United States Patent [19]

Hayman, Jr.

[11] **3,819,527**

[45] **June 25, 1974**

[54] **COMPOSITION AND METHOD FOR INHIBITING ACID ATTACK OF METALS**

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[22] Filed: **Nov. 6, 1972**

[21] Appl. No.: **303,956**

[52] **U.S. Cl.** **252/149**, 252/148, 252/151, 252/391

[51] **Int. Cl.** **C11d 7/34**

[58] **Field of Search** 252/148, 149, 151, 391; 134/3

[56] **References Cited**

UNITED STATES PATENTS

1,719,649	7/1929	Chamberlain	252/148
2,049,517	8/1936	Saukaitis	252/149
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2,959,555	11/1960	Martin et al.	252/149
3,668,137	6/1972	Gardner	252/149

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Assistant Examiner—Harris A. Pitlick
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[57] **ABSTRACT**

A composition comprising a cyclic trimer of methylene ortho-toluidine, thiourea, and a sulfonium salt for use in an acidic aqueous composition for the purpose of inhibiting acid attack on metallic surfaces which are contacted with the acidic composition.

18 Claims, No Drawings

COMPOSITION AND METHOD FOR INHIBITING ACID ATTACK OF METALS

FIELD OF THE INVENTION

This invention relates to reducing the attack of acid on metals which are contacted with an acidic aqueous composition. More particularly, this invention relates to a composition and its use in an acidic aqueous solution for the purpose of inhibiting or reducing the tendency of acid attack of metallic surfaces which are subjected to the acidic aqueous solution.

There are many applications in which a metallic surface is contacted with an acidic aqueous composition. For example, it is known to utilize acidic aqueous compositions for the purpose of cleaning or pickling metallic surfaces to remove therefrom unwanted oxide scales and other undesirable corrosion products or unwanted deposits. Another example of such an application is the use of metallic conduits to convey acidic compositions.

In such applications, it is known to add inhibitory compositions to the acid composition for the purpose of inhibiting acid attack on the metallic surfaces that are contacted with the acidic composition. The inhibitory composition functions to reduce or prevent the tendency of the acid to corrode, degrade or otherwise attack the metallic surface without adversely affecting the desired properties of the acidic composition. Materials which so function generally are referred to as "acid inhibitors."

This invention relates to an acid inhibitor composition and to its use.

REPORTED DEVELOPMENTS

Examples of acid inhibitors are disclosed in the following U.S. Pat. Nos. 2,758,970; 2,807,585; 2,941,949, 3,077,454 and 3,668,137. Acid inhibitors disclosed in the aforementioned patents include nitrogen-containing compounds, triphenyl sulfonium chloride, and acetylenic alcohols. These acid inhibitors are a few examples of the many that are known. Some examples of other known inhibitors are arsenic compounds, thioureas, heterocylic compounds containing sulfur and/or nitrogen, such as mercapto benzothiazole and Schiff's bases, and aldehydes, such as formaldehyde and benzaldehyde. Mixtures of such acid inhibitors have been used also.

There are various problems encountered in the manufacture or use of heretofore known acid inhibitors. The present invention is directed to the provision of an acid inhibitor that can be prepared readily from relatively low cost ingredients that are readily available, and an acid inhibitor that has excellent acid inhibiting properties.

It is an object of this invention to provide an improved acid inhibitor.

It is still another object of this invention to provide an acidic composition comprised of an acid of the type that attacks metals and an improved acid inhibitor which inhibits the tendency of the acid to attack metals which are contacted with the composition.

An additional objective of this invention is to provide an improved process for reducing acid attack on metallic surfaces by acidic compositions which come into contact therewith.

SUMMARY OF THE INVENTION

In accordance with this invention, there is provided a composition comprising a cyclic trimer of methylene orthotoluidine, thiourea, and a sulfonium salt which composition can be used in an acidic aqueous composition for the purpose of inhibiting acid attack on metallic surfaces which are contacted therewith.

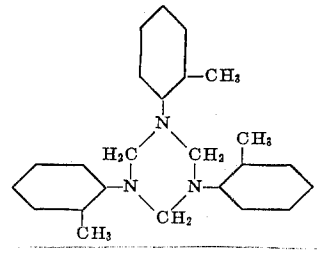
Generally speaking, the acid inhibitor composition of this invention, which can contain optional ingredients and additives, can be used in any application in which it is desired to prevent acid attack of metals. This includes applications wherein an acidic cleaning solution is utilized to clean or rid metallic surfaces of oxide scales and other undesired deposits and corrosion products. It includes also applications wherein an acidic solution comes into contact with a metallic conduit during use.

DETAILED DESCRIPTION OF THE INVENTION

In preferred form, the acid inhibitor composition of this invention comprises an aqueous solution containing the following ingredients in the amounts indicated.

Ingredients	Approximate Amounts, Wt. %	Preferred Approximate Amounts, Wt. %
cyclic trimer of methylene ortho-toluidine	30–60	40–50
thiourea	1–15	1–5
sulfonium salt	0.5–25	1–5

The cyclic trimer of methylene ortho-toluidine is prepared by reacting formaldehyde and o-toluidine to form a Schiff's base, namely, methylene o-toluidine. This Schiff's base which is unstable forms the cyclic trimer of methylene ortho-toluidine having the formula



Formula 1

Thiourea or substituted thioureas, such as alkyl substituted thioureas wherein the alkyl groups contain about one to about four carbon atoms, is also an essential ingredient of the acid inhibitor of the present invention. The term "thiourea" when used herein includes within its meaning thiourea and substituted thioureas.

The third essential component of the inhibiting composition of this invention is a sulfonium salt of the formula

Formula 2

wherein R^1, R^2, and R^3 are each hydrocarbon radicals, such as for example, those selected from the group consisting of alkyl, aryl and aralkyl and wherein X is an acid anion, preferably an anion of a strong mineral acid. Formula 2 above includes within its scope compounds wherein said R^1, R^2 and R^3 radicals are the same radicals or are different radicals.

Formula 2 above includes also compounds wherein one or more of the said R^1, R^2 and R^3 radicals contain one or more of the same or different substituents, examples of which include hydroxy, halo and alkyl groups.

Examples of the radicals R^1, R^2 and R^3 of Formula 2 above are propyl, nonyl, dodecyl, isobutyl, phenyl, hydroxy-phenyl, dodecyl phenyl, benzyl and 4-hydroxy-3,5-dimethylphenyl. It is preferred that at least one of the aforesaid R^1, R^2 and R^3 radicals be aryl or aralkyl and most preferably, each of said radicals is aryl, such as for example phenyl or p-chlorophenyl.

Examples of X, the acid anion, in Formula 2 above, are chloride, bromide, iodide and sulfate, the first mentioned being preferred.

Sulfonium salts and methods for their preparation are known. For example, they can be prepared by the reaction of an aromatic hydrocarbon with a sulfur monohalide in the presence of anhydrous aluminum chloride and a halogen.

Triphenyl sulfonium chloride is the preferred sulfonium salt for use in this invention.

The foregoing description has been concerned with those ingredients which are essential components of the composition of this invention. A composition containing said ingredients is effective as an acid inhibitor. However, it is preferred that additives be combined with the aforementioned essential ingredients in order to increase the overall effectiveness of the inhibiting composition. Such additives include materials which function as foaming agents and which increase the solubility of one or more of the essential ingredients of the composition. In general, these additives are surface active agents and solvents for the components comprising the composition. Any surface active agent compatible with the other components of the composition can be used including cationic and nonionic surface active agents with the last mentioned being preferred. Examples of such additives are non-ionic surface active agents, such as ethoxylated secondary alcohols and ethoxylated nonyl phenols and related compounds, such as thiols, and polar solvents such as alcohols, for example the lower alcohols, such as methanol and isopropanol.

Additives, such as those described above, have been used previously with acid inhibitors and the amounts employed in the composition of this invention can be determined readily from past experience. In general, the total amount of additives present in the composition should be no more than about 20 percent.

In utilizing the composition of this invention to inhibit acid attack on metal, the composition is added to the particular acidic composition utilized in an amount effective to inhibit the attack of the acid on the metal which is exposed to the acid. The amount of inhibiting composition that will be effective to the extent desired will vary depending on a number of conditions. Such conditions include the particular components and amounts comprising the inhibiting composition, the particular acidic composition (including concentration) that is utilized, the type of metal cleaning operation or acidizing operation that is being performed and also the particular metal which is being subjected to said operations.

In view of the various applications and conditions under which the inhibiting composition of this invention can be used, it will be appreciated that the most effective amount should be determined from experience gained in using the composition in a particular application. For guidance purposes, it is noted that it has been observed that generally good results can be obtained by adding the inhibiting composition to an acidic composition in an amount such that the inhibiting composition comprises from about 0.01 percent to about 5 percent by weight of the total weight of the inhibitor-containing acid composition and preferably from about 0.025 percent to about 1 percent by weight.

If less than about 0.05 percent inhibitor is employed then the desired inhibiting effect, particularly when it is used with the more concentrated acids, is not as apparent. If more than about 5 percent of the inhibiting composition is employed, the inhibiting properties seem to increase very slightly over that observable when the inhibiting composition comprises about 4.5 percent to about 5 percent. Indeed, it has been observed that about 1 percent of the inhibiting composition gives maximum inhibition in many applications.

The inhibitor composition of this invention can be employed in any application where, for example, it is desired to inhibit the attack of an acid on metals, including particularly metal cleaning operations. The inhibiting composition of this invention can be utilized with hydrochloric acid or other of the metal cleaning or pickling acids — the so-called non-oxidizing acids. Included in this category are inorganic acids such as phosphoric, sulfamic and sulfuric and organic acids such as acetic, citric, formic, glycolic and oxalic. The acid inhibitor of the present invention performs particularly well in sulfuric acid pickling solutions.

Of the various types of metal that can be protected from acid attack by utilizing the acid inhibitor of this invention, particularly effective results have been obtained for iron and steel. However, the acid inhibitor can also be utilized to protect from acid attack other metals such as for example, copper, brass, bronze and other alloys such as stainless steel.

EXAMPLES

The following examples are illustrative of compositions within the scope of the present invention.

Ingredients	Amounts, % by Weight Example 1	Example 2	Example 3	Example 4
cyclic trimer of methylene ortho-toluidine	35%	41%	48%	58%
thiourea	5%	5%		12%
diethyl thiourea			4%	

-Continued

Ingredients	Amounts, % by Weight Example 1	Example 2	Example 3	Example 4
triphenyl sulfonium chloride	15%	2%	4%	10%
nonionic surfactant	1%	2%	15%	1%
water	44%	50%	29%	19%

The aqueous solution of the acid inhibitor of Example 2 above is used in a pickling bath containing 10 percent by volume of 66° Be H_2SO_4. The acid inhibiting solution was added to the pickling bath in an amount of 0.5 percent by volume of the 66° Be H_2SO_4. A metallic panel of 1010 hot rolled steel having an area of 10 sq. inches is immersed in the pickling bath containing the acid inhibitor for 30 minutes. The temperature of the pickling bath is maintained at 180°F. Prior to immersing the panel in the bath, it is weighed, and after the panel is withdrawn from the bath it is rinsed, dried and reweighed to determine metal loss. For comparative purposes, another test panel of the same type is immersed in the same pickling bath except that it does not contain an acid inhibitor. Upon comparing the weight losses of both panels, it is found that the panel subjected to the pickling bath that contained no acid inhibitor lost almost 65 times more weight than the panel subjected to the bath that contained the acid inhibitor of Example 2. Other calculations show that the panel subjected to the pickling bath containing the acid inhibitor of Example 2 lost about 0.2 percent of its weight whereas the panel subjected to the pickling bath containing no acid inhibitor lost about 14 percent of its weight.

It has been found that the acid inhibitors of the present invention have excellent stability in acidic aqueous compositions. The acid inhibitors can be prepared readily and exhibit excellent acid inhibiting properties.

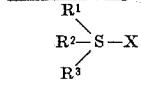
I claim:

1. An aqueous solution consisting essentially of, in weight percent based on the total weight of the solution:

a. about 30 to about 60 percent of a cyclic trimer of methylene ortho-toluidine;

b. about 1 to about 15 percent of a thiourea compound selected from the group consisting of thiourea and substituted thiourea having alkyl groups of from one to about four carbon atoms; and

c. about 1 to about 25 percent of a sulfonium salt having the formula:



wherein R^1, R^2, and R^3 are hydrocarbon radicals selected from the group consisting of alkyl, aryl and aralkyl and wherein X is an acid anion.

2. A solution according to claim 1 wherein said ingredients are present in the amounts of:

a. about 40 to about 50 percent of said cyclic trimer of methylene ortho-toluidine;

b. about 1 to about 5 percent of said thiourea compound; and

c. about 1 to about 5 percent of said sulfonium salt.

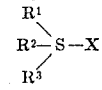
3. A solution according to claim 1 wherein said thiourea compound is $NH_2—CS—NH_2$ and wherein said sulfonium salt is triphenyl sulfonium chloride.

4. A solution according to claim 2 wherein said thiourea compound is $NH_2—CS—NH_2$ and wherein said sulfonium salt is triphenyl sulfonium chloride.

5. A solution according to claim 1 wherein said thiourea compound is diethyl thiourea and said sulfonium salt is triphenyl sulfonium chloride.

6. A solution according to claim 2 wherein said thiourea compound is diethyl thiourea and said sulfonium salt is triphenyl sulfonium chloride.

7. A method for inhibiting acid attack of metallic surfaces comprising contacting a metallic surface with an acidic aqueous composition comprising a non-oxidizing acid of the type that tends to attack metals which are contacted therewith and, in acid inhibiting amounts, an inhibitor composition consisting essentially of about 30 to about 60 wt. percent of a cyclic trimer of methylene ortho-toluidine, about 1 to about 15 wt. percent of a thiourea compound selected from the group consisting of thiourea and substituted thioureas having alkyl groups of from one to about four carbon atoms, and about 1 to about 25 wt. percent of a sulfonium salt having the formula:



wherein R^1, R^2, and R^3 are hydrocarbon radicals selected from the group consisting of alkyl, aryl and aralkyl and wherein X is an acid anion.

8. A method according to claim 7 wherein said inhibitor composition consists essentially of about 40 to about 50 wt. percent of a cyclic trimer of methylene ortho-toluidine, about 1 to about 5 wt. percent of thiourea and about 1 to about 5 wt. percent of triphenyl sulfonium chloride.

9. A method according to claim 7 wherein said inhibitor composition consists essentially of about 40 to about 50 wt. percent of a cyclic trimer of methylene ortho-toluidine, about 1 to about 5 wt. percent of diethyl thiourea and about 1 to about 5 wt. percent of triphenyl sulfonium chloride.

10. A method according to claim 8 wherein said acid is sulfuric acid.

11. A method according to claim 9 wherein said acid is sulfuric acid.

12. A method according to claim 9 wherein said inhibitor composition consists essentially of about 40 to about 50 wt. percent of said cyclic trimer of methylene orthotoluidine, about 1 to about 5 wt. percent of said thiourea compound, and about 1 to about 5 wt. percent of said sulfonium salt.

13. A method according to claim 12 wherein said acid is sulfuric acid.

14. An acidic aqueous solution containing a non-oxidizing acid of the type that tends to attack metallic surfaces and, in an amount at least sufficient to reduce said acid attack of said metallic surface, the composition of claim 1.

15. An acidic aqueous solution containing a non-oxidizing acid of the type that tends to attack metallic

surfaces and about 0.01 to about 5 percent by weight of an aqueous solution consisting essentially of:

a. about 40 to about 50 wt. percent of a cyclic trimer of methylene ortho-toluidine;

b. about 1 to about 5 wt. percent of thiourea or diethyl thiourea; and

c. about 1 to about 5 wt. percent of triphenyl sulfonium chloride.

16. A composition according to claim **15** wherein said aqueous solution is present in an amount of about 0.025 to about 1 percent by weight of the composition.

17. A composition according to claim **15** wherein said acid is sulfuric acid.

18. A composition according to claim **16** wherein said acid is sulfuric acid.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,819,527 Dated June 25, 1974

Inventor(s) Edgar S. Hayman, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In THE CLAIMS

Claim 12, line 1, "claim 9" should read --claim 7--.

Signed and sealed this 15th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

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Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
U.S. GOVERNMENT PRINTING OFFICE 869-930

UNITED STATES PATENT OFFICE

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FORM PO-1050 (10-69)

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