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ACID CORROSION INHIBITING COMPOSITIONS

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No Drawing. Original application Apr. 4, 1960, Ser. No. 19,480, now Patent No. 3,197,403, dated July 27, 1965. Divided and this application Sept. 2, 1964, Ser. No. 394,033

10 Claims. (Cl. 260—294.8)

This application is a division of my application Serial No. 19,480, filed April 4, 1960, now Patent No. 3,197,403.

This invention relates to compositions of matter effective for inhibiting the corrosion of metals by aqueous acid solutions. More particularly, the present invention concerns additives for aqueous solutions of mineral acids capable of inhibiting the corrosive effect of the acid upon ferrous metals. Specifically, this invention relates to corrosion inhibitors of the aforementioned type comprising the reaction products of a mercapto compound and a basic nitrogen-containing compound.

In many industrial practices, the need to contact ferrous metal surfaces with strong acidic agents constantly arises. Particularly under numerous industrial circumstances, equipment fabricated of ferrous metals such as boilers and the like often accumulate scale formations which must be periodically removed in order to maintain the efficiency of the equipment involved. For example, it is common within the petroleum industry to utilize heater tubes in contact with crude oil containing emulsified aqueous solutions of inorganic salts, particularly those of calcium, in order to effect separation of oil and water. The briny solution upon contacting the heated metallic surfaces deposit a substantial portion of their mineral content upon said surfaces in a form of insoluble calcareous formations. Consequently, in order to maintain adequate efficiency of the heaters and to obviate burning out of the heater tubes, it is necessary to remove periodically the scale formations that have formed. The latter is but one example of many of such operations in the petroleum field alone requiring frequent acidizing treatment of various pieces of equipment made of iron or a ferrous alloy. Also in many chemical processes, it is necessary to store or transport acids, such as the common mineral acids, while in contact with ferrous metals. Accordingly, it can be seen that the practical situations necessitating the minimizing or obviating the corrosive effect acidic materials, especially those of mineral origin, upon ferrous metal surfaces are legion.

An object of this invention is to provide novel compositions of matter which are effective metal corrosion inhibitors.

This and other objects of the invention are attained by preparing a heat reaction product of the hereinafter enumerated mercapto compounds with various designated organic compounds containing a basic nitrogen atom.

I am aware that the art has hitherto taught that mercapto compounds as a class, and additionally that various basic nitrogen-containing compounds, are capable of inhibiting ferrous metal corrosion. I have found, however, that when certain members of these respective classes of compounds are combined to yield a heat reaction product, surprising results are obtained in that the resultant products are markedly more effective in arresting corrosion than are either of the reactants from whence they are derived.

As might be expected, the concept of metal corrosion inhibition is a relative one. Thus, the criterion of the effectiveness of a particular material as an inhibitor for acid solutions is whether the material will provide substantially complete protection in relatively small amounts.

In the art directed to the prevention of metal corrosion, it is a practical requisite that any acceptable corrosion arrester be capable of inhibiting in this manner. This is especially so because of the economics encountered in many acidizing operations such as in the conditioning of oil well piping and the like, where it conceivable could be less expensive to use thicker casings as opposed to using large amounts of a chemical inhibitor in the acidizing solution. In this respect, all of the novel inhibitor compositions of the present invention are extremely effective in that they will substantially obviate corrosion of ferrous metals even in the presence of comparatively strong acid solutions in very small amounts, oftentimes in amounts of 1% or less based on the total weight of the acid solution.

The mercapto compounds useful for preparing the inhibitors in accordance with this invention are: thiol acetic acid, mercapto succinic acid, toluene thiol and orthomercapto benzoic acid. The applicable toluene thiols can be any of the isomeric configurations than can be attributed to this substance. However, with regard to the mercapto benzoic acid, it is preferred that the functional substituents, that is, the carboxylic acid and mercapto groups be in ortho relationship to one another.

The organic nitrogen compounds contemplated as suitable reactants for the mercapto compounds enumerated above include various basic nitrogen-containing compounds. Suitable among such compounds are the various 2-alkyl-pyridines. Of the applicable alkyl pyridines, the alkyl group should be in the ortho position relative to the ring nitrogen. The alkyl substituents of the applicable pyridines contain from 4 to 12 carbon atoms. Obviously, mixtures of the various pyridines mentioned may be satisfactorily used. In pointing up the critical nature of each of the types of reactants specifically contemplated herein, it is mentioned that a product derived by reacting picoline, or any of the picolines for that matter, with the mercapto-compounds will not yield satisfactory inhibitors. As a matter of fact, certain of the reaction products of a picoline with one or another of the mercapto compounds contemplated will yield products which accelerate corrosion of ferrous metals in the presence of mineral acids.

Another suitable class of nitrogen compounds is represented by a series of aliphatic polyamines. I have determined that there is no restriction with respect to the molecular structure of this particular class of nitrogen compounds as was observed for the class of pyridines mentioned. However, especially preferable among the polyamines are those compounds corresponding to the following formula:

$$H_2N—CH_2CH_2—(NH—CH_2—CH_2)_n—NH_2$$

wherein n is an integer preferably 3 or greater. Specific examples of this series of aliphatic polyamines are such as: triethylene tetramine, tetraethylene pentamine, pentaethylene hexylamine, etc.

Particularly suitable nitrogenous materials corresponding generally to the above-given formula are the bottoms fraction obtained in the commercial manufacture of the polyamines specifically identified above.

Another class of applicable aliphatic polyamines are the diamines corresponding to the following general formula:

$$(C_nH_{2n+1})—NH—(CH_2)_3—NH_2$$

wherein n represents an integer from about 12 to 18. Exemplary of such diamines are the products manufactured by the Armour Chemical Division of Armour Company under the trademark Duomeen. These products are fatty diamines of the general formula:

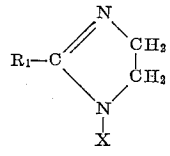
$$\begin{matrix} R \\ | \\ HN(CH_2)_3NH_2 \end{matrix}$$

wherein the R represents an alkyl group derived from a fatty acid which is identified as follows:

Duomeen 12; lauric; M.W.=242
Duomeen C; coconut; M.W.=257
Duomeen S; soya; M.W.=321
Duomeen T; tallow; M.W.=320

Alkyl substituted mono amino benzene (aniline) likewise may be used to react with the mercapto compounds set forth hereinabove. The alkyl group of this type of basic nitrogen-containing compound preferably has from 1 to 6 carbon atoms. As in the case with the pyridine derivatives, the alkyl substitutents of the amino benzene is preferably attached at the ortho position relative to the amino substituent.

Still another class of suitable basic nitrogen-containing compounds is the imidazolines, as represented by the following general formula:



wherein R_1 is either an alkyl or an alkenyl group preferably containing from about 12 to 22 carbon atoms and x represents a substituent containing a replaceable or reactive hydrogen such as hydroxy, amino or imino. These heterocyclic nitrogen bases may be readily prepared by various methods known to those skilled in the art. A particularly preferred method of preparing these compounds consists of reacting a substituted ethylene amine such as aminoethylethanolamine, ethylene diamine, diethylene triamine, etc., with one of the higher fatty acids such as for example, oleic, stearic, or coconut oil fatty acids, etc.

The inhibiting compositions contemplated herein as previously mentioned are the reaction products of a mercapto compound such as described with any one of the organic basic nitrogen-containing compounds enumerated hereinabove. The reaction involved is essentially the formation of a salt of the mercapto compound and the organic nitrogen compound which can be readily accomplished simply by heating these respective reactants at elevated temperatures for various lengths of time. Applicable reaction temperatures range from as low as 65° C. to 200° C. or even higher. The upper limit of temperature is primarily dictated by the volatility of the particular types of reactants utilized. I have found that a particularly suitable temperature at atmospheric conditions is in the order of 150° C. The time required to effect reaction or salt formation also can be varied over wide limits depending upon the particular temperature utilized, the nature of the specific reactants among other factors and can be noted in most instances when there is a subsidence of evolved gases. Accordingly, a suitable time ranges from about 30 minutes to 4 hours or even longer.

As indicated, the primary reaction involved in preparing the inhibitors of this invention is generally that of salt formation. However, I cannot be sure whether a limited degree of another type or types of reactions occur, and in some instances the main reaction that takes place is not clearly understood. Accordingly, I prefer to empirically refer to the reaction product as being one which is heat induced in view of the fact that in many instances the resultant product defines precise chemical characterization. This is obviously particularly so say where one of the reactants consists of undetermined composition such as the organic nitrogen materials derived from still bottoms in the preparation of polyamines.

Suitable amounts of the respective reactants is represented by approximately equal molar amounts. However, this relation can be varied extensively depending, for instance, upon the number of functional groups contained by either of the reactants. Thus, where the organic nitrogen compound contains a plurality of amino substituents

and the mercapto reactant is mono functional, a relatively high molar ratio of mercapto reactant to amino compound can be employed. Conversely, when a mercapto compound such as mercapto succinic acid is reacted with an appropriate pyridine, smaller molar ratios of the acid with respect to the base can be used. With these considerations in mind, the proportions of the respective reactants usually range from about 0.7 to 0.3 mole of the mercapto compound and correspondingly from about 0.3 to 0.7 mole of the organic nitrogen compound.

In order to further show those skilled in the art how the present invention is practiced, the following specific examples are given in which all parts are parts by weight unless otherwise indicated. These examples are given primarily by way of illustration and any enumeration of details contained therein should not be interpreted as a limitation on the invention except as indicated in the appended claims.

EXAMPLE I

Into a suitable reaction vessel equipped with a thermometer, stirrer and a provision for venting to the atmosphere were charged equi-molar amounts of thiol acetic acid and a mixture of alkyl pyridines, the alkyl substituents of the latter ranging in carbon chain length from 4 to 12, with an indicated average of 6.

With stirring, the mixture was heated to about 80° C. and held in the order of this temperature for approximately one hour. The reaction mixture was then discharged from the reaction vessel and cooled to room temperature. The product upon cooling was a viscous liquid capable of being readily dissolved in acidic aqueous systems.

EXAMPLE II

Into a reaction vessel equipped as in Example I were charged one part of mercapto succinic acid and one part of an alkyl pyridine mixture identical in composition to that utilized in Example I.

The charged ingredients were rapidly heated to 150° C. and held at this temperature with stirring for approximately 1½ hours, whereupon the reaction product was discharged from the vessel and allowed to cool to room temperature.

EXAMPLE III

Into a suitable reaction vessel equipped as in Example I were charged one part of mercapto succinic acid and one part of 2-heptadecenyl-1-hydroxyethyl imidazoline. The charged ingredients were heated to 150° C. and held at that temperature was stirring for 2 hours. The reaction product was then discharged from the vessel and cooled to room temperature and designated inhibitor III*a*.

An inhibitor was prepared in a similar manner as above from one part of toluene thiol and one part of 2-heptadecenyl-1-hydroxyethyl imidazoline and was designated inhibitor III*b*.

An inhibitor made following the procedure outlined initially in this example from one part of o-mercaptobenzoic acid and one part of the above imidazoline was designated inhibitor III*c*.

EXAMPLE IV

An inhibitor was made in substantially the manner indicated in the previous examples by reacting one part of a polyamine corresponding generally to the following formula:

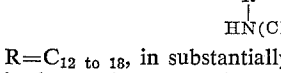
$$H_2N—CH_2CH_2—(NH—CH_2CH_2)_n—NH_2$$

when n represents an integer between about 3 and 6 obtained as a bottoms fraction in the manufacture of polyamines and one part of toluene thiol. The resultant reaction product was designated inhibitor IV*a*.

Another inhibitor (IV*b*) was prepared by reacting one part of the polyamine of this example with one part of o-mercaptobenzoic acid.

EXAMPLE V

An inhibitor composition was prepared by reacting one part of toluene thiol with one part of a diamine mixture corresponding to the following formula:



$R = C_{12 \text{ to } 18}$, in substantially the same manner described in the previous example.

EXAMPLE VI

A heat reaction product (50 minutes at 110° C.) was prepared substantially in accordance with the procedure set forth in the previous examples from one part of toluene thiol and one part of mixed toluidines consisting predominantly of o-toluidine.

EXAMPLE VII

Equal parts of a mixture of picolines (o, m, p) and o-mercapto succinic acid were reacted at about 90° C. for approximately one hour.

EXAMPLE VIII

This example illustrates the effectiveness of the various reaction compositions described in the previous examples as acid corrosion inhibitors. The test for corrosion efficiency was determined by utilizing an aqueous hydrochloric acid solution obtained by diluting 37.5° HCl with 5% aqueous NaCl solution in a ratio of 50:50 respectively. To various portions of the solution was added 1% by weight of the reaction products described in the previous examples. Into each inhibited solution was submerged a freshly abraided 1020 mild steel coupon of a predetermined area (1" x 8" by about ⅛"). Each coupon was exposed in the respective solution for one hour in a static condition. At the end of the exposure period, the coupon was removed, cleaned, dried, and weighed. After the weight of the exposed coupon was ascertained, a calculation for determining the effectiveness of the particular inhibitor expressed in terms of percent protection was made. The basis for these determinations was that corrosion (loss of weight) observed for a coupon exposed in a similar manner in an uninhibited acid solution, which basis was considered to be 0.0% protection.

Table I

Inhibitor	Inhibitor Composition	Percent Protection
Example I	Thiol acetic acid—alkyl pyridine	93
Example II	Mercapto succinic acid—alkyl pyridine	88
Example III*a*	Mercapto succinic acid—imidazoline	91
Example III*b*	Toluene thiol—imidazoline	90
Example III*c*	o-mercapto-benzoic acid—imidazoline	94
Example IV*a*	Toluene thiol—polyamine	93
Example IV*b*	o-mercapto-benzoic acid—polyamine	91
Example V	Toluene thiol—diamine	94
Example VI	Toluene thiol—mixed toluidines	98
Example VII	o-mercapto-benzoic acid—picoline	−15

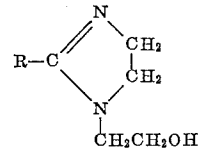
We claim:

1. A metal corrosion inhibiting composition comprising the product obtained by reacting at a temperature between 65° C. and 200° C. from 0.7 to 0.3 mole of a mercapto compound selected from the group consisting of thiol acetic acid, mercapto succinic acid, toluene thiol, and o-mercapto-benzoic acid, with correspondingly from 0.3 to 0.7 mole of an organic nitrogen compound selected from the group consisting of a 2-alkyl-pyridine, the alkyl group of which contains from 4 to 12 carbon atoms, an o-alkyl-aniline the alkyl group of which contains from 1 to 6 carbon atoms, a polyethylene polyamine, a N-alkyl-trimethylene-diamine in which the alkyl group is derived from a fatty acid, and an imidazoline substituted in the number one position with an aliphatic group containing a radical selected from the class consisting of hydroxy, amino and imino and substituted in the number two position with a C_{12}–C_{22} hydrocarbon group selected from the class consisting of alkyl and alkenyl.

2. A metal corrosion inhibiting composition according to claim 1 wherein said mercapto compound is thiol acetic acid and said organic nitrogen compound is a 2-alkyl-pyridine containing from 4 to 12 carbon atoms in the alkyl substituent.

3. A metal corrosion inhibiting composition according to claim 1 wherein said mercapto compound is o-mercapto succinic acid and said organic nitrogen compound is a 2-alkyl-pyridine containing from 4 to 12 carbon atoms in the alkyl substituent.

4. A metal corrosion inhibiting composition according to claim 1 wherein said mercapto compound is o-mercapto succinic acid and said organic nitrogen compound is an imidazoline corresponding to the following formula:



in which R is a member selected from the group consisting of alkyl and alkenyl radicals containing from 12 to 22 carbon atoms.

5. A metal corrosion inhibiting composition according to claim 1 wherein said mercapto compound is toluene thiol and said organic nitrogen compound is a 2-alkyl-pyridine containing from 4 to 12 carbon atoms in the alkyl substituent.

6. A metal corrosion inhibiting composition according to claim 1 wherein said mercapto compound is toluene thiol and said organic nitrogen compound is a polyamine corresponding to the following formula:

$$H_2N—CH_2CH_2—(NH—CH_2CH_2)_n—NH_2$$

where n represents an integer greater than 2.

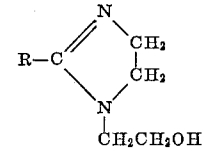
7. A metal corrosion inhibiting composition according to claim 1 wherein said mercapto compound is toluene thiol and said organic nitrogen compound is a diamine corresponding to the following formula:

$$(C_nH_{2n+1})—NH—(CH_2)_3—NH_2$$

where n represents an integer greater than 15 but less than 19.

8. A metal corrosion inhibiting composition according to claim 1 wherein said mercapto compound is toluene thiol and said organic nitrogen compound is o-toluidine.

9. A metal corrosion inhibiting composition according to claim 1 wherein said mercapto compound is o-mercapto-benzoic acid and said organic nitrogen compound is an imidazoline corresponding to the following formula:



in which R is a member selected from the group consisting of alkyl and alkenyl radicals containing from 12 to 22 carbon atoms.

10. A metal corrosion inhibiting composition according to claim 1 wherein said mercapto compound is o-mercapto-benzoic acid and said organic nitrogen compound is a polyamine corresponding to the following formula:

$$H_2N—CH_2—CH_2—(NH—CH_2CH_2)_n—NH_2$$

where n represents an integer greater than 2.

No references cited.

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