

United States Patent Office

3,277,012

Patented Oct. 4, 1966

1

3,277,012

AGENT FOR UNRUSTING IRON AND IRON-CONTAINING ARTICLES

Ernest-Wilhelm Krockow, Kleinkarlbach at Grunstadt, Germany, assignor to Dr. Spiess G.m.b.H., Kleinkarlbach Rheinpfalz, near Grunstadt, Germany
 No Drawing. Filed Jan. 14, 1963, Ser. No. 250,999
 16 Claims. (Cl. 252-152)

This invention relates to an unrusting agent.

It is known to unrust articles of iron by treating them with acids in which the rust is dissolved. The method has the disadvantage that when working within the acid range the ferrous metal itself is also attacked to a greater or lesser extent. This has the result that especially fine details of the iron articles such as threads, thin wires and the like are so seriously attacked when treated with acids for the purpose of removing the rust that these articles become useless alone by the treatment with acids.

It is desirable for these reasons to operate at a neutral or alkaline pH when unrusting articles of iron by means of chemical agents since the risk that the ferrous metal is dissolved in addition to the rust is not encountered in this case.

It has now been found that articles of iron can be unrusted particularly advantageously by chemical means by using organic compounds which contain one or more —SH groups. This class of thiol compounds is in general outstandingly suited to remove rust from articles of iron both within the neutral and within the alkaline range without attacking the ferrous metal itself. Aqueous solutions of these compounds, provided that they are water-soluble, will be used in general for the purpose mentioned above. However, solutions in organic solvents are also suitable and offer the additional advantage that the material being unrusted is easily dried after unrusting so that the risk of renewed formation of rust during the drying process is absent.

Examples of thiol compounds which are suitable in accordance with the invention to dissolve rust include ethyl mercaptan, thioglycol, thioglycerol, thiophenol, thio-salicylic acid, thiobenzoic acid, thioglycolic acid, thio-lactic acid, thiomalic acid, cysteine, their salts, esters and derivatives in which the —SH group is preserved completely or partially. These compounds are only mentioned as examples, it being not intended to restrict the invention to these examples. Similarly, suitable compounds include those which give rise to the formation of such compounds containing —SH groups during the unrusting process, e.g. from rhodamines or thiocarbonyl-bis-thioglycolic acid in an ammoniacal solution.

It is advantageous to add to these compounds materials having a basic action such as, for example, sodium hydroxide solution, potassium hydroxide solution, ammonia or organic primary, secondary, tertiary amines such as ethanalamine, triethylamine, pyridine or piperidine, which appear to be suitable to combine with the —SH group and the rust being dissolved to form a soluble compound of a salt-like or complex nature. In many cases, the rust-dissolving action of the above-mentioned thiol compounds is enhanced to practical utilization only by the addition of such bases.

2

Solutions of any concentration of the materials mentioned above are suited for unrusting, the rule being generally applicable that in case of lower concentrations the time of action must be longer than when using higher concentrations. However, the efficiency will again drop to some extent in case of very high concentrations. In general, concentrations of 1 to 100% and particularly of 3 to 30% are of advantage. However, rust will also be dissolved with concentrations ranging below 1%. This is easily perceptible by the violet color which appears if, for example, rusty iron is placed into an aqueous solution which contains 0.3% of ammonium thioglycolate. If it is desired to work in an organic solvent, the periods of action should generally be chosen somewhat longer than in case of the corresponding aqueous solutions.

The amount of basic material to be added may be low and will be such that the pH value is not substantially affected and may still range below pH 7. However, the amount of the base added may also be sufficiently high that a neutral solution or even a very strong alkaline solution will be obtained. In general, one will desirably operate at a pH value which ranges between 6 and 13 and particularly between 6 and 9.

Particularly suitable for unrusting metallic articles in accordance with the invention are thiol compounds of acids such as, for example, thioglycolic acid, thiolactic acid and thiomalic acid. Equally well suitable are salts, esters and derivatives of these acids in which the —SH group is preserved. Examples of salts of these compounds the solutions of which are outstandingly suited for unrusting including the salts of alkalis, ammonium salt and salts of alkaline earth metals. Examples of suitable esters include esters of lower and higher alcohols. A derivative of thiolactic acid is, for example, cysteine which may, for example, be used successfully in an ammoniacal solution for unrusting. Of the acids mentioned above, thioglycolic acid, its salts, esters and derivatives are particularly efficient and this acid appears to be particularly suitable for the purpose of the invention since it can be produced at low cost on a commercial scale.

When using thiol-carboxylic acids, unrusting can also be effected at an acid pH. In this case, the ferrous metal is not attacked at all or to a far lesser extent by the thiol acids than in those cases where other acids are used which do not contain thiol groups. This is perceptible by the fact that rust is removed by these acids much more rapidly than in those cases where acids such as sulfuric acid are used which do not contain thiol groups.

Unrusting of iron or articles containing iron can be effected with the above-mentioned substances in a simple manner by suspending the parts into a solution of these substances. In doing so, it is desirable to agitate or stir the solution. It is possible to use temperatures which are higher or lower than room temperature, the dissolution of rust taking place more rapidly at higher temperatures. As the rust is dissolved at an acid pH, the solution acquires an increasingly deep color as the pH increases, the solution being colorless at about pH 3, pink at about pH 5 and violet at pH 7 and becoming deep violet above pH 7, i.e. within the alkaline range. It is, for example, immediately perceptible by the appearance of color at an alkaline pH that the rust is being dissolved.

3

Unrusting may also be effected by brushing the solution of the invention on the articles to be unrusted, particularly in those cases where the articles cannot be suspended in said solution. For this purpose, inert materials such as talc, chalk and the like or thickening agents or glue-like substances may additionally be incorporated in the solution which is thereby given a paste-like consistency and, therefore, may be applied to vertical surfaces by brushing or trowelling. Examples of thickening agents of this kind include pectin, glue, Tylose (methyl cellulose), and the like. After adequate exposure, the paste is rinsed off. The thiol compounds may also be in solid form when mixed with inert materials such as precipitated silica. A slurry is made of this solid mixture briefly before its application.

Wetting agents and/or emulsifiers may be added to the solutions of the invention to achieve better wetting.

The treatment periods until complete removal of rust is achieved are also dependent upon the degree of rusting. Thicker layers of rust necessarily require longer exposure of the article being unrusted. For this reason, plate or sheet having the same degree of rust attack if possible was used for the tests described in the following examples.

EXAMPLE 1

To an aqueous solution containing 28.4% of thioglycolic acid, there was added sufficient ammonia that the pH of the solution was 7. Then a rusty piece of iron sheet was placed into the solution. The solution acquired a deep violet color and the rust was completely dissolved after an exposure of 7 minutes. The loss in weight was 2.9%. After another exposure of 24 hours, a further loss in weight could not be observed.

EXAMPLE 2

To an aqueous solution containing 14.2% of thioglycolic acid there was added sufficient ammonia that the pH was 8.4. Then a piece of rusted sheet iron was placed into the solution. The solution acquired a deep violet color and the sheet was completely free from rust after an exposure of somewhat less than 8 minutes. The loss in weight was 3.05%. The sheet iron was suspended into the solution for additional 24 hours but showed no further loss in weight after this time.

EXAMPLE 3

To an aqueous solution containing 7.1% of thioglycolic acid there was added sufficient ammonia that the pH was 6. Then a piece of rusted iron plate was suspended in the solution. After 8 minutes, the plate was completely free from rust. The loss in weight was 3.4%. Although this solution had an acid reaction, dissolution of iron metal could not be detected.

EXAMPLE 4

To an aqueous solution containing 3.5% of thioglycolic acid there was added sufficient concentrated ammonia that the pH ranged between 11 and 12. A piece of rusted iron plate was suspended into the solution. The solution acquired a deep violet color and the plate was free from rust after an exposure of 11 minutes. The loss in weight was 2.12%.

EXAMPLE 5

To an aqueous solution containing 1.7% of thioglycolic acid there was added sufficient ammonia that the pH value was 9. Then a piece of rusted iron plate was suspended into the solution. The solution acquired a deep violet color and the plate was completely free from rust after 30 minutes. The same result was obtained when an equivalent amount of ammonium thioglycolate was immediately added when preparing the solution.

EXAMPLE 6

Into a solution containing about 0.3% of thioglycolic acid and brought to about pH 8 by addition of ammonia

there was suspended a rusted piece of sheet iron. The solution acquired an intense red color at those spots where it contacted the rust which was dissolved. Thus, unrusting is also possible by means of an ammonium thioglycolate solution of such a low concentration if sufficiently long exposure of the metal is provided. When suspending a rust-free iron plate into such a solution, the same is not discolored.

EXAMPLE 7

In a solution of 25 gms. of thioglycolic acid (98%) in 100 ml. of water, the rust of a rusted iron plate was dissolved in 6 minutes while the solution was hardly discolored. If some sodium hydroxide is previously added to the solution to bring its pH to 9.5, a piece of sheet iron could be unrusted with such a solution within the same time. The solution acquired a deep violet color. The same behavior is shown by an aqueous solution of thioglycolic acid having the same concentration and having added thereto sufficient 25% ammonia to adjust the pH to about 10.

EXAMPLE 8

A piece of rusted iron plate was placed into concentrated sulfuric acid. The rust was dissolved irregularly and had disappeared completely only after an exposure of 1 hour. The loss in weight of the rusted iron plate was 5.5%. Since a loss in weight of about 3% had to be expected from dissolution of rust alone, some of the iron metal must also have gone into solution. This is also recognizable by inspection of the modified surface of the iron plate.

EXAMPLE 9

A piece of rusted sheet iron was suspended in 10% sulfuric acid. The rust was dissolved irregularly with vigorous evolution of hydrogen. After rust could no longer be detected, the sheet was removed from the medium, rinsed and dried. The loss in weight was 9.77%. It is clearly illustrated by tests 8 and 9 that when dissolving rust with sulfuric acid, not only rust but also some metal is dissolved in addition.

EXAMPLE 10

Ethanolamine was added to an aqueous solution containing about 25% of thioglycolic acid until the pH of the solution was between 9 and 10. Then a piece of rusted sheet iron was placed into the solution. The solution acquired a deep violet color and the sheet was rust-free after an exposure of 7 minutes. The loss in weight was 3.1%.

EXAMPLE 11

5 gms. of thiomalic acid were dissolved in 40 ml. of water and a piece of rusted iron plate was placed into the solution. The plate was rustfree after an exposure of 15 minutes.

EXAMPLE 12

5 gms. of thiomalic acid were dissolved in 30 ml. of water and 10 ml. of 25% ammonia were added to the solution which had a weak alkaline reaction. A piece of rusted sheet iron was placed into the solution. The solution acquired a deep violet color and the rust was completely dissolved after an exposure of 20 minutes.

EXAMPLE 13

Some thiosalicylic acid was mixed with ammoniacal liquor, the amounts being such that a solution of ammonium thiosalicylate having a weak alkaline reaction was obtained. A piece of rusted sheet iron was placed into this solution which acquired a black-brown color while the rust was dissolved slowly.

EXAMPLE 14

A piece of rusted sheet iron was placed into an ammoniacal solution of thiobenzoic acid. The rust was slowly dissolved while the solution acquired a dark color.

5

EXAMPLE 15

Some thiophenol was mixed with anhydrous piperidine and then a piece of rusted sheet iron was placed into the mixture which acquired a red-brown color while the rust was dissolved slowly.

In the same manner, thiophenol is capable of dissolving rust from a seriously rusted iron plate when some ammonia gas is introduced into the thiophenol.

EXAMPLE 16

A small amount of ethyl mercaptan was mixed with aqueous ammonia in a test tube and a piece of rusted sheet iron was added thereto. After a short period of time, the solution acquired a reddish color and the rust went into solution.

EXAMPLE 17

2 ml. of thioglycol were mixed with 2 ml. of 10% ammonia and a piece of rusted sheet iron was placed into the solution which immediately acquired a red-brown color while the rust was dissolved, the dissolution being complete after about 30 minutes.

EXAMPLE 18

2 ml. of thioglycol were diluted with twice the amount of absolute alcohol and the solution was mixed with some piperidine. When a piece of rusted sheet iron was suspended into the solution, it became clearly obvious that the rust was dissolved.

EXAMPLE 19

2 ml. of thioglycol were diluted with twice the amount of absolute alcohol and the solution was mixed with water and piperidine. Then a piece of rusted sheet iron was placed into the mixture which acquired a red-brown color while the rust was dissolved slowly.

EXAMPLE 20

2 ml. of thioglycol were diluted with twice the amount of absolute alcohol and some aqueous ammonia was added to the solution. A piece of rusted sheet iron was suspended into the solution which acquired a red-brown color while the rust was dissolved.

EXAMPLE 21

A piece of rusted sheet iron was placed into thioglycolic acid nonyl ester. In doing so, the red-brown rust acquired a dark color but was dissolved only slightly. When a small amount of an organic base such as, for example, piperidine was added to the solution, the rust was dissolved and the solution acquired an intense red-brown color. The sheet was free from rust after an exposure of an hour.

EXAMPLE 22

2 ml. of thioglycolic acid nonyl ester were mixed with twice the amount of methanol and the resultant solution mixed with some piperidine. A piece of rusted sheet iron was suspended into this solution which acquired a deep violet color while the rust went into solution. The sheet iron was rustfree after an exposure of 40 minutes. Alcohols in general, acetone and other organic solvents may be used in place of methanol. In place of piperidine, some ammonia could be passed into the solution or some ammoniacal liquor could be added thereto. While two layers were obtained in the latter case, the rust dissolved nevertheless in the thioglycolic acid nonyl ester while a deep red color appeared.

EXAMPLE 23

2 ml. of thioglycolic acid methyl ester were diluted with 5 ml. of methanol and mixed with some ethanol-

6

amine. A piece of rusted sheet iron was placed into the solution which acquired a red-violet color. The rust was dissolved after an exposure of 1 hour.

EXAMPLE 24

200 mg. of cysteine hydrochloride were dissolved in 5 ml. of water and the solution was made alkaline by adding some dilute ammonia. A piece of rusted sheet iron was suspended into the solution which acquired a deep violet color. The rust went into solution and was completely removed after an exposure of 15 minutes.

EXAMPLE 25

A sufficient amount of a weakly ammoniacal ammonium thioglycolate solution was added to a Tylose mucilage that the pasty Tylose solution contained about 10% of ammonium thioglycolate. This solution was applied to a rusty sheet iron by brushing and rinsed off after 5 to 10 minutes. Such a treatment is adequate for the removal of rust in case of thin rust layers. In case of thicker rust layers, the treatment must be repeated as required.

What is claimed is:

1. A rust removing composition consisting of 0.1-100% of an organic thiol compound having at least one —SH group selected from the group consisting of mercaptans, thio alcohols, thio acids, and salts of thio acids, as active rust-removing ingredient, the remainder consisting of a solvent selected from the group consisting of water and alcohols.

2. A rust removing composition according to claim 1 wherein said organic thiol compound is present in an amount of 3-30%.

3. A rust removing composition according to claim 1 wherein said organic thiol compound is a thiol carboxylic acid selected from the group consisting of thiosalicylic acid, thiobenzoic acid, thioglycolic acid, thiolactic acid and thiomalic acid.

4. A rust removing composition according to claim 1 wherein said organic thiol compound is a salt of a thiol carboxylic acid selected from the group consisting of thiosalicylic acid, thiobenzoic acid, thioglycolic acid, thiolactic acid and thiomalic acid.

5. A rust removing composition according to claim 1 wherein said organic thiol compound is thio glycolic acid.

6. A rust removing composition according to claim 1 additionally including an alkaline reacting compound which when added to said composition produces a pH of between 6 and 13.

7. A rust removing composition according to claim 1 additionally including an alkaline reacting compound which when added to said composition produces a pH of between 6 and 9.

8. A rust removing composition according to claim 6 wherein said alkaline reacting compound is a member selected from the group consisting of sodium hydroxide, potassium hydroxide, ammonia, lower alkanolamines, tri-lower-alkylamines, pyridine and piperidine.

9. A rust removing composition according to claim 1 wherein said solvent is water.

10. A rust removing composition according to claim 1 wherein said solvent is an alcohol.

11. A rust removing composition according to claim 1 additionally including an inert thickening material selected from the group consisting of talc, chalk, glue, pectin, and methyl cellulose in an amount sufficient to impart a paste-like consistency to said composition.

12. A method of removing rust from metallic iron-containing articles comprising contacting such an article with a rust removing composition, consisting of 0.1-100% of an organic thiol compound having at least one —SH group selected from the group consisting of mercaptans, thio alcohols, thio acids, and salts of thio acids, as active rust removing ingredients, the remainder if any

7

consisting of a solvent selected from the group consisting of water and alcohols.

13. Method according to claim 12 wherein said composition additionally includes an alkaline reacting compound which when added to said composition produces a pH of between 6 and 13. 5

14. Method according to claim 12 wherein said solvent is water.

15. Method according to claim 12 wherein said solvent is alcohol.

16. Method according to claim 12 wherein said composition is in the form of a paste.

8

References Cited by the Examiner**UNITED STATES PATENTS**

2,488,832 11/1949 Rossi ----- 252—105

OTHER REFERENCES

The Condensed Chemical Dictionary, 6th ed., Reinhold Publ. Co. (1962), pages 77, 712, 1135.

LEON D. ROSDOL, *Primary Examiner*.

10 JULIUS GREENWALD, *Examiner*.

W. E. SCHULZ, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,277,012

October 4, 1966

Ernest-Wilhelm Krockow

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 65, for "thiosalicyclic" read -- thiosalicylic --; column 6, lines 37 and 42, for "thiosalicyclic", each occurrence, read -- thiosalicylic --; column 8, after line 8, insert the following reference:

Gregory Uses and Applications of Chemicals
and Related Materials, Reinhold Publi. Corp. (1939)
Page 52 TP 9 G 79.

Signed and sealed this 22nd day of August 1967.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents