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3,458,354

# METHOD OF REMOVING COPPER-CONTAINING SCALE FROM METAL SURFACES

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## ABSTRACT OF THE DISCLOSURE

A method of removing copper-containing iron oxide incrustation from a metal surface employing a scale-removing material without redeposition of copper thereon nor objectionable decomposition of said material, which consists in bringing into contact with such surface an aqueous solution having dissolved therein between about 2 and 70 percent by weight of sulfuric acid, preferably an inhibitor to the corrosivity of acid to metal, and an alkenylthiourea wherein said alkenyl group contains between 2 and 6 carbon atoms per molecule, the amount of the alkenylthiourea being about 4 and about 40 pounds per pound of copper in the incrustation, said aqueous solution being maintained in contact with the incrustation for a time sufficient to solubilize substantially the incrustation.

This application is a continuation-in-part of S.N. 290,644, filed June 26, 1963 now abandoned.

The invention relates to the removal of scale from metal surfaces and especially to the removal of scale comprising iron oxide incrustations containing copper, of the nature commonly formed on the internal surfaces of tubes, pipes, casing, tanks, boilers, heat exchangers, and the like. The term "vessels" will be used hereinafter to designate any of the above or similar storage, transfer, cooling or heating containers or conduits.

The formation of tenaciously adhering scale on the interior surfaces of vessels, of which a number are mentioned above, has been a source of trouble in the employment of such vessels. The formation or deposition of scale markedly reduces the heat transfer through the walls of such vessels. Accordingly, greater heat must be provided to the vessel walls, thereby often subjecting the metal to excessive heat. Furthermore, the capacity of scale-incrusted vessels is reduced and flowage or passage therethrough is restricted by the presence of the scale. Accordingly, more pressure is applied to the contained fluid in attempting to maintain the original through-put. The metal of which the containers are made, due to the scale formation on the surfaces thereof, is therefore subjected to greater strain due to the increased pressure. The metal itself deteriorates more rapidly because of the corrosive effect of scale adhered thereto. These conditions often lead to leaks and ruptures which necessitate undesirable down-time and increased maintenance costs.

As a natural consequence of the bad effects of scale, efforts to remove it satisfactorily from various types and shapes of vessels (of the type suggested) have been rather numerous. Although a great many efforts have been more-or-less fruitless in a practical sense, some efforts have met with an encouraging degree of success. A particularly successful effort is that described in U.S. Patent 2,959,555, wherein a copper-containing iron oxide incrustation on a ferrous metal surface is removed by subjecting the incrustation to the action of a suitable acid solution in which is dissolved thiourea or one of the following derivatives of thiourea: 1,3-dimethylthiourea, ethylenethiourea, and 1,3-diisopropylthiourea. Although the removal of the scale,



by the practice of the above-identified patent, has been highly successful in a broad sense, under some circumstances, e.g., where an advanced temperature for the descaling operation is required, some of the thiourea compounds undergo limited decomposition which is undesirable. It has also been found less effective than is desired when used in sulfuric acid cleaning or descaling compositions.

The principal object of the present invention is to provide an improved method of removing copper-containing iron oxide incrustations from metal surfaces, particularly from ferrous and copper metal surfaces and particularly when employing a descaling composition containing $H_2SO_4$ and more particularly at advanced temperatures such are often encountered in boiler cleaning jobs.

The manner of attaining this and related objects is made clear in the ensuing description and is defined in the appended claims.

According to the present invention, a copper-containing iron oxide incrustation on a ferrous metal surface, e.g., such as that of any of the vessels mentioned above, and particularly from steam generating boilers, is removed by subjecting the incrustation to the action of an aqueous solution of sulfuric acid and a small but effective amount of a monoalkenylthiourea, e.g., 1-butenyl-2-thiourea or 1-allyl-2-thiourea, or mixture of such alkenylthiourea. 1-allyl-2-thiourea is sometimes known as thiosinamine. The alkenyl group may contain from 2 to 6 carbon atoms per molecule.

It is recommended that an inhibitor to the corrosivity of acids on metal be admixed with the aqueous solution of $H_2SO_4$ and alkenylthiourea.

Methods of preparing an alkenylthiourea such as 1-allyl-2-thiourea are known. One method consists essentially of reacting allyl chloride with ammonium thiocyanate to yield allyl isothiocyanate. The allyl isothiocyanate so produced is then reacted with ammonia to yield the allylthiourea.

The amount of the monoalkenylthiourea to employ in the practice of the invention should be not less than about 4 pounds thereof per pound of copper contained in the incrustation sought to be removed. The maximum amount of the monoalkenylthiourea to employ is not highly critical, being largely guided by economic considerations. An amount in excess of 40 pounds per pound of copper in the scale to be removed is not generally employed. The preferred amount of the alkenylthiourea to employ in the practice of the invention is between about 6 and about 12 pounds per pound of copper to be removed.

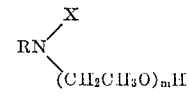
A convenient technique for ascertaining the amount of the alkenylthiourea to employ in the practice of the invention is to procure a small sample of the scale to be removed, analyze it for its copper content, and calculate the weight of the alkenylthiourea to employ dependent upon the amount of copper present in the scale. The invention is usually carried out at a somewhat advanced temperature because the action of the composition employed is more rapid at such temperature. The preferred temperature range to employ is between about 100° and 200° F., although temperatures as low as 40° and 50° F. may be used. Temperatures in excess of about 200° F. are not recommended. The concentration of the sulfuric acid solution may be from about 2 to about 70 percent but is preferably between about 5 and about 15 percent. The amount of the inhibitor employed is usually between 0.1 and 1.0 percent by weight of the aqueous acidic solution.

Any of the known inhibitors to the corrosivity of acids may be employed. Among such inhibitors are those containing a bound nitrogen atom, which may be considered as being a substituted ammonia compound of which the primary, secondary and tertiary aliphatic and aromatic amines and substituted amines are illustrative. Such in-

hibitors are commonly referred to as amine-type inhibitors and reference to them as such is sometimes made hereinafter.

Among amine-type inhibitors are any of those set out in the above-identified patent, e.g., pyridine, alpha-picoline, beta-picoline, gamma-picoline, 2-n-amylpyridine, 4 - n-amylpyridine, 2-hexylpyridine, 2,4-lutidine, 2,6-lutidine, 2,4,6-collidine, quinoline, lepidine, and quinaldine. An amine-type inhibitor may be considered to be any amine or amine derivative which inhibits the corrosive action of an acid on metal (e.g. as described under amines in chapter 10, page 224 et seq. of Organic Chemistry, third edition by Fieser and Fieser (1956), published by Reinhold Publishing Company, New York or under the term "amino" as defined on pages 43 to 45 in Hackh's Chemical Dictionary, third edition (1944), published by the McGraw-Hill Book Company, Inc., New York.

Other inhibitors than amine-type are useful in the practice of the invention. Inhibitors to the corrosivity of acid on metal described in other U.S. patents which are effective in sulfuric acid to inhibit attack on iron and steel are the following materials which are described in the U.S. patents set out opposite the inhibitor below:

| Inhibitor to Corrosion | U.S. patents in which described |
|---|---|
| $H_3AsO_4$; $As_2O_3$; S; organic nitrogen bases, e.g. aniline or pyridine | 1,877,504 |
| Propargyl sulfide | 2,880,180 |
| 2-(2-propynyloxy)tetrahydropyran | 2,952,509 |
| Synergistic mixture of propargyl sulfide and one or more of ethanedithiol, thiolacetic acid, mercaptoacetic acid, ethyl sulfide, hydrogen sulfide, or ferrous sulfide | 2,963,439 |
| One or more of 2-furfurylmethanethiol, 1,2-ethanedithiol; 1,3-propanedithiol, furfurylthiol | 2,989,485 |
| R—$NR_2$ amines wherein each R represents a lower aliphatic hydrocarbon, at least one of which contains ethylenic or acetylenic unsaturation and the total number of carbon atoms is from 4 to 10 | 2,977,507 |
| A glycol ether of an ethanolamine having the formula:  where R is selected from abietyl, hydroabietyl, and dehydroabietyl, X is H or $(CH_2CH_2O)_nH$, and $m$ and $n$ are intergers from 2 to 10 the sum of which is within the range of about 4 and 20 | 2,510,063 |
| An ethylene oxide condensate of an ethanol rosin amine prepared by reacting one molar equivalent of an N-ethanol rosin amine with from 2 to 18 molar equivalents of ethylene oxide in presence of an alkaline catalyst at 80° to 200° C | 2,510,284 |
| A reaction product of a rosin amine, HCHO, and acetophenone in an HCl medium to produce:  wherein R is abietyl, hydroabietyl or dehydroabietyl; Y is $CH_2R$; and X is H or $CH_2R$ and wherein R is an $\alpha$-ketonyl group, the total number of carbon atoms in the three R's being from 4 to 10, e.g. 3,dimethylamino-3-methyl-1-butyne | 2,758,970 |
| Synergistic mixture of an amine, e.g. pyridine, amylamine, or dibutylamine, and a propargylsulfide | 3,017,355 |
| The reaction product of 1,3-dichloropropene and a salt of a hydrosulfuric acid | 3,044,958 |
| A propargyl mercaptan | 3,037,934 |
| Synergistic mixture of an acetylenic alcohol, e.g. propargyl alcohol and a stannous ion-yielding component, e.g. propargyl alcohol and a stannous ion-yielding component, e.g. $SnCl_4$ or SnO, and an alkylamine having from 2 to 6 carbon atoms in each alkyl group | 3,077,453 |
| Synergistic mixture of (1) an amine or amide; (2) acetophenone; (3) a ketone e.g. an aldehyde e.g. formaldehyde, and (4) a fatty acid, e.g. acetic octanoic, or pelargonic | 3,077,454 |
| Synergistic mixture of (1) an amine and (2) an acetylenic alcohol, e.g. butynediol or $\alpha$-ethynylbenzyl alcohol | 3,107,221 |

The following examples are illustrative of the practice of the invention:

Organic sulfur-containing and nitrogen-containing compounds are preferred corrosion inhibitors to employ in the invention.



Series 1

A solution was prepared consisting of a 5 percent by weight aqueous sulfuric acid, containing 0.4 percent by volume of the inhibitor described below and 1 percent by weight 1-allyl-2-thiourea.

The inhibitor employed was an amine-type prepared by reacting a rosin amine, formaldehyde, and acetophenone in the presence of hydrochloric acid as a catalyst. The method of its preparation is stated in detail in U.S. Patent 2,758,970, more specifically in column 2, lines 12 to 31 and as claimed in claims 8 to 10 thereof. This inhibitor is preferably employed in a mixture of water and a water-miscible alcohol containing a small amount of a surfactant.

A section of a carbon-molybdenum steel alloy boiler tubing 5 inches in length, 2 inches in outside diameter, and having a wall 0.25 inch thick, upon the interior surface of which there was a tenaceously adhering copper-containing iron oxide incrustation, was filled with the solution thus prepared and both ends of the tubing section tightly stoppered and allowed to stand for 6 hours at 150° F. At the end of this period, the thus used solution was removed from the tubing section and the tubing examined. All of the incrustation had been dissolved and removed therefrom; there was no evidence that any of the copper had plated out on the surfaces of the metal tubing. The so-used solvent was analyzed and found to contain 0.02 percent by weight copper. There was no evidence of undesriable decomposition of the 1-allyl-2-thiourea.

Series 2

To show the efficacy of the method of the invention, the example above was repeated except, for comparative purposes, no allylthiourea was employed. A clearly visible copper plating appeared on the surface of the tubing section.

To show further the efficacy of the method of the invention, a second comparative test was run, following substantially the example above except that thiourea was employed in place of the allylthiourea of the example. Decomposition of the thiourea occurred as evidenced by the presence of free sulfur in the solution at the completion of the test period.

Series 3

Nine aliquot portions of 150 milliliters each of the 5% by weight inhibited sulfuric acid descaling solution containing 1% by weight of 1-allyl-2-thiourea (as prepared in Series 1 above) were made.

The ingredients shown in the table below were admixed with the inhibited sulfuric acid solutions. An AISI, number 1010 carbon steel coupon (1 inch x 2¾ inch x ⅛ inch), was placed in each aliquot portion. The beakers were then covered and put in a 150° F. constant temperature bath for 6 hours of contact time. Boiler cleaning operations are usually conducted at at least 150° F. Each test was identified by the designation shown in the table below, wherein the results obtained by the tests are also set forth:

| Test Identification | Additives | Precipitation | Copper Plating |
|---|---|---|---|
| 1a | 1% by wt. 1-allyl-2-thiourea | None | No. |
| 1b | 1% by wt. 1-allyl-2-thiourea, 0.1% $Cu_2O$. | do | No. |
| 1c | 1% by wt. 1-allyl-2-thiourea, 0.1% $Cu_2O$+1.0% $Fe_3O_4$. | do | No. |
| 2a | 1% thiourea | do | No. |
| 2b | 1% thiourea, 0.1% $Cu_2O$ | do | No. |
| 2c | 1% thiourea, 0.1% $Cu_2O$+1.0% $Fe_3O_4$. | Heavy | Yes. |
| 3a | 2% by vol. methylol thiourea | None | No. |
| 3b | 2% by vol. methylol thiourea, 0.1% $Cu_2O$ | Heavy | No. |
| 3c | 2% by vol. methylol thiourea, 0.1% $Cu_2O$+1.0% $Fe_2O_4$. | do | Yes. |

The results of the above tests, show that thiourea and methylol thiourea are not suitable as copper

complexing agents in sulfuric acid solutions to remove scale containing iron oxide in the presence of copper ions at the temperature employed. As shown in the table, a heavy flocculent precipitate formed in test numbers 2c, 3b, and 3c. The presence of a precipitate of the type formed renders the use of a composition unacceptable for use in any chemical cleaning operation. Where both iron oxides and metallic copper are to be removed from iron or steel surfaces, as shown by the above tests, these materials would not prevent redeposition of the copper onto such surfaces. The steel coupon intest number 3b was coated with a heavy white precipitate. Such precipitate would be practically impossible to remove from pipes, cores, and conduits. The copper in test number 3b was so intermixed with the heavy precipitate that it could not separate to plate out but remained, nevertheless unremoved from the coupon.

In the case of tests 1a, 1b, and 1c, where 1-allyl-2-thiourea was used as the copper complexing agent, according to the invention, there was no precipitation and no copper plating or deposition on the steel surfaces. This shows that 1-allyl-2-thiourea does prevent copper from replating onto ferrous surfaces during chemical cleaning operations wherein iron oxides and copper deposits are sought to be removed and that no undesirable precipitate forms which would interfere with functioning or removal of the cleaning solution.

Series 4

This series of tests was conducted to show that, when an allylthiourea is used in an amount adequate as a corrosion inhibitor (as opposed to its use according to the invention as a copper complexing agent) together with thiourea in an amount adequate as a copper complexing agent according to known practice, in the presence if iron oxides (chiefly $Fe_3O_4$) which is being sought to be removed by aqueous sulfuric acid, the results were very unsatisfactory. The tests were conducted as follows:

Test 4a

150 milliliters of a 5% by weight aqueous sulfuric acid solution was prepared. To this solution were admixed (1) 0.1% by weight of 1-allyl-2-thiourea, as a corrosion inhibitor (which was insufficient as a copper sequestering agent), (2) 1% by weight thiourea, as an intended copper complexing agent according to the art, and (3) 1% by weight of iron oxides (substantially all of which was $Fe_3O_4$) to simulate a solubilized iron oxide scale to be solubilized and removed. An AISI, number 1010 carbon steel coupon (1 inch x 2¾ inch x ⅛ inch) was placed in the test solution, the solution covered, and placed in 150° F. constant temperature bath. After 6 hours the solution was very cloudy and thereafter a heavy white precipitate formed. The thiourea had decomposed and was ineffective for use as a copper sequestering or complexing agent in the sulfuric acid soluition at the temperature employed.

Test 4b

Part 1 was repeated exactly except that the 1% thiourea was replaced by the same amount of 1-allyl-2-thiourea according to the invention. The solution remained perfectly clear showing that the 1-allyl-2-thiourea was completely stable in the sulfuric acid at the advanced temperature employed and that it dissolved the $Fe_3O_4$ scale whereby it could be removed.

Series 5

The following tests were conducted to show the effect of known inhibitors against corrosivity of sulfuric acid on metal. One test was made employing only sulfuric acid for further comparison.

All tests employed AISI No. 1010 coupons 2¾" x 1" x ⅛" in size. The sulfuric acid used was 5% by weight $H_2SO_4$. The coupons were weighed before immersion in the sulfuric acid at 150° F. and, after immersion, were washed, dried, and reweighed.

The test solutions employed were 5% by weight sulfuric acid identified at follows and containing, if used, the inhibitor and/or alkenylthiourea copper sequestering agent, by weight:

| Test Number | Allyl-2-thiourea | Corrosion Inhibitor in Weight Percent |
|---|---|---|
| 5a | 0.1% | 0.2% made according to U.S. Patent 2,510,284. |
| 5b | None | 0.2% made according to U.S. Patent 2,403,153. |
| 5c | do | 0.2% made according to U.S. Patent 3,003,898. |
| 5d | do | None. |

The solutions employed and the test results are shown in the following table:

| Test Number | Weight in Grams | | | Length of Time Immersed in Hours | Corrosion Rates | |
|---|---|---|---|---|---|---|
| | Before Immersion | After Immersion | Loss | | In Pound/ Sq. Ft. | Average Per Day |
| 5a | 43.1104 | 43.1034 | 0.007 | 6 | 0.0014 | 0.0016 |
| 5b | 43.3714 | 43.0084 | 0.3630 | 6 | 0.0715 | 0.0709 |
| 5c | 43.8147 | 43.7879 | 0.0268 | 6 | 0.0053 | 0.0060 |
| 5d | 43.6537 | 43.4689 | 0.1848 | 1 | 0.2185 | 0.2190 |

Reference to the table above shows that known corrosion inhibitors may be used in sulfuric acid at an advanced temperature, although the efficacy varies.

It particularly shows a most satisfactory inhibition of corrosion of sulfuric acid when both a small amount of allylthiourea and a well known amine-type inhibitor are used together.

It shows also that, without a corrosion inhibitor, the sulfuric acid corrosivity is excessive.

When the test on the corrosion of the steel coupons was repeated employing sulfuric acid containing allylthiourea only, the corrosivity of the steel was also excessive.

When the tests were repeated employing small amounts of alkylthiourea with various well known amine-type corrosion inhibitor (of which a number are named hereinabove) a synergistic effect on corrosion inhibition was consistently shown.

It is clear, therefore, that the allylthiourea functions superbly as a copper sequestering agent in sulfuric acid but contributes to inhibiting metal corrosion only in the presence of a known inhibitor to the corrosivity of sulfuric acid on steel.

Having described my invention, what I claim and desire to protect by Letters Patent is:

1. A method of removing copper-containing iron oxide incrustation, scale, and deposits from a metal surface employing a scale-removing material without redeposition of copper thereon nor objectionable decomposition of said material, which consists in bringing into contact with such surface an aqueous solution having dissolved therein between about 2 and 70 percent by weight of sulfuric acid, a small but effective amount of an inhibitor to the corrosivity of an acid on metal and an alkenylthiourea wherein said alkenyl group contains between 2 and 6 carbon atoms per molecule, the amount of the alkenylthiourea being between about 4 and about 40

pounds per pound of copper in the incrustation, scale or deposits, said aqueous solution being maintained in contact with the incrustation for a time sufficient to solubilize substantially the incrustation.

2. The method according to claim 1 wherein the amount of the inhibitor to the corrosivity of an acid on metal is between about 0.1 and about 1.0 percent by weight of said aqueous solution.

3. The method according to claim 1 wherein said inhibitor is an amine type inhibitor prepared by reacting a rosin amine, formaldehyde, and acetophenone in the presence of hydrochloric acid as a catalyst.

4. The method of removing copper-containing iron oxide incrustation, scale, and deposits from a metal surface according to claim 1 wherein the temperature at which said metal surface is contacted is between about 40° F. and 200° F., the aqueous solution contains between about 5% and 30% by weight of sulfuric acid, and



the amount of alkenylthiourea is between about 6 and about 12 times the weight of copper in said incrustation, scale, and deposits.

5. The method according to claim 1 wherein the alkenylthiourea is 1-allyl-2-thiourea.

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