PROCESS OF CONDITIONING METAL SURFACES AND COMPOSITIONS THEREFOR

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17 Claims. (Cl. 21—2.5)

This invention relates to a process for conditioning metal surfaces and compositions therefor. More particularly, the invention relates to the acid pickling of metals and especially to the acid pickling of steel and to new and useful pickling compositions.

One of the objects of the invention is to provide a new and improved process for pickling metals which is especially adapted to the pickling of ferrous metals and can be employed for the pickling of a wide variety of ferrous metals.

Still another object of the invention is to provide a new and improved process for pickling ferrous metal rods and wire.

Another object of the invention is to provide an acid pickling process for ferrous metals, the operation of which means better quality products, saves on the acid requirement and reduces the heat requirements.

Still a further object also of the invention is to provide new and useful pickling compositions which can be added to acid pickling baths in order to produce new and improved results. Other objects will appear hereinafter.

These objects are accomplished in accordance with this invention by providing a pickling bath containing a compound capable of liberating colloidal sulfur, preferably sodium thiosulfate, and an organic acid pickling inhibitor, preferably dihydroxythioureia.

The invention will be illustrated but is not limited by the following examples.

Example I
A composition suitable for use as an addition agent to an acid pickling bath was prepared by mixing together the following ingredients:

<table>
<thead>
<tr>
<th>Pounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium thiosulfate (Na₂S₂O₃, anhydrous powder)</td>
</tr>
<tr>
<td>Dihydroxythioureia</td>
</tr>
<tr>
<td>Santomser No. 1</td>
</tr>
<tr>
<td>Sodium sulfate</td>
</tr>
<tr>
<td>Ethofat 242/25</td>
</tr>
</tbody>
</table>

The Ethofat 242/25 is spread over one-half the Santomser No. 1 and sodium sulfate and mixed therewith. The dihydroxythioureia is then added and mixed with the previous mixture followed by the sodium thiosulfate and the balance of the Santomser No. 1 and sodium sulfate. The resultant product is a dry mixture which is suitable for addition to acid pickling baths.

Example II
A sulfuric acid pickling bath was prepared containing 8% H₂SO₄. The composition prepared as described in Example I was added to said bath in proportions corresponding to one-fourth part by weight of said composition per 100 parts by weight of H₂SO₄ in said bath. Hot rolled SAE 1010 steel rods were pickled in said bath at 165° F. for 3 to 5 minutes.

Example III
The procedure was the same as in Example II except that the H₂SO₄ concentration of the bath was 4% by weight and the pickling temperature was 135° F.

Example IV
The procedure was the same as in Example II except that a 15% by weight solution of hydrochloric acid was used instead of the sulfuric acid and the temperature was around 120° F.

In a similar manner other types of ferrous metals, including SAE 1020 steels, SAE 1060 steels, SAE 1100 series steels and SAE 2100 series steels, have been processed in accordance with the invention with excellent results. The invention is especially useful in pickling wire, rods, billets, sheet and pipe formed from many of the well known mild alloy steels. It is useful in pickling wire which has been cold drawn and has to be repickled before being chemically coated. It is useful in pickling valve spring alloys.

In the composition of Example I the sodium thiosulfate constitutes about 5.25% by weight of the composition. Since 1 pound of the composition is used for 400 pounds of acid weight in this example, the amount of sodium thiosulfate is approximately 0.5 pound per 400 pounds of acid weight, e.g., H₂SO₄. Inasmuch as only about one-fifth of the Na₂S₂O₃ is effective to produce colloidal sulfur, the amount of colloidal sulfur formed in the bath by the use of 1 pound of the composition of Example I per 400 pounds of H₂SO₄ is approximately 0.01 pound per 400 pounds of acid weight.

The quantity of the composition which is added to the acid pickling bath is subject to some variation but is preferably within the range of 1% to 2 pounds per 400 pounds of acid weight or, in other words, 1% to 2% of the acid weight in the bath. Thus, the amount of colloidal sulfur liberated would generally be in the range of 0.005 to 0.02 part per 400 parts of acid weight. In terms of percentage this amounts to approximately 0.00125% to 0.0025% of colloidal sulfur based on the acid weight in the bath. In terms of the sodium thiosulfate used, the preferred quantities are within the range of 0.025 to 0.1 part of sodium thiosulfate per 400 parts of acid weight, i.e., 0.00025% to 0.0025% of the acid weight.

The employment of a substance, such as sodium thiosulfate, which liberates colloidal sulfur in the pickling solution is not claimed herein per se but is the subject of my U.S. Patent 2,636,009. It will be understood that other substances capable of liberating colloidal sulfur as, for example, sodium polysulfide, may be employed in the practice of the invention. The only essential requirements are that the sulfur compound must be capable of liberating colloidal sulfur in an acid bath and the amount used must be sufficiently small so that the colloidal sulfur liberated remains dispersed in colloidal form.

The dihydroxythioureia is representative of a class of organic acid inhibitors which have heretofore been employed in acid pickling baths to decrease acid attack on the basis metal without appreciably altering the rate of scale removal. For the purpose of this invention any organic inhibitor of a kind and in an amount which will provide at least 50% protection against weight loss of the basis metal can be employed in the practice of this invention but the inhibitors containing nitrogen atoms are especially suitable. A list of organic inhibitors which may be employed for the purpose of the present invention in conjunction with a sulfur liberating compound as herein described is given in "Corrosion Handbook," Ullagic, John Wiley & Sons (1948), Table 1, pages 910-912, and is incorporated herein by reference. All of the compounds listed in Table 1 are known as anticorrosive agents in acidic media and give at least 50% protection. Of the 112 anticorrosive agents listed 59 give 90% protection.
Of the anticorrosives listed, four are thioureas, viz., thio-urea, phenyl thiourea, o-tolylthiourea, and p tolyl thiourea; seven are alkyl thioureas, viz., butyl sulfaide, butyl disulfide, propyl sulfaide, propyl disulfide, butyl methyl sulfide, and methyl sulfide; forty-five are amines; ten are mercaptans, including o, m and p thiocresol, 2-thiophenol, and thiophenol; and the remainder are aldehydes, ketones and miscellaneous compounds. The method of determining the percentage of protection is defined in U.S. Patent No. 2,059,864 at page 909. The percentage of protection is determined by a series of tests in which cold rolled steel specimens with ground surfaces are immersed in 1 N (4.9%) sulfuric acid at 25° C. (77° F.) with and without various amounts of the inhibitor to be tested and the weight loss is measured. After 48 hours in 250 ml. of acid the percentage protection P is calculated from the overall rate of attack in grams per square centimeter per hour according to the following equation:

\[ P = \frac{(\text{Rate uninhibited} - \text{rate inhibited}) \times 100}{\text{Rate uninhibited}} \]

In general, the organic pickling inhibitors which are employed in conjunction with the colloidal sulfatric le- crating compound for the purpose of the invention con- sist of a hydrocarbon group attached to a polar or ioniz- able group. They contain nitrogen, oxygen, sulfur, or other elements in the fifth and sixth groups of the Periodic Table and are compounds such as amines, mercaptans, heterocyclic nitrogen compounds, substituted amines and thioureas, sulfides and aldehydes. The quantity of the organic inhibitor required in order to provide at least 50% protection of a ferrous metal is subject to wide variation depending upon the particular inhibitor but it is generally within the range of 0.003 to 2.5 weight percent of the acid weight. In Example I the diorthotolylthiourea constitutes approximately 5.5% by weight of the composition added to the pickling bath. Hence, if the composition is added in proportions of 1 pound to 400 pounds of acid in the pickling bath the proportion of the organic inhibiting agent will be .05 pound of the pickling inhibitor per 400 pounds of acid weight or 0.0125% of the acid weight. A preferred range of proportions of the organic pickling inhibitor is 0.005% to 0.025% by weight of the acid weight. In terms of parts per acid weight the preferred range is 0.025 part to 0.1 part of the organic pickling inhibitor per 400 parts of acid weight.

The Santonorse No. 1 in the composition of Example I is employed to provide a foam head on the bath and is an alkylarylsulfonate known technically as a keryl benzene sulfonate. The preparation of this composition is described in Schwartz and Perry, Surface Active Agents, pages 122-31, Santonorse No. 1 being mentioned spe- cifically on page 123. The foam producing agent per se does not form a part of the invention and it will be un- understood that any other acid-stable foam producing agent can be employed.

The sodium sulfate is an optional ingredient which is inert in the acid pickling bath and is employed primarily to add bulk to the composition so that the relatively small amounts required can be properly proportioned.

The Ethofat 242-25 used in the composition of Example I is oxyethyalted refined tall oil and is employed primarily for the purpose of preventing dusting of the composition. The amounts used are too small to have any substantial effect on the acid pickling bath to which the composition is added. Other oxyalkylated fatty acids can be employed, such as, for example, products obtained by oxyethyaling coconut oil fatty acids, oleic acid, hydroxy stearic acid, ricinoleic acid, stearic acid, and/or resin fatty acids with 5 to 50 moles of ethylene oxide per mole of acid. These oxyethyalted monocarboxylic acid materials are essentially nonionic.

The acid concentration used in the bath is subject to

variation depending upon the particular type of acid em- ployed. In the case of sulfuric acid the general range of concentration is 1% to 25% by weight H_2SO_4. In the case of hydrochloric acid the general range of concentra- tion is 5% to 33% by weight HCl.

The pickling temperatures are generally within the range of 120° F. to 220° F. in sulfuric acid pickling baths and within the range of 60° F. to 160° F. in hydrochloric acid pickling baths.

The time of pickling of the metal in the pickling bath depends upon the kind of metal but is generally anywhere from 3 to 5 minutes in the case of most mild alloy steels to 2 hours in the case of special kinds of steels.

The invention provides a number of advantages over conventional processes now being used in commercial practice. For example, in one such process a 10–11% sulfuric acid pickling bath containing a well known acid inhibitor is operated at a temperature of 180° F. to 200° F. By the practice of the present invention improved results were obtained in a pickling bath containing 7% to 8% H_2SO_4 at 165° F. and in a sulfuric acid pickling bath containing 4% by weight H_2SO_4 at 135° F. The surface conditioning of the metal with the present process was better than with the commercial process and there was no significant difference in hydrogen embrittlement. The present process permitted more overcleaning without undue harm to the sur- face and the deep pitting that occurred in steel cleaned with the commercial process. It was possible with the present process to obtain the same production at a lower acid concentration and lower temperature than in the conventional process. In one series of tests there was a saving of about 22% in acid per ton of product, a re- duction of about 20% in steel requirements per ton of product and a reduction of .2% in rejects in subsequent operations that might be attributed to poor cleaning.

The expression "percentage protection of the metal" is defined herein to mean the percentage protection P as calculated in the manner described in Corrosion Hand- book, supra, page 909.

The invention is hereby claimed as follows:

1. A method of protecting iron and steel surfaces against electrochemical corrosion in an acidic aqueous medium having a corrosive action of the acidic type on said metal surfaces and against the penetration of hy- drogen developed in such media, comprising the steps of adding to said acidic medium an organic inhibi- tor, in corrosion-inhibiting amounts, and adding also to the acidic medium a chemical compound which is capable of forming in situ in the acidic medium finely divided sulfur.

2. A process of pickling a steel in an acid pickling bath from the group consisting of a sulfuric acid pickling bath and a hydrochloric acid pickling bath which comprises adding to such a bath an organic inhibitor known as an anti-corrosive agent in acidic media, in corrosion-inhibiting amounts, and forming also in said bath elemental colloidal sulfur which is liberated in situ in said bath.

3. A process as claimed in claim 2 in which the organic inhibitor is from the group consisting of thiourea, orthothiolylthiourea, para tolly thiourea and dithiorthiol- thiourea.

4. A process as claimed in claim 2 in which the quan- tity of organic inhibitor is 0.003 to 2.5 weight percent of the acid weight.

5. A process as claimed in claim 2 in which the organ- ic inhibitor is from the group consisting of thiourea, orthothiolylthiourea, para toly thiourea and dithiortholyl- thiourea.

6. A process of pickling a steel in a sulfuric acid pickling bath which comprises pickling the steel in a sulfuric acid pickling bath to which has been added 0.005% to 0.025% of dithiorthiolthiourea calculated on the acidity weight and 0.00625% to 0.025% sodium thio- sulfate, calculated on the acid weight.

7. A process as claimed in claim 5 in which the sul-
furic acid concentration is 4% to 8% by weight \( \text{H}_2\text{SO}_4 \) and the temperature is 135°F to 165°F.

8. An acidic cleaning bath affording enhanced protection to corrosive attack of ferrous metals by acid in said bath, said bath consisting essentially of an aqueous acidic solution of corrosion-inhibiting amounts of an organic acid inhibitor, and finely distributed colloidal sulfur formed in situ.

9. An acidic cleaning bath affording enhanced protection to corrosive attack of ferrous metals by acid in said bath, said bath consisting essentially of an aqueous acidic sulfuric acid solution of corrosion-inhibiting amounts, of an organic acid inhibitor, and finely distributed colloidal sulfur formed in situ.

10. An acidic cleaning bath affording enhanced protection to corrosive attack of ferrous metals by acid in said bath, said bath consisting essentially of an aqueous acidic hydrochloric acid solution of corrosion-inhibiting amounts of an organic acid inhibitor, and finely distributed colloidal sulfur formed in situ.

11. An aqueous acid solution containing 1% to 26% by weight of \( \text{H}_2\text{SO}_4 \), 0.00125% to 0.005% colloidal sulfur based on the acid weight of said solution and 0.003% to 2.5% based on the acid weight of the solution of an organic inhibitor known as an anti-corrosive agent in acidic media.

12. An aqueous hydrochloric acid solution containing 5% to 33% by weight of \( \text{HCl} \), 0.00125% to 0.005% colloidal sulfur based on the acid weight of said solution, and 0.003% to 2.5% based on the acid weight of the solution of an organic inhibitor known as an anti-corrosive agent in acidic media.

13. An aqueous sulfuric acid pickling solution containing 4% to 8% by weight \( \text{H}_2\text{SO}_4 \), 0.00125% to 0.005% colloidal sulfur based on the weight of \( \text{H}_2\text{SO}_4 \) and 0.003% to 2.5% by weight of \( \text{H}_2\text{SO}_4 \) of an organic inhibitor known as an anti-corrosive agent in sulfuric acid solution.

14. An aqueous sulfuric acid solution containing 1% to 26% by weight of sulfuric acid to which has been added 0.005% to 0.025% of the acid weight of diorthotolythioure and 0.00625% to 0.025% of the acid weight of sodium thiosulfate.

15. An aqueous hydrochloric acid solution containing 5% to 33% \( \text{HCl} \) to which has been added 0.005% to 0.025% of the acid weight of diorthotolythioure and 0.00625% to 0.025% of the acid weight of sodium thiosulfate.

16. An additive for acidic aqueous solutions which when added to such solutions affords enhanced protection to corrosive attack of ferrous metals by acid in such solutions, said additive consisting essentially of an organic acid inhibitor known as an anti-corrosion agent in acidic aqueous media, in corrosion inhibiting amounts, and a compound liberating colloidal sulfur in acidic aqueous media.

17. An additive for acidic aqueous solutions which when added to such solutions affords enhanced protection to corrosive attack of ferrous metals by acid in such solutions, said additive consisting essentially of an organic acid inhibitor known as an anti-corrosion agent in acidic aqueous media, in corrosion inhibiting amounts, and sodium thiosulfate.

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WILLIAM B. KNIGHT, Examiner.