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CORROSION INHIBITION

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20 Claims. (Cl. 252—392)

This application is a divisional application of our co-pending application Serial No. 21,891, filed April 13, 1960, now Patent Number 3,152,187, isued October 6, 1964.

This invention relates to an improved corrosion inhibiting composition and its method of preparation and use. More particularly it relates to the reaction of an unsaturated diol and a polyalkylene polyamine in the presence of a small concentration of a metallic ion, to form a reaction product 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 existance 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 alkanol amines; lacquers used to coat ferrous metals sometimes contain such compounds; and aqueous alkanolamine (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 characteristic 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 the co-pending application of Barnes et al., Serial No. 672,117, filed July 16, 1957, now abondoned, the reaction product of the unsaturated diol and the polyalkylene polyamine is disclosed. As indicated in this co-pending application, the butynediols may be prepared by the condensation of acetylene with aldehydes or ketones in the presence of copper acetylide as taught by Reppe et al., in U.S. Pats. Nos. 2,232,867 and 2,300,969, while the butenediols may be prepared by the partial reduction of the corresponding butynediols by treatment of the butynediol in an aqueous alkali solution with zinc in accordance with the Reppe et al. Pat. No 2,267,749. See also the following reports of the British Intelligence Objectives Sub-Committee Surveys (published by His Majesty's Stationary Office, London): Report No. 30, "The Acetylene Industry and Acetylene Chemistry in Germany during the period 1939–1945," 1951, p. 78; Report No. 367, "Manufacture of 1:4-Butinediol at I. G. Lugwigshafen."

During the initial work performed prior to the filing of the above-identified application, it was observed that water was formed during the reaction process, which water was trapped and removed. It was accordingly assumed that the product was not merely an adduct, but was a new compound resulting from the splitting-off of water. In order to check these conclusions, purified diols and amines were employed in reactions, and the resulting products were analyzed. In one instance, for example, reactants having the following properties were employed in equimolar quantities:

	Boiling pt. at 7 mm.	n_D^{25}
Diethylene triamine	82-84° C	1.4812
Butenediol (purified by distillation).	130–132° C	1.4765

The reaction product was distilled in a Claisen flask at 7 mm. taking the fraction from 129–130° C. as the major fraction (69 percent of the total product) having the following properties:

	Percent Carbon	Percent H	Percent N	n_D^{25}
Observed for product	51.5	10.7	16.6	1.4880
Calculated for simple addition product	50.5	11.0	22.1	

These data, together with the fact that no water was trapped in the Dry Ice trap used on the vacuum line during distillation, suggested that the reaction product was a simple addition product rather than a new compound. When distillation was attempted in a spinning band column to obtain a purer product, decomposition occurred, leading to the formation of diol and triamine. The molecular weight of the product could not be determined because of its tendency to disassociate. The distillation cut was acetylated, and the resulting acetylated material showed ester groups but no amide linkages by infrared analysis, indicating that there were free hydroxyl groups in the reaction product but no free amine groups. Vapor phase chromatography of the product showed the absence of any free triamine, further indicating that a mere mechanical mixture was not involved.

Similar results were obtained using other purified diols of the class indicated above. The solid diols were purified by recrystallization; for example, butynediol was purified by the following technique:

40 gms. of solid butynediol was added to a mixture of
80 cc. of ethyl acetate and
20 cc. of toluene plus
0.25 gm. Norit (activated carbon)

The mixture was heated on the steam bath to 60° C. and gravity filtered. The filtrate was then cooled, with stirring, by means of a cold water bath. At 35° C. precipitation began. At 25° C. about 70 percent of the material had been removed by precipitation. (Further cooling may cause the slurry to become too thick for handling.) The product was collected on a Büchner funnel and sucked as dry as possible. It was then dried for 30 hours in a vacuum desiccator over sulfuric acid at room temperature.

Another method of purifying 2-butyne-1,4-diol is disclosed in U.S. Patent 2,789,147, involving technique of slowly cooling the material to crystallize the diol, removing the liquid, and then slowly raising the temperature to sweat out the remaining liquid impurities.

Thus it appeared that when a diol prepared by the Reppe et al. method was employed, the reaction thereof with the amine involved the formation of water to yield a condensation product, while the use of a purified diol resulted in the formation of a simple addition product without the splitting-off of water. It was discovered that the condensation product of our invention had corrosion inhibiting properties far superior to the simple addition product. It then became of importance to determine how to prepare the condensation product from a pure diol, in view of the fact that the principal manufacturers of diols were—and still are—preparing and marketing diols of such purity that only the addition product could be prepared therefrom using the technique of the above-mentioned co-pending application.

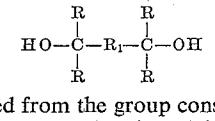
The principal object of this invention is therefore to provide a new composition matter effective to prevent the corrosion of ferrous metals. Another object is to provide a method for preventing the oxygen corrosion of ferrous metals, involving the addition of a new corrosion inhibiting composition to 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. Another object of this invention is to provide a novel and effective method of reacting an unsaturated diol and a polyalkylene polyamine involving the use of small amounts of a metal in ionic form to promote or catalyze the reaction. Further objects will become apparent from the consideration of the disclosure which follows.

We have found that the desired condensation products may be prepared from pure diols by incorporating into the reaction mixture of diol and amine a small amount of a metal compound affording a metal ion. Broadly stated, our invention comprises the condensation reaction of an unsaturated diol and a polyalkylene polyamine in the presence of a small amount of a metal compound affording a metal ion, the reaction product formed thereby, and the use of said products to prevent the corrosion of metal surfaces.

Although several metals are suitable, we prefer to use an ionizable copper compound. Although we do not wish to be bound by any theory, it is our opinion that the unpurified diols successfully employed in the reactions of Barnes et al. (Serial No. 672,117) contained a catalytic amount of copper ion in the form of a copper containing derivative of propargyl alcohol carried over with the propargyl alcohol formed as a by-product during the manufacture of the unsaturated diol. We believe that the copper ion acts as a catalytic agent to promote the condensation reaction between the amine and the diol, possibly involving chelation as a first step followed by condensation, since we have observed that the copper promotes the exothermic formation of an adduct prior to the carrying out of the condensation step of the reaction. The origin of the copper probably lies in the use of copper acetylide as a catalyst for the reaction of the aldehyde and acetylene. It is further believed that when the unsaturated diols were purified to remove the propargyl alcohol therefrom, the copper was removed along with the propargyl alcohol, thus removing the catalyst necessary for the desired reaction of the unsaturated diol with the polyalkylene polyamines. (U.S. Patent 2,789,147 discloses a method for purifying 2-butyne-1,4-diol to remove propargyl alcohol and other compounds.)

THE UNSATURATED DIOL

The unsaturated diols are those of the formula:



where R is selected from the group consisting of hydrogen, methyl, and ethyl, and R_1 is selected from the group consisting of

—C≡C— and —CH=CH—

Specific diols include, but are not limited to, the following:

2-butynediol-1,4
1-methyl-2-butynediol-1,4
1,4-dimethyl-2-butynediol-1,4
1,1-dimethyl-2-butynediol-1,4
1,1,4,4-tetramethyl-2-butynediol-1,4
1-ethyl-2-butynediol-1,4
1,4-diethyl-2-butynediol-1,4
1,1-diethyl-2-butynediol-1,4
1,1,4,4-tetraethyl-2-butynediol-1,4
1-methyl-1-ethyl-2-butynediol-1,4
1-methyl-4-ethyl-2-butynediol-1,4
1,1-dimethyl-4-ethyl-2-butynediol-1,4
1,1-diethyl-4-methyl-2-butynediol-1,4
1,4-diethyl-1-methyl-2-butynediol-1,4
1,1-dimethyl-4,4-diethyl-2-butynediol-1,4
1,1,4-trimethyl-2-butynediol-1,4
1,1,4-triethyl-2-butynediol-1,4
1,4-dimethyl-1-ethyl-2-butynediol-1,4
1,1,4-trimethyl-4-ethyl-2-butynediol-1,4
1,4-dimethyl-1,4-diethyl-2-butynediol-1,4
1,1,4-triethyl-4-methyl-2-butynediol-1,4

The butenediols corresponding to the above butynediols, as for example, 2-butenediol-1,4; 1,1-dimethyl-2-butenediol-1,4; 1,1,4,4-tetramethyl-2-butenediol-1-4; and 1,4-diethyl-1-methyl-2-butenediol-1,4 to name only a few, are also suitable for preparing the reaction products of this invention. The butynediols are preferred, however, because both of the hydroxyl groups are reactive, whereas the butenediols react with more difficulty, so that in actual practice lower yields may be obtained. It is postulated that this is a consequence of the unequal reactivity of the cis and trans forms of the butenediols.

THE POLYALKYLENE POLYAMINE

The suitable polyalkylene polyamines may be structurally represented by the formula

$$H_2N(R_2—NH)_n—CH_2CH_2—NH_2$$

where R_2 is a radical selected from the group consisting of ethylene and propylene, and n is an integer varying from 1 to 4.

Exemplary, but not limitative of the polyalkylene polyamines suitable for preparation of the reaction products of our invention, are diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexylamine, dipropylene triamine and tripropylene tetramine.

THE METAL COMPOUND

The selection of the metal compound is preferably made from ionizable compounds of chelate-forming metals, which are those metals other than the alkali, alkaline earth, and lanthanide metals. In general, the best chelate-formers are cations of small size and high nuclear of ionic charges, such as the metals having atomic numbers of 24–30, 42–48, and 74–80, although we may employ metals selected from the somewhat broader group of metals including those having atomic numbers of 22–30, 41–48, 49–50, and 73–83, inclusive. As indicated above, we prefer to use a copper compound. Although chloride salts may be employed, we prefer to use other ionizable compounds such as metal acetates or other compounds of organic acids. A particularly suitable compound is copper acetate.

The amount of metallic compound depends somewhat upon the particular reactants and metal used; for example, titanium is more active than copper and, therefore, may be employed in smaller quantities. The amount of metal employed affects the rate of reaction, and since the reaction is exothermic, the desired amount will also depend upon the heat transfer characteristics of the equipment in which the reaction is carried out. It has been established, however, that in the case of copper the amount of metal should preferably not exceed about one-half gram of metal ion per mole of the unsaturated diol. If this limit is exceeded, the reaction proceeds very rapidly and the resulting product generally contains an excess of a high molecular weight resinous fraction and therefore lacks certain desired physical characteristics such as viscosity and water solubility. We have also found that mere trace quantities of copper in the order of 10 parts of copper acetate, per million parts of diol, are effective to promote the desired reaction involving the splitting-off of water to form the condensation product. We generally use from about 10–500, and preferably from about 25–100 parts of copper acetate per million parts of diol. In Examples 1 and 3–6, below, we used considerably more metal than is required. Example 7 illustrates a preferred amount of 50 parts of copper acetate per million parts of diol.

PREPARATION OF THE REACTION PRODUCT

The unsaturated diol and the polyalkylene polyamine may be simply mixed (preferably in equimolar quantities, but possibly from about ½–2 mole equivalents of amine per mole equivalent of the diol) and the metal compound added thereto. We prefer, however, to dissolve the metal compound in a small quantity of water,

and then mix the solution with the diol prior to addition of the amine. The diol is preferably heated slightly to facilitate mixing of the metal compound therewith.

The mixture of diol, amine, and metal compound 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, and heating should be discontinued. The water which is formed is trapped and removed and the temperature is allowed to rise slowly until the condensation of water has ceased. After the water of reaction has been removed, the mixture is allowed to cool, an azeotropic solvent such as benzene or toluene is added, and azeotropic distillation conducted to trap out residual water. The solvent is stripped from the mixture after which the then-existing temperature is preferably maintained for about 45 minutes to insure completion of the reaction.

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 chemical structure of the product has not been elucidated. Depending upon reaction conditions the product is found to contain mixtures of substances of various molecular weights. Gas-liquid phase chromatography studies indicate that more than twelve compounds are formed during the reaction and that individual distillation cuts of the reaction product also contain more than one compound. Infrared analysis showed several groups and various linkages, but positive identification of the reaction product (or any of its constituents) was not deemed feasible. It is believed that this variety of compounds having a wide range of molecular weights is responsible for the corrosion-inhibiting properties of the product.

The following examples illustrate the method of preparation of the corrosion inhibitors of this invention, Example 7 setting forth the preferred procedure.

Example 1

One gram of $CuCl_2 \cdot 2H_2O$, containing 0.37 gm. of copper ion, was dissolved in about 10 ml. of water, and was then added to 87 gm. of 2-butyne-1,4-diol. The mixture was placed in a standard 3-necked round bottom reaction flask equipped for refluxing and for the removal of water by azeotropic distillation. 189 gm. of tetraethylene pentamine was then poured into the flask, and the temperature raised to about 126° C. At this time the temperature began to rise, and water began to condense. The heating mantle was removed and the flask cooled to prevent a sudden increase in temperature. At 153° C., 31 ml. of water had been trapped. At 200° C., 22 ml. of a light yellow distillate had been trapped, and while the temperature climbed from 200° C. to 225° C., 15 ml. of a dark yellow distillate was trapped. The mixture was cooled to 75° C., and 100 ml. of toluene was added. The heating mantle was replaced, and the mixture was heated to about 110° C., when reflux of the azeotrope began. Refluxing was continued until the residual water had been trapped-out, as evidenced by the condensation of a small amount of the low boiling reaction mixture which was somewhat yellow in color and which discolored the trapped water slightly. Then the toluene was stripped, commencing at about 117° C. and ending at about 228° C., after which the mixture was held at the latter temperature for 45 minutes.

Example 2

The procedure of Example 1 was attempted without the use of either the metal salt or the water. The temperature was raised to 140° C., but there was no pronounced exothermic reaction observed and no distillate obtained. The temperature was raised to 180° C. before a slight amount (about 4 ml.) of a clear distillate was obtained. Upon raising the temperature to 190° C., about 10 ml. of a yellow distillate was obtained. There was still no pronounced exothermic effect as in Example 1. The mixture was then cooled to about 90° C., and 100 ml. of toluene was added for azeotropic distillation and refluxing. After refluxing until it was apparent that no water was being trapped, the toluene was stripped from about 115° C.–225° C., and the mixture was held at the latter temperature for about 2 hours. At no time was any water detected.

Example 3

The procedure of Example 1 was followed except that pentaethylene hexylamine was substituted for tetraethylene pentamine. The reaction proceeded in the same manner as in Example 1. 43.5 gm. of 2-butyne-1,4-diol, 116 gms. of pentaethylene hexylamine, and 1 gm. of $CuCl_2 \cdot 2H_2O$ were used. The temperature was raised to 156° C., when the first distillate (colorless) began to come over. When the temperature reached 174° C., the mixture was cooled to 60° C. and 100 ml. of toluene added. The toluene was stripped commencing at 108° C. and ending at 200° C., and 96 ml. of toluene were recovered. The mixture was held at 200° C. for 2 hours and no additional toluene was recovered.

Example 4

The procedure of Example 1 was repeated except that a cobalt salt was employed instead of $CuCl_2 \cdot 2H_2O$. 1.4 gm. of $CoCl_2 \cdot 6H_2O$ were dissolved in 10 ml. of water and the solution was mixed with 87 gm. of 2-butyne-1,4-diol, which was placed in the flask. 189 gm. of tetraethylene pentamine was then poured into the flask. The temperature was raised to 125° C. to initiate the reaction, at which time the temperature began to rise. At 159° C., 31 ml. of water had been trapped, and at 190° C. an additional 14 ml. was obtained. A light yellow distillate came over beginning at about 191° C. After reaching 210° C., the temperature rose rather sharply. The heat was removed, but the temperature rose to 245° C. 33.5 ml. of a dark yellowish distillate was obtained. The mixture was cooled to about 70° C., 100 ml. of toluene added, and the residual water removed by azeotropic distillation. Then the toluene was stripped at from 112° C.–228° C. The mixture was held at 228° C. for about 1 hour.

Example 5

The procedure of Example 1 was followed using 1.2 gm. of $MnCl_2 \cdot 4H_2O$ instead of $CuCl_2 \cdot 2H_2O$.

Water began to distill—130° C.
Trapped 21 ml. water—163° C.
Trapped 25 ml. distillate—200° C.

The heat was removed, but the temperature continued to rise to 230° C. 13 ml. of a dark yellow distillate was trapped. After cooling to 75° C., 100 ml. of toluene was added. The azeotrope was refluxed to remove residual water, and the toluene was then stripped (117° C.–228° C.). The mixture was then held at 225° C. for about 2 hours.

Example 6

Example 1 was repeated using 1.4 gm. of $SnCl_2 \cdot 2H_2O$ instead of $CuCl_2 \cdot 2H_2O$.

Water began to distill—121° C.
Trapped 38 ml. water—166° C.
Trapped 12 ml. light yellow distillate—205° C.

The heat was removed but the temperature climbed to 246° C. 10 ml. of a dark yellow distillate was obtained. Residual water was removed by azeotropic distillation while refluxing, and the toluene was then stripped (111° C.–228° C.). The mixture was held at about 225° C. for about 2 hours.

Example 7

Into a 500 ml., 3-necked, round bottom flask, place one mole (86 gm.) of 2-butyne-1,4-diol and 0.86 ml. of a stock solution of copper acetate. (This stock solution consists of 5 gm. of $Cu(C_2H_3O_2)_2H_2O$ dissolved in 1,000 ml. of de-ionized water heated to 50° C.) The temperature is raised to the melting point of the diol (57–58° C.), while stirring, to mix in the copper. To the warm solution add one mole of tetraethylene pentamine (189 grams) while continuing to stir the mixture. Raise the temperature to 180° C. and hold. Water begins to distill over at approximately 170° C. Continue distillation until 18–20 ml. of distillate has been trapped. Cool ingredients to 70° C. and add 30 ml. toluene for azeotrope of remaining water. Raise the temperature. Azeotropic distillation begins at approximately 134° C. Trap and remove water only as thimble fills. The temperature will slowly rise with removal of residual water. As the temperature reaches 190° C., measure the water (it should be near 16 ml. volume). Continue to let the temperature rise as toluene is stripped free of the reaction product. The temperature should not be allowed to exceed about 225° C. A few ml. of a yellow distillate will be trapped out in the toluene at temperatures between 190° C.–225° C. The product forms a bright, clear solution in water.

The compositions of Examples 1–7 were tested for inhibition of oxygen corrosion, and the results are shown in Table 1. The indicated quantities of the corrosion inhibitor were dissolved in 250 ml. of an aerated 5 percent sodium chloride solution, and mild steel coupons immersed therein and allowed to stand for the periods of time specified. Thereafter, the coupons were removed, descaled by scrubbing with a nylon bristle brush and a cleaning powder, weighed, and the weight loss determined. The same procedure was followed in the absence of inhibitor to obtain a blank. The percent protection was calculated as follows:

$$\text{P.C.P.} = \frac{(Wb_i - Wb_f) - (Wc_i - Wc_f) \times 100}{(Wb_i - Wb_f)}$$

where:

P.C.P.=Percent protection afforded by inhibitor
Wb_i=Initial weight of coupon subjected to test in the absence of inhibitor
Wb_f=Final weight of coupon subjected to test in the absence of inhibitor
Wc_i=Intial weight of coupon subjected to test in presence of inhibitor
Wc_f=Final weight of coupon subjected to test in the presence of inhibitor

TABLE 1

Example	Metal	Concentration of inhibitor (p.p.m.)	Time of exposure (days)	Percent protection
1	Copper	286	6	91
1	do	143	4	92
2		143	4	63
3	Copper	143	4	90
4	Cobalt	286	6	95
5	Manganese	286	6	92
6	Tin	286	6	89
7	Copper	286	7	93

The compositions of Examples 1–7 were also tested and found to be effective in preventing filiform corrosion. Mild steel coupons were immersed in an unstirred, aerated 5 percent sodium chloride solution containing 1 percent diethanolamine. The corrosion inhibitor was employed in the concentrations indicated in Table 2 which sets

forth the results obtained. (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, thread-like filaments.)

TABLE 2

Example	Metal	Concentration of inhibitor (p.p.m.)	Time of exposure (days)	Filiform corrosion
1	Copper	286	7	No.
1	do	715	7	No.
2		286	2	Yes (slight).
2		715	5	Yes.
3	Copper	286	7	No.
3	do	715	7	No.
4	Cobalt	286	6	No.
5	Manganese	286	6	No.
6	Tin	286	6	No.
7	Copper	286	7	No.
7	do	715	7	No.

While the foregoing tests were conducted at 143 p.p.m., 286 p.p.m., and 715 p.p.m., corresponding to 100 p.p.m., 200 p.p.m., and 500 p.p.m., respectively of active inhibitor (assuming that the product is 70% active), we have found that concentrations as low as 100 p.p.m. (total inhibitor) or less are effective to inhibit oxygen corrosion, and that concentrations as low as 200 p.p.m. (total inhibitor) are effective to prevent filiform corrosion. Optimal concentration is dependent upon the nature of the corrosive fluid and upon the quantity of corrosive constituents present. Where, for example, the system approaches oxygen saturation, the desired degree of inhibitor may be attained through incorporation of from 250–500 or more parts per million. On the other hand, where the system contains very low dissolved oxygen only a few parts per million of the reaction product will give satisfactory results. The quantity to be employed will be readily determinable from the corrosiveness of the solution.

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.

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 covenient point or combination of points. The preferred inhibitor is the reaction product of 2-butyne-1,4-diol and tetraethylene pentamine, although other products are suitable, as indicated above.

Example 8

Several known corrosion inhibitors were added to the filiform-producing diethanolamine (DEA) and monoethanolamine (MEA) systems. These systems consisted of unstirred, aerated, 1% amine, 5% sodium chloride brine solutions. 1020 mild steel strips were immersed in such solutions for periods of 168 hours. The results are presented in Table 3.

TABLE 3.—EFFECTS OF CHEMICAL ADDITIVES ON FILIFORM CORROSION IN MEA AND DEA BRINE SYSTEMS

Chemical treatment, 100 p.p.m.:	Filiform occurs
Tetraethylenepentamine—butynediol reaction product	No
Diethylenetriamine—butynediol reaction product	No
Triethylenetetramine—butynediol reaction product	No
Commercial Imidazoline inhibitor	Yes
Commercial Rosin Amine D inhibitor	Yes
Sodium chromate	Yes
Sodium nitrite	Yes
Tetraethylenepentamine	Yes
Diethylenetriamine	Yes
Triethylene tetramine	Yes
Imidazoline sulfate	Yes
n-Acetyl ethanolamine	Yes
Aminoethylethanolamine	Yes
Dibutylisopropanolamine	Yes
Phenyl ethanolamine	Yes
Pyrogallic acid (as an oxygen scavenger)	Yes
Tetraethylenepentamine—pyrogallic acid	Yes

Example 9

In order to more closely simulate the actual conditions present in a commercial diethanolamine gas treating unit and to thus more vividly illustrate the results afforded by this invention by presenting quantitative data, the following tests were performed.

A 3-necked, 1-liter, round-bottom flask was assembled with a steel test coupon suspended therein, and a solution the same as that employed in Example 8 was placed in the flask. The solution was continuously stirred during the test period. A mixture of H_2S and CO_2 gases was passed through the liquid at the rate of 0.5 liter per min. A vertical condenser attached to one neck of the flask prevented evaporation loss. The temperature was maintained at 200° F. during the test period (24 hours). Surface-corrosion observations were made at the end of the test. The weight-loss measurements were determined, from which corrosion rates and percent protection were calculated. The results of this test are shown in Table 4.

TABLE 4.—EFFECT OF INHIBITORS ON CORROSION IN A 1 PERCENT DEA, 5 PERCENT SODIUM CHLORIDE BRINE SATURATED WITH HYDROGEN SULFIDE AND CARBON DIOXIDE

Chemical	Concentration, (parts per million)	Corrosion rate (mils per year)	Surface corrosion
None	0	96	Pitting.
Commercial Imidazoline	250	7.3	Slight pitting.
Commercial Rosin Amine D.	250	8.4	Do.
Tetraethylenepentamine—butynediol reaction product.	250	0.8	None detected.

The corrosion which occurred during this test was of the pitting type rather than the threadlike filiform type, because the fluid environment was under agitation which prevents build-up of the threadlike formations. As indicated above, filiform will occur in an unagitated system.

Example 10

In a commercial diethanolamine gas sweetening unit, small amounts of the reaction product of tetraethylenepentamine and 2-butyne-1,4-diol were added to the regenerator overhead line by means of a proportioning pump. The dosage rate was such that the concentration of the inhibitor was maintained at 200 parts per million of liquid phase in the system.

In order to determine quantitatively the effectivness of the corrosion inhibitor, steel test coupons were placed in the liquid in the bottom of the regenerator tower. The corrosion of the coupons was measured, and the results obtained are shown in Table 5.

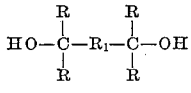
TABLE 5

Chemical treatment	Time-exposure interval	Corrosion rates of exposed coupons, liquid phase (mils per year)
None	11-18-57 to 1-21-58	7.8
Tetraethylenepentamine-butynediol.	1-21-58 to 1-28-58	5.9
Do	1-28-58 to 2-4-58	4.0

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.

We claim:

1. The method of inhibiting the corrosion of ferrous metals in contact with a corrosive aqueous medium which comprises incorporating into said medium a product formed by the reaction of about one mole equivalent of an unsaturated diol of the formula



where R is selected from the group consisting of hydrogen, methyl, and ethyl, and R_1 is selected from the group consisting of

$$-C\equiv C- \text{ and } -CH=CH-$$

with about ½–2 mole equivalents of a polyalkylene polyamine of the formula

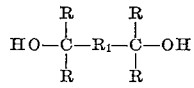
$$H_2N(R_2—NH)_n—CH_2CH_2—NH_2$$

wherein R_2 is a radical selected from the group consisting of ethylene and propylene, and n is an integer varying from 1 to 4; said reaction being carried out in the presence of a small amount of a compound affording a chelate-forming metal ion, the amount of said metal compound being sufficient to cause an exothermic reaction between the unsaturated diol and the polyalkylene polyamine and to cause the formation of water.

2. The method of claim **1** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is tetraethylene pentamine.

3. The method of claim **1** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamnie is pentaethylene hexylamine.

4. The method of inhibiting the corrosion of ferrous metals in contact with an aqueous medium containing oxygen which comprises incorporating into said medium a product formed by the rection of about one mole equivalent of an unsaturated diol of the formula



where R is selected from the group consisting of hydrogen, methyl, and ethyl, and R_1 is selected from the group consisting of

$$-C\equiv C- \text{ and } -CH=CH-$$

with about ½–2 mole equivalents of a polyalkylene polyamine of the formula

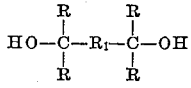
$$H_2N(R_2—NH)_n—CH_2CH_2—NH_2$$

wherein R_2 is a radical selected from the group consisting of ethylene and propylene, and n is an integer varying from 1 to 4; said reaction being carried out in the presence of a small amount of a compound affording a chelate-forming metal ion, the amount of said metal compound being sufficient to cause an exothermic reaction between the unsaturated diol and the polyalkylene polyamine and to cause the formation of water.

5. The method of claim **4** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is tetraethylene pentamine.

6. The method of claim **4** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is pentaethylene hexylamine.

7. The method of inhibiting the corrosion of ferrous metals in contact with an aqueous medium containing oxygen and sodium chloride which comprises incorporating into said medium a product formed by the reaction of about one mole equivalent of an unsaturated diol of the formula



where R is selected from the group consisting of hydrogen, methyl, and ethyl, and R_1 is selected from the group consisting of

$$-C\equiv C- \text{ and } -CH=CH-$$

with about ½–2 mole equivalent of a polyalkylene polyamine of the formula

$$H_2N(R_2—NH)_n—CH_2CH_2—NH_2$$

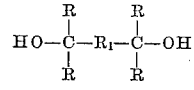
wherein R_2 is a radical selected from the group consisting of ethylene and propylene, and n is an integer varying from 1 to 4; said reaction being carried out in the presence of a small amount of a compound affording a chelate-forming metal ion, the amount of said metal compound being sufficient to cause an exothermic reaction between the unsaturated diol and the polyalkylene polyamine and to cause the formation of water.

8. The method of claim **7** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is tetraethylene pentamine.

9. The method of claim **7** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is pentaethylene hexylamine.

10. The method of inhibiting the corrosion of ferrous metals in contact with an aqueous medium containing oxygen, sodium chloride and an amine selected from the

group consisting of monoethanolamine and diethanolamine which comprises incorporating into said medium a product formed by the reaction of about one mole equivalent of an unsaturated diol of the formula



where R is selected from the group consisting of hydrogen, methyl, and ethyl, and R_1 is selected from the group consisting of

—C≡C— and —CH=CH—

with about ½–2 mole equivalent of a polyalkylene polyamine of the formula

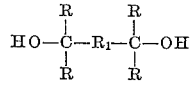
$$H_2N(R_2—NH)_n—CH_2CH_2—NH_2$$

wherein R_2 is a radical selected from the group consisting of ethylene and propylene, and *n* is an integer varying from 1 to 4; said reaction being carried out in the presence of a small amount of a compound affording a chelate-forming metal ion, the amount of said metal compound being sufficient to cause an exothermic reaction between the unsaturated diol and the polyalkylene polyamine and to cause the formation of water.

11. The method of claim **10** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is tetraethylene pentamine.

12. The method of claim **10** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is pentaethylene hexylamine.

13. The method of inhibiting the corrosion of ferrous metals in contact with an aqueous medium containing oxygen, H_2S, CO_2, and an amine selected from the group consisting of monoethanolamine and diethanolamine which comprises incorporating into said medium a product formed by the reaction of about one mole equivalent of an unsaturated diol of the formula



where R is selected from the group consisting of hydrogen, methyl, and ethyl, and R_1 is selected from the group consisting of

—C≡C— and —CH=CH—

with about ½–2 mole equivalent of a polyalkylene polyamine of the formula

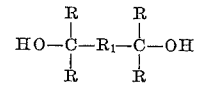
$$H_2N(R_2—NH)_n—CH_2CH_2—NH_2$$

wherein R_2 is a radical selected from the group consisting of ethylene and propylene, and *n* is an integer varying from 1 to 4; said reaction being carried out in the presence of a small amount of a compound affording a chelate-forming metal ion, the amount of said metal compound being sufficient to cause an exothermic reaction between the unsaturated diol and the polyalkylene polyamine and to cause the formation of water.

14. The method of claim **13** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is tetraethylene pentamine.

15. The method of claim **13** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is pentaethylene hexylamine.

16. The method of inhibiting the corrosion of ferrous metals in contact with an aqueous medium containing oxygen, H_2S, CO_2, sodium chloride and an amine selected from the group consisting of monoethanolamine and diethanolamine which comprises incorporating into said medium a product formed by the reaction of about one mole equivalent of an unsaturated diol of the formula



where R is selected from the group consisting of hydrogen, methyl, and ethyl, and R_1 is selected from the group consisting of

—C≡C— and —CH=CH—

with about ½–2 mole equivalent of a polyalkylene polyamine of the formula

$$H_2N(R_2—NH)_n—CH_2CH_2—NH_2$$

wherein R_2 is a radical selected from the group consisting of ethylene and propylene, and *n* is an integer varying from 1 to 4; said reaction being carried out in the presence of a small amount of a compound affording a chelate-forming metal ion, the amount of said metal compound being sufficient to cause an exothermic reaction between the unsaturated diol and the polyalkylene polyamine and to cause the formation of water.

17. The method of claim **16** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is tetraethylene pentamine.

18. The method of claim **16** wherein the metal ion is copper, the unsaturated diol is 2-butyne-1,4-diol, and the polyalkylene polyamine is pentaethylene hexylamine.

19. The method of inhibiting the corrosion of ferrous metals in contact with an aqueous medium containing oxygen, H_2S, CO_2, and diethanolamine which comprises incorporating into said medium the product formed by the reaction of approximately equimolar quantities of 2-butyne-1,4-diol and tetraethylene pentamine, said reaction being carried out in the presence of a small amount of copper ion sufficient to cause the liberation of heat and formation of by-product water of reaction.

20. The method of inhibiting the corrosion of ferrous metals in contact with an aqueous medium containing oxygen, H_2S, CO_2, and diethanolamine which comprises incorporating into said medium the product formed by the reaction of approximately equimolar quantities of 2-butyne-1,4-diol and pentaethylene hexylamine, said reaction being carried out in the presence of a small amount of copper ion sufficient to cause the liberation of heat and formation of by-product water of reaction.

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