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AMINOPHENOL CORROSION INHIBITOR

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ABSTRACT OF THE DISCLOSURE

Corrosion in metal surfaces contacting liquids, particularly hydrocarbonaceous liquids, can be inhibited by adding to said liquid a corrosion inhibiting amount of aminophenol or a derivative thereof.

This invention pertains to a method for minimizing or preventing corrosion. More particularly, this invention pertains to the prevention of corrosion of metals which are exposed to various corrosive solutions such as solutions containing HCl. More particularly still, this invention pertains to a method for minimizing or preventing corrosion which occurs in the petroleum, petrochemical and related industries such as corrosion caused in the refining of crude oil and the shipping of various petroleum and petrochemical compounds. The corrosion is prevented by adding aminophenol or derivatives thereof, particularly para-aminophenol, directly or indirectly into the corrosive solution.

It is well known that various organic and inorganic materials when found in a solution cause extensive damage to any metallic surfaces with which they come in contact. Examples of especially destructive inorganic compounds include HCl and H₂SO₄. With respect to organic compounds, acetic acid, phenolic solutions and naphthenic acids are extremely troublesome. Various metals which are utilized differ to a great extent concerning their ability to withstand these corrosive compounds. However, unfortunately, carbon steel, an extremely widely used material, is quite susceptible to the corrosiveness of the various corrosive agents. Generally, these corrosive materials fall within the bounds of a Brönsted acid. A Brönsted acid is defined as any substance that can lose one or more protons. Additionally, a Lewis acid or electron donor may also on occasion cause corrosiveness.

In particular, the petroleum industry has suffered greatly in loss of equipment and time because of the presence of the various corrosion-causing compounds. Most crude petroleum contains numerous naturally occurring constituents and impurities which will cause severe corrosion of the metals from which conventional petroleum refining equipment is constructed. This is, of course, predominately carbon steel. The corrosive or corrosion-causing materials are varied in scope and composition. Among the more troublesome corrosive agents is hydrogen sulfide, which is dissolved both in crude oil and in any water which is found within the system. Needless to say, hydrochloric acid is particularly destructive and this is found in substantially all petroleum systems. A major source of the HCl is its generation by the high temperature hydrolysis, i.e. 200° F. or higher of magnesium and calcium chlorides which are contained in the water phase of crude oil.

The high temperatures within a refinery encourage the formation of HCl. The elevated temperatures utilized force the hydrolysis reaction mentioned above to the right because the hydrochloric acid formed is volatile and thereby constantly removed from the reaction zone.

Another area where corrosion is becoming particularly troublesome is in the shipping of crude oils and other corrosive containing materials such as various refinery products, fertilizer solutions, petrochemicals and chemicals containing acidic materials. Shipping these materials in

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cargo ships has resulted in the pitting of the interior of the vessel. Prolonged exposure to these corrosive materials may result in deterioration of the hull of the ship with disastrous consequences. This, of course, would also be true of any container used for small or large scale storage of liquids which contain corrosive agents.

Attempts to rectify these corrosion problems in the prior art have been varied in their scope.

In U.S. Patent 2,366,074, a composition is disclosed which is used to prevent the corrosion of iron or steel surfaces which are in contact with organic materials. The composition comprises a mixture of an aromatic amine and an alkylated aromatic acid. Patentee teaches that the alkylated hydroxy aromatic acid causes increased resistance to corrosion when used alone. The presence of the aromatic amine serves to increase the life of oils such as turbine oils which are in contact with the iron or steel surfaces and at the same time the corrosion resisting effect of the acid is retained. Patentee has no teaching to the effect that the aromatic amine would serve to enhance the anti-corrosion effect of his additive.

In U.S. Patent 2,496,595, there is disclosed the use of a solution of formaldehyde and an organic compound containing an amino-reactive group such as an alkyl aminophenol. It is indicated within the specification that amino-reactive compounds when utilized alone are individually less effective than formaldehyde as corrosion inhibitors for oil brines. A minor portion of these amino-reactive compounds utilized in conjunction with formaldehyde provide an unexpectedly successful inhibiting effect. Thus, patentee is relying on a synergistic effect to compensate for the ineffective results obtained with alkyl aminophenol.

None of these corrosion inhibitors has produced the kind of corrosion inhibition which would be desired in certain areas where corrosion is severe. Previously used corrosion inhibitor systems also have limited efficiency at elevated temperatures.

According to this invention, a corrosion inhibitor has been discovered which provides the extent of corrosion inhibition which was not previously obtainable with previously known inhibitors. Severe corrosive agents are inhibited successfully even when temperatures are elevated.

It has unexpectedly been discovered that the addition of aminophenols particularly para-aminophenol to the corrosive solutions prevent corrosion of metals which are utilized to contain various corrosive solutions. It should be emphasized that substantially all metals will be protected, however, for purposes of this invention and in the interest of brevity, the invention will be described in terms of preventing the corrosion of carbon steel.

Aminophenols are partially soluble in water and soluble in acid solutions and can be used directly in the pure form or technical grade as well as being diluted with other additives as an inhibitor formulation. It is essential to the operation of this invention that the benzene ring have both hydroxy and NH₂ groups attached directly to it. Derivatives of aminophenol such as having C₁ to C₃ alkyl groups present on the benzene ring may also be utilized. Thus, a compound such as 1-hydroxy, 2-methyl and 4-amino benzene is within the scope of this invention. In addition, two or more condensed ring aromatics may be used so long as at least one ring has a hydroxy and an amino group attached to it.

Other derivatives of aminophenol include the compound resulting from the addition of either hydroxy or amino groups onto at least one of the four remaining unsubstituted carbon atoms of the benzene rings. It should be noted that particularly outstanding results are obtained with para-aminophenol. Ortho aminophenol provides results which are less effective and the least effective results are obtained with meta-aminophenol.

The following explanation is offered for the effective-

ness of the instant invention. There is no intention to be bound by any particular mechanism and the mechanism offered is just for the purposes of clarity. The benzene ring is an excellent carrier of electrons. The nitrogen makes contact with the metal surface whose corrosion is intended to be limited. The greater the number of electrons around the nitrogen the stronger the bond which is formed between the nitrogen and the metal. The function of the hydroxide group is to act as an electron donor and thus increase the electron density in the nitrogen atom of the amino group. Thus, the combination of the benzene ring, the amine and the hydroxy group forms an excellent corrosion inhibitor. The acids which may be inhibited by the instant invention include the organic acids such as fumaric acid, citric acid, succinic acid, acetic acid, naphthenic acid, organic acid halides, non-aqueous solutions such as formamide, dimethyl sulfoxide, etc. The various inorganic acids are also corrosive and the presence of the aminophenol of the instant invention also serves to inhibit metal corrosion caused by these inorganic acids. Examples of these inorganic acids include hydrochloric acid, sulfuric acid, nitric acid, sulfurous acid, hydrofluoric acid, perchloric acid, polyphosphoric acid, etc.

The metals which may be protected from corrosion by the process of the instant invention include carbon steel, nickel steel, copper and its alloys, stainless steels, etc. However, it should be emphasized that this invention will be most useful in preventing the corrosion of carbon steel, particularly as it is used in storage and refinery facilities, i.e. transfer lines, pipestills and other process vessels as well as ships and pipelines.

A further area where this invention would be applicable is in the area of chemical reactions wherein at least one of the reactants, catalysts or products is corrosive in nature. This would include acid catalyzed reactions, reactions of an acid with another reactant and reactions wherein an acid is formed either as the main product or a secondary product. Reactions such as these when carried out on a large scale or under pressure often make use of carbon steel vats as well as other metallic vessels which may be subjected to the corrosive attack of any of these acidic materials. Examples of the various reactions wherein corrosion is a problem would include alkylation particularly the formation of isooctane. The additive should be substantially unreactive with the reactants, catalyst or product so as not to interfere with the reaction. The corrosion of overhead pipestill may also be successfully inhibited by this invention by direct injection of the additive. In fact, the corrosion of all metallic components in the distillation of crude oil has been extremely troublesome. A variety of methods have been attempted to prevent the corrosion of metallic surfaces by the previously enumerated corrosive agents. However, they have met with little success because of the limited inhibition efficiency of the available inhibitors.

With respect to concentrations of aminophenol which may be utilized, 10^{-5} moles to 2×10^{-1} moles of aminophenol per liter of corrosive solution may be used. Preferably 5×10^{-3} moles to 10^{-1} moles of aminophenol may be utilized and most preferably 10^{-2} moles to 10^{-1} moles of aminophenol may be added to every liter of corrosive solution. The exact amount will be a function of the particular solution and may be determined by one skilled in the art. The aminophenol is added directly and may be mixed by conventional means.

The addition of the aminophenol inhibits corrosion in all metallic constituents of equipment utilized to distill crude oil. Particularly susceptible to this corrosion is the overhead pipestill which may be successfully protected by the instant invention by the previously mentioned injection of aminophenol.

The aminophenol additive prevents corrosion at temperatures of 0° to 350° F. It is effective about 200° F., a temperature where corrosion inhibitors have been extremely ineffective in the past.

In a specific embodiment which is illustrative of the success of the instant invention, aminophenol is added to a ship's hold in which crude oil is transported. The aminophenol is para-aminophenol added in the amount of 5×10^{-3} moles to 10^{-1} moles per liter of crude oil. After a period of several days, essentially no evidence of corrosion was found in areas that had been in contact with the ship's hold. Without the para-aminophenol extensive damage would have been apparent.

EXAMPLE 1

This example illustrates the effectiveness of the use of aminophenols to control corrosion in severe corrosive environments. The protective properties of the inhibitor were evaluated by immersing 1020 carbon steel test panels in HCl solution. The HCl was 0.1 normal (pH=1.0). The temperature of the solution was 25° C.

TABLE I.—PROTECTIVE PROPERTIES OF AMINOPHENOLS TO CONTROL CORROSION OF 1020 CARBON STEEL IN 0.1 N HCl (pH=1.0), 25° C.

Inhibitor concentration moles of inhibitor/ liter of solution	Corrosion rate (mdd.), mgr./dec. ² /day	Percent inhibitor efficiency
Blank.....	1,168	-----
m-Aminophenol:		
1 $\times 10^{-5}$ M.P.L.....	890	23.8
1 $\times 10^{-4}$ M.P.L.....	886	24.1
5 $\times 10^{-3}$ M.P.L.....	361	69.1
1 $\times 10^{-2}$ M.P.L.....	317	72.9
1 $\times 10^{-1}$ M.P.L.....	43.8	96.2
p-Aminophenol:		
1 $\times 10^{-5}$ M.P.L.....	920	21.2
1 $\times 10^{-4}$ M.P.L.....	891	23.7
5 $\times 10^{-3}$ M.P.L.....	877	24.6
1 $\times 10^{-2}$ M.P.L.....	306	73.8
1 $\times 10^{-1}$ M.P.L.....	34.1	97.1

The above table, Table I, indicates that either meta aminophenol brought about satisfactory results when one is desirous of controlling the corrosion of carbon steel. As indicated above, the most preferred range of aminophenol produces very desirable results. Furthermore, 5×10^{-3} M.P.L. of meta aminophenol produces an inhibition of 69.1% whereas 10^{-1} M.P.L. produces 96.2%. Using para-aminophenol at concentrations of 1×10^{-1} M.P.L. produced an inhibitor which was 97.1% effective. The blank produced a corrosion rate of 1168; small amounts of aminophenol such as 1×10^{-5} M.P.L. brought about an inhibition of 23.8%. Thus indicating that a small amount of aminophenol was effective as a corrosion inhibitor although somewhat improved results were obtained with slightly higher concentrations.

EXAMPLE 2

This example illustrates the effect on inhibition efficiency of other groups such as the NO_2 group, methyl, or hydrogen in the place of the hydroxyl group. The inhibition properties of aniline, para toluidine and para and meta nitroaniline are given in Tables II, III and IV, respectively. These tests were run using the same 1020 carbon steel under the same conditions as in Example 1.

TABLE II

Protective properties of aniline to control corrosion of 1020 carbon steel in 0.1 N HCl (pH=1.0), 25° C.

Inhibitor Concentration Moles of Inhibitor/Liter of Solution	Percent Inhibitor Efficiency
Aniline 1 $\times 10^{-4}$ M.P.L.....	7.6
Aniline 5 $\times 10^{-3}$ M.P.L.....	21
Aniline 1 $\times 10^{-2}$ M.P.L.....	34
Aniline 1 $\times 10^{-1}$ M.P.L.....	88.4

TABLE III

Protective properties of p-toluidine to control corrosion of 1020 carbon steel in 0.1 N HCl (pH=1.0), 25° C.

Inhibitor Concentration Moles of Inhibitor/Liter of Solution	Percent Inhibitor Efficiency
p-toluidine 1×10^{-4} M.P.L. -----	7.2
p-toluidine 5×10^{-3} M.P.L. -----	10.3
p-toluidine 1×10^{-2} M.P.L. -----	40.2

TABLE IV

Protective properties of para and meta nitroaniline to control corrosion of 1020 carbon steel in 0.1 N HCl (pH=1.0), 25° C.

Inhibitor Concentration Moles of Inhibitor/Liter of Solution	Percent Inhibitor Efficiency ¹
m-nitroaniline 1×10^{-5} M.P.L. -----	19.3
m-nitroaniline 1×10^{-4} M.P.L. -----	31.3
m-nitroaniline 5×10^{-3} M.P.L. -----	18.7
m-nitroaniline 1×10^{-2} M.P.L. -----	-28.8
m-nitroaniline 1×10^{-1} M.P.L. -----	-29.3
p-nitroaniline 1×10^{-5} M.P.L. -----	15.5
p-nitroaniline 1×10^{-4} M.P.L. -----	22.4
p-nitroaniline 5×10^{-3} M.P.L. -----	-10.8
p-nitroaniline 1×10^{-2} M.P.L. -----	-55.5

¹ Negative number for percent inhibitor efficiency indicates acceleration of corrosion.

A comparison of the data in Tables II, III and IV with these in Table I indicate the superior performance of abinophenols. When utilizing 5×10^{-3} M.P.L. of m-aminophenol, an inhibitor efficiency of 69.1% was achieved. The same quantity of aniline produced an inhibitor efficiency of 34%, 10.3% in p-toluidine, 18.7% in m-nitroaniline and -10.8% in p-nitroaniline.

The corrosion inhibition with 1×10^{-1} M.P.L. of p-aminophenol was 97.1%. Utilizing the same amount of aniline produced only 88.4% efficiency.

Although this invention has been described with some degree of particularity, it is intended to be limited only by the attached claims.

What is claimed is:

1. The method of protecting metal surfaces which are subject to the corrosive action of liquid containing acidic corrosive agents which comprises treating said metal surfaces when in contact with said corrosive agents with an amount of a corrosion inhibitor selected from the group consisting of aminophenol and its C_1 to C_3 alkyl derivatives sufficient to inhibit the corrosion of said metal surfaces.

2. The process of claim 1 in which the metal is carbon steel.

3. The process of claim 2 in which the corrosive agent is hydrochloric acid.

4. The process of claim 2 in which the corrosive liquid is a crude oil.

5. The process of claim 2 in which the corrosive agent is selected from the group consisting of organic and inorganic acids.

6. The method for protecting carbon steel surfaces which are subject to the corrosive action of liquids containing acidic corrosive agents which comprises treating said carbon steel surfaces when in contact with said liquids with from 5×10^{-3} to 10^{-1} moles of para-aminophenol per liter of corrosive liquid.

7. A process for protecting metal surfaces in the cargo area of a ship, said cargo area being utilized to transport crude oil and said metal surfaces being thereby subject to the corrosive action of said crude oil, which comprises treating said metal surfaces when in contact with said

crude oil with from 10^{-5} to 2×10^{-1} moles per liter of crude oil of a corrosion inhibitor selected from the group consisting of aminophenol and its C_1 to C_3 alkyl derivatives.

8. A process for protecting the metal surfaces of an oil pipeline which is subject to the corrosive action of petroleum products carried thereby which comprises treating the metal surfaces of said pipeline when in contact with petroleum products with an amount of aminophenol sufficient to inhibit the corrosion of said metal surfaces.

9. A process for protecting the metal surface in vessels used to store or transport crude oil which comprises treating said metal surfaces when in contact with said crude oil with 10^{-5} to 2×10^{-1} moles of aminophenol per liter of crude oil.

10. A process for protecting the metal surfaces of equipment used for the distillation of crude oil and subject to the corrosive action of said crude oil which comprises treating said metal surfaces when in contact with said crude oil with an amount of aminophenol sufficient to inhibit the corrosion of said metal surfaces.

11. The process of claim 10 in which the aminophenol is selected from the group consisting of para and meta aminophenol.

12. A process for protecting metal surfaces which are subject to the corrosive action of a liquid containing an organic acid which comprises treating said metal surfaces when in contact with said liquid with an amount of para-aminophenol sufficient to inhibit the corrosive effects of said organic acid.

13. A process for protecting metal surfaces which are subject to the corrosive action of a liquid containing an inorganic acid which comprises treating said metal surfaces when in contact with said liquid with an amount of a corrosion inhibitor selected from the group consisting of aminophenol and its C_1 to C_3 alkyl derivatives sufficient to inhibit the corrosive effects of said inorganic acid.

14. The process of claim 13 in which said metal is selected from the group consisting of copper and carbon steel and said inorganic acid is hydrochloric acid.

15. The method for protecting copper and carbon steel surfaces which are subject to the corrosive action of a liquid containing at least one acidic corrosive agent capable of corroding said copper and carbon steel which comprises treating the surfaces of said copper or carbon steel when in contact with said liquid with 10^{-5} to 2×10^{-1} moles per liter of liquid of aminophenol in which at least one of the four remaining unsubstituted carbon atoms is combined with one molecule selected from the group consisting of NH_2 and OH .

16. A process for protecting metallic surfaces selected from the group consisting of copper and carbon steel which are subject to the corrosive action of an acidic corrosive liquid which consists essentially of treating said metallic surfaces when in contact with said liquid of 10^{-5} to 2×10^{-1} moles of aminophenol per liter of liquid.

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