

1

3,135,632

METHOD OF PROTECTING FERROUS METAL SURFACES FROM RERUSTING

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The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalties thereon.

This invention relates to the protection of ferrous metal surfaces against rerusting. In particular, it is directed to a new and improved method for the prevention of the rerusting which normally occurs upon the removal of freshly pickled carbon or low alloy ferrous metals from a pickling bath by the addition of acridine, certain substituted acridines and mixtures thereof to the pickling acid bath.

It is well known that after various mill operations and at numerous stages in the fabrication of finished products, for instance, for galvanizing, tinning, electroplating and painting, it is necessary to remove oxides and other scales from various metal surfaces. Commercially for carbon or low alloy ferrous metals, this is done by the process called "pickling" wherein the ferrous metals being treated are immersed in acid solutions. Various acids are used in commercial pickling, such as sulfuric, hydrochloric and phosphoric acids. Because of its relative commercial availability, sulfuric acid is more widely used than all others.

It is also known that in order to reduce the attack of the pickling acids on the base ferrous metal and thus to prevent the waste both of the acid and the metal, additives termed "inhibitors" are incorporated into the pickling baths. Many satisfactory commercial inhibitors exist which accomplish this function of protecting the metal surfaces from acid attack while the metal is immersed in the pickling bath.

To the knowledge of the inventors however, none of these inhibitors had the attribute of protecting the highly active, freshly pickled metal surfaces from rerusting upon removal from the bath.

After the metal has been removed from the pickling bath, by known methods, portions of the thin residual film of pickling acid and salts, as well as portions of the inhibitor additive, are then rinsed from the metal. At this stage and in order to protect the metal surfaces while in temporary or semi-permanent storage from the rusting caused by exposure to the elements, i.e., the effects of atmospheric type oxidation, it is necessary to treat the highly active, freshly pickled metal immediately by methods well known to the art. It is therefore an object of the present invention to eliminate the necessity for this immediate rust preventing treatment of ferrous metals following pickling.

Some of the methods presently employed to accomplish this rust preventive treatment involve coating the ferrous metal surfaces with an impervious oily film such as oil, grease, etc. Another object of this invention is to provide for the protection of the metal surface against rerusting by the use of a substance which is non-oily.

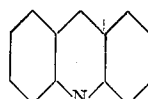
2

A further objection to this type of treatment arises as the result of the fact that the oily film must subsequently be removed by any of the well-known methods when further use of the metal is desired. Accordingly, it is an additional object of the present invention to eliminate the operational necessity for removal of a rust protective coating when further use of the ferrous metal is desired.

It can then be seen that the elimination of these repetitive coating and removal operations during the processing of the metal would expedite and simplify overall production-line type fabrication processes. It is a further object of this invention to provide a method to expedite and simplify the overall fabrication process by the elimination of the coating, coating removal and recoating operations.

According to our method, once the pickling bath operation has been completed the freshly pickled metal may be simply allowed to dry or, alternately, rinsed in water and then allowed to dry. Accordingly, it is a still further object of the present invention to provide a method whereby freshly pickled ferrous metal surfaces are rendered resistant to rerusting. Other objects will in part be apparent and will in part appear hereinafter.

Unexpectedly it was found that the addition to the pickling bath of a small amount of acridine, 1-aminoacridine, 1-bromoacridine or mixtures thereof, either alone or in combination with other inhibitors, would result in rendering the highly active, freshly pickled metal resistant to rerusting upon exposure to atmospheric or other elemental effects. Acridine is a benzolog of quinoline having a structural formula corresponding to:



Relatively, acridine appears to afford more protection than the substituted acridines mentioned, as will more fully appear from the following examples.

It can be seen that by this new and novel method the coating, coating-removal and recoating operational steps of presently available methods can be entirely eliminated from pickling bath procedures. Furthermore, the use of this new and novel method wherein the more effective inhibitors are also incorporated in the pickling bath will tend to give the optimum for not only the protection from pickling acid action on the ferrous metals, but after-rust protection as well.

It has been our experience that samples of ferrous metals removed from pickling baths, if not otherwise treated, will be almost completely covered with rust within 24 hours. Samples of steel surfaces pickled in a solution containing acridine, an additional inhibitor and sulfuric acid have been exposed to ambient laboratory temperatures for several months without the slightest evidence of rust.

This peculiar property of acridine, 1-aminoacridine, 1-bromoacridine and mixtures thereof could not be deduced from either test comparisons with other substituted acridines or from comparisons with other related heterocyclic compounds, for instance, acridone, quinoline, pyridine or B-naphthoquinoline. Although some of these compounds are acid attack inhibitors, as shown in our

compending application, Serial No. 668,283, filed January 25, 1957, now U.S. Patent 2,981,617, they afford, as will be indicated by the test data contained in the examples hereafter set forth, no protection to the metal against rerusting after pickling.

Thus the value of this invention can be appreciated when it is considered that, by the addition of a small amount of acridine, 1-amino acridine, 1-bromo-acridine, and mixtures thereof to the pickling bath, the necessity for immediate rust prevention treatment of the metal following pickling is eliminated. Furthermore, without any additional treatment, ferrous metals thus protected may be primed and painted at any time up to one year after pickling.

The following examples are given by way of illustration only and are not intended to limit the scope of this invention in any way:

The hydrogen evolution method was employed to determine the percentage retardation (inhibition) in each of the following examples. This method consists of immersing the metal samples in a gas burette filled with the pickling acid under consideration. Below this specimen, a small orifice leads to the overflow tube so that the system is at atmospheric pressure, and the rate of attack of the acid upon the metal could be followed by reading the volume of hydrogen evolved. An inhibited acid test is always compared with an uninhibited acid test for control purposes, and the percentage retardation is calculated as follows:

Percent retardation

$$= \frac{\text{volume H}_2 \text{ uninhibited} - \text{volume of H}_2 \text{ inhibited}}{\text{volume of H}_2 \text{ uninhibited}} \times 10$$

The employment of this method makes it possible to obtain data at very frequent intervals which is not feasible when using the weight-loss method. The sample immersions hereinafter described were continued for 24 hours; the specimens were then removed from the bath; rinsed with water and placed on a rack to dry. Within 24 hours after being placed on the drying rack, the metal samples were examined to determine the extent of the protection against rerusting. This determination was made by measuring the percentage of surface covered by rust. In all cases, the samples of uninhibited metals were found to be almost completely covered by rust within one hour.

EXAMPLE I

Table I contains the results of tests which indicate the type of inhibition and after-rust protection afforded by acridine when tested alone. Samples of SAE 1010 steel were cut to give a surface area of 37 cm.² and were ground to a smooth surface. After degreasing, the specimens were placed in different gas burettes completely filled with 1-N sulfuric acid. The results of the tests in which acridine alone was added to the acid are shown in Table I:

Table I

AFTER RUST OF SAE 1010 STEEL WHEN PICKLED IN SULFURIC ACID TO WHICH ACRIDINE WAS ADDED

Number of specimens	Concentration of sulfuric acid (Normality)	Acridine by weight percent	After rust protection, percent
4	1-N	0.1	100
1	1-N	0.1	90
1	1-N	0.2	90
2	1-N	0.05	90
2	1-N	0.05	100
1	1-N	0.025	100
1	1-N	0.01	90
1	1-N	0.005	90

As indicated in Table I, a number of specimens were tested for the different concentrations by weight percent of the acridine.

EXAMPLE II

Table II involves a comparison of the protective effect afforded by acridine, 1-amino acridine and 1-bromo acridine as well as a comparison of the effectiveness of acridine, 1-bromo acridine and 1-amino acridine with respect to the ineffectiveness of the other substituted acridines tested.

Tests were performed under the same conditions and in the same manner as in Example I except that varying concentrations by weight percent of the acridine and substituted acridines were used. This table illustrates both the retardation effectiveness and the after-rust protection afforded by the various concentrations of acridine, 1-bromo acridine and 1-amino acridine.

Table II

INHIBITION AND AFTER RUST PROTECTION FROM THE ATTACK OF 1-N SULFURIC ACID ON MILD STEEL BY ACRIDINE AND SUBSTITUTED ACRIDINES

Samples	Concentration, weight percent	Retardation, percent	After-pickling rust protection, percent
Acridine.....	0.1	57	100
Do.....	0.05	67	100
Do.....	0.025	62	100
1-bromo acridine.....	0.1	69	90
Do.....	0.05	62	90
Do.....	0.025	62	90
1-amino acridine.....	0.05	77	100
Do.....	0.025	76	80
5-amino acridine.....	0.1	92	0
Do.....	0.05	90	0
Do.....	0.025	85	0
3,6-diamino acridine.....	0.1	70	0
Do.....	0.05	74	0
Do.....	0.025	71	0
1-nitro acridine.....	0.1	81	0
Do.....	0.05	86	0
Do.....	0.025	79	0

EXAMPLE III

Tests were conducted under the same conditions and in the same manner as in Example I except that different concentrations of acridine and different concentrations of various pickling acids were tested. Table III further illustrates the control specimens ineffectiveness in comparison with that of the particular acid solution to which acridine had been added.

Table III

AFTER RUST PROTECTION OF SAE 1010 STEEL WHEN PICKLED IN VARIOUS ACIDS TO WHICH ACRIDINE WAS ADDED

Acid	Concentration of acid normality	Concentration of acridine	After rust protection, percent
H ₂ SO ₄	1-N	nil	0
H ₂ SO ₄	2-N	nil	0
H ₂ SO ₄	5-N	nil	0
H ₂ SO ₄	1-N	0.05	100
H ₂ SO ₄	2-N	0.05	100
H ₂ SO ₄	5-N	0.05	90
HCl.....	1-N	nil	0
HCl.....	1-N	0.1	100
HCl.....	1-N	0.05	100
HCl.....	1-N	0.025	100
H ₃ PO ₄	1-N	nil	0
H ₃ PO ₄	1-N	0.1	100
H ₃ PO ₄	1-N	0.05	100
H ₃ PO ₄	1-N	0.025	100

5 EXAMPLE IV

Tests were conducted under the same conditions and in the same manner as in Example I. However, other inhibitors were added to the acid solution along with the acridine for the purpose of illustrating that a more effective combined inhibition-after-rust protection could be obtained by the addition of a more effective inhibitor in combination with the acridine. The compounds used were inhibitors of acid attack, but which, of themselves, afforded no protection against rerusting.

Table IV

AFTER RUST OF SAE 1010 STEEL WHEN PICKLED IN INHIBITED SULFURIC ACID TO WHICH ACRIDINE WAS ADDED

Concentration of acridine	Concentration of inhibitor	Concentration of acid normality	Percent after rust protection when inhibitor used alone	Percent after rust protection acridine plus inhibitor
0.05	0.025 acridine orange	1-N	20	100
0.05	0.05 8-nitroquinoline	1-N	10	90
0.05	0.1 5-nitroquinoline	1-N	10	80
0.1	0.1 2-aminobenzene thiol	1-N	20	100
0.1	0.2 2-aminobenzene thiol	1-N	20	100
0.05	do	1-N	20	100
0.025	do	1-N	20	100
0.01	do	1-N	20	80

EXAMPLE V

To illustrate that mixtures of acridine and the specified substituted acridines were as effective when mixed together as when used alone, tests were conducted under similar conditions and in the same manner as in Example I except that both SAE 1010 and SAE 4130 steels were tested. A mixture of 0.05% acridine and 0.025 1-bromo acridine resulted in a 100% after rust protection for SAE 1010 steel. When tested with different samples of SAE 1010 and SAE 4130 steel, a mixture of 0.05% acridine and 0.025% 1-bromo acridine resulted in a 90% after rust protection in each case.

EXAMPLE VI

To test the effectiveness of acridine and 1-bromo acridine with low alloy steels, experiments were conducted in the same manner and under similar conditions as those of Example I except that SAE 4130 steel was used and 0.05% acridine added to 1-N sulfuric acid. The results indicated an 80% after rust protection. 0.025% 1-bromo acridine added to a 1-N acid bath which contained a sample of SAE 4130 low alloy steel gave an 80% after rust protection.

EXAMPLE VII

Although the tests listed in the previous examples ran 24 hours, much less time is required for the reaction which affords the protection against rerust. Tests were conducted in the same manner and under the same conditions as discussed in Example I except that specimens were removed from the solution after short, graduated periods of time, rinsed and allowed to air-dry. The specimens were examined for rust 24 hours after rinsing. The results of these tests are listed in Table V.

6 Table V

AFTER RUST OF SAE 1010 STEEL WHEN PICKLED IN 1-N SULFURIC ACID

Acridine, weight percent	Length of pickle	After rust protection, percent
0.05	5 min.	90
0.05	15 min.	100
0.05	30 min.	100
0.05	45 min.	100
0.05	60 min.	100
0.05	7 hours	100
0.05	24 hours	100

The foregoing examples are intended merely as illustrations of our invention. Since modifications in the examples will occur to those skilled in the art, we wish to be limited, not by the scope of the specific examples, but solely by the scope of the appended claims.

We claim:

1. In the method of protecting metal surfaces selected from the group consisting of ferrous metal surfaces, carbon-ferrous metal surfaces, and low alloy ferrous metal surfaces from rerusting after removal from acid pickling baths, the steps which comprise: adding to the acid pickling bath a small amount of an organic compound selected from the group consisting of acridine, 1-amino acridine, 1-bromo acridine and mixtures thereof, whereby the metal surfaces are rendered substantially inactive to the normal effect of atmospheric oxidation; removing the inactivated freshly pickled metal from the acid pickling bath; and allowing the metal to dry.

2. The method of claim 1 wherein the organic compound is an amount between .005 and .2% by weight acridine.

3. The method of claim 1 wherein the organic compound is an amount between .025 and .1% by weight 1-amino acridine.

4. The method of claim 1 wherein the organic compound is an amount between .025 and .1% by weight 1-bromo acridine.

5. The method of claim 1 wherein the organic compound is a mixture of acridine and 1-amino acridine.

6. The method of claim 1 wherein the organic compound is a mixture of acridine and 1-bromo acridine.

7. The method of claim 1 wherein the organic compound is a mixture of 1-amino acridine and 1-bromo acridine.

8. In the method of protecting metal surfaces selected from the group consisting of ferrous metal surface, carbon-ferrous metal surfaces, and low alloy ferrous metal surfaces from rerusting after removal from acid pickling baths, the steps which comprise: adding to the acid pickling bath a small amount of an organic compound selected from the group consisting of acridine, 1-amino acridine, 1-bromo acridine and mixtures thereof, whereby the metal surfaces are rendered substantially inactive to the normal effect of atmospheric oxidation; removing the inactivated freshly pickled metal from the acid pickling bath; rinsing the metal with water; and allowing the metal to dry.

References Cited in the file of this patent

UNITED STATES PATENTS

1,503,443	Gravell	July 29, 1924
1,678,775	Gravell	July 31, 1928
2,037,762	Cole	Apr. 21, 1936
2,814,593	Beiswanger	Nov. 26, 1957