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2,474,526

PICKLING OF STAINLESS STEELS

John J. Healy, Jr., Brookline, Maurice H. Taylor, Stoneham, and Furio A. Abbiati, Longmeadow, Mass., assignors to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

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2 Claims. (Cl. 252-142)

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This invention relates to pickling solutions for steels and has particular application to the pickling of the so-called stainless steels which are in most cases essentially chromium-nickel-iron alloys. These alloys are characterized by their resistance to the action of common pickling reagents used with success in connection with ordinary steels.

The main objects of the invention are to provide a pickling bath for the removal of heat scale from stainless steels which will not pit, etch or otherwise damage the surface of the alloy; which will impart to it the pleasing light gray, dull, satiny finish desired by manufacturers of a high grade product and resembling, to a remarkable degree, the appearance of a piece of dull-finished aluminum; which is relatively economical to use; for which it is not difficult to obtain a suitably resistant container; and from which there is no possibility of the evolution of nitrogen oxide gases.

It is common practice in the removal of scale from ordinary irons and steels to dip them in dilute solutions of sulfuric or muriatic acid, either inhibited or uninhibited. Such treatment is usually satisfactory, especially with inhibited acids which have very little action on the steel itself and which therefore result in a greatly decreased consumption of acid and much less damage to the surface of the metal. In the case of stainless steels, however, this treatment is very unsatisfactory since either the scale is not all removed if a short treatment is given, or in the case of a prolonged pickling the surface of the metal is badly pitted or etched, dark colored and very unattractive in appearance. Even an inhibited acid, which will not pit the stainless steel, leaves it with a dirty black surface.

The present invention is based on the discovery that mixtures of a soluble ferric salt, such as ferric sulfate, and hydrofluoric acid, or of ferric fluoride and a mineral acid, such as sulfuric acid, in aqueous solution are very effective in removing scale from stainless steel and imparting to it the desired light gray, dull, aluminum-like finish. Other soluble ferric salts may be employed in combination with hydrofluoric acid, or with hydrogen fluoride salts or with fluoride salts and mineral acids, so that broadly stated, this invention contemplates the use of mixtures of a soluble ferric salt and an ionizable fluoride in baths having an acid reaction. Such solutions can safely be used in lead-lined tanks, which would be attacked by nitric acid, and since they contain none of that acid, they cannot evolve nitrogen oxide gases, 55

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small amounts of which are very deleterious to the workmen engaged in the pickling operation.

Baths containing or developing both ferric and fluoride ions have been used in the past for pickling stainless steels, but in these baths the ferric salts present have not been the active pickling agent. For example, the Kiefer Patent No. 1,974,570 describes the pickling of stainless steels with baths containing from 5 to 25% by volume of commercial nitric acid and up to 5% by volume of commercial hydrofluoric acid, while the Blaut and Lang Patent No. 2,115,005 describes the electrolytic pickling of stainless steels with baths containing from 30 to 80% of commercial concentrated sulfuric acid and from 2 to 20% of commercial concentrated hydrofluoric acid. Although the baths of both of these patents tend to develop ferric salts as the result of the pickling action of the acids on the steel in the presence of an oxidizing agent (nitric acid or electricity), the resulting ferric salts are incapable of exerting any pickling action due to the continued presence of said oxidizing agent. Thus, in accordance with the prior art baths, the amount of ferric ions continually increases during the life of the bath, while in the baths described herein a predetermined amount of ferric salts is initially employed and this amount gradually decreases as the bath is used for its intended purpose, thereby showing that the ferric salts employed in accordance with the present invention constitute an active pickling agent.

Examples of combinations, with which satisfactory pickling of stainless steel may be accomplished according to this invention, follow: ferric sulfate and hydrofluoric acid; ferric fluoride and sulfuric acid; ferric fluoride and hydrofluoric acid; ferric sulfate and sodium fluoride; ferric sulfate, sodium fluoride and sulfuric acid; ferric sulfate and potassium fluoride; ferric sulfate, potassium fluoride and sulfuric acid; ferric sulfate, calcium fluoride and sulfuric acid; ferric sulfate and sodium hydrogen fluoride; ferric sulfate and potassium hydrogen fluoride. In some cases when the scale formation is very light or of an easily removable nature, solutions of ferric sulfate alone or ferric fluoride alone may be used. For example, such a scale is removed by immersing the stainless steel in a solution containing 5% ferric sulfate at 80° C. for 2½ hours or at 65° C. for 5 hours or in a solution containing 5% ferric fluoride at 80° C. for one hour or 30% ferric fluoride at 80° C. for 40 to 90 minutes, or 15% ferric fluoride at 80° C. for 20 minutes. However, in order to obtain the greatest efficiency from the

baths of this invention, acid and preferably fluoride ions should be present as indicated herein.

The relative proportion of ferric sulfate and hydrofluoric acid to be used in pickling stainless steel is important to obtain the best results. A range within which very satisfactory results have been obtained comprises by weight

Ferric sulfate	Per cent
Hydrofluoric acid	1 to 30
Water	.3 to 10
	98.7 to 60

It is preferable that the hydrofluoric acid be present in a smaller amount than the ferric sulfate. Two specific formulae within the range above contain: 6% ferric sulfate with 1.5% hydrofluoric acid; and 15% ferric sulfate with 5.7% hydrofluoric acid.

With these pickling baths temperatures between 25° and 95° C. may be used depending on the condition of the scale and the article to be pickled. The duration of pickling may vary from 1 minute to 35 minutes, depending on the temperature and concentration of the bath and the condition of the scale on the steel. Increasing the temperature decreases the time.

The following table will give some idea of the results obtained at 60° C. with solutions containing different amounts of ferric sulfate and hydrofluoric acid on an annealed stainless steel of the usual 18-8 composition, i. e., containing 18% chromium and 8% nickel. The percentage figures under "Composition of the bath" are by weight. For example, 100 grams of the mixture designated 15% ferric sulfate and 5.7% hydrofluoric acid contains 15 grams of 100% ferric sulfate and 5.7 grams of 100% hydrofluoric acid, or in other terms 16.3 grams of 92% ferric sulfate and 11.9 grams of 48% hydrofluoric acid.

Composition of the bath

Per cent Ferric Sulfate	Per cent Hydrofluoric Acid	Results
5	2.3	Satisfactory pickling in 10 minutes.
15	2.3	Satisfactory pickling in 8 minutes.
30	2.3	Satisfactory pickling in 11 minutes.
5	5.7	Satisfactory pickling in 10 minutes.
15	5.7	Satisfactory pickling in 5 minutes.
30	5.7	Satisfactory pickling in 4 minutes.

The necessary time of immersion of the alloy in the ferric sulfate-hydrofluoric acid solutions may be substantially reduced by means of a short preliminary treatment in a conventional acid pickling bath, not long enough to pit the metal but enough to partly loosen the scale. For example, in the case of a hot rolled unannealed 18-8 stainless steel with a very difficultly removable scale, a 5-minute dip in an 8% sulfuric acid solution at 75° C. reduces the time in a 15% ferric sulfate-5.7% hydrofluoric acid mixture from 20 to 3 minutes. Similarly, the time is cut from 20 minutes to 2½ minutes by a preliminary pickle of 30 minutes in an inhibited 8% sulfuric acid bath at 75° C. which does not pit, etch or otherwise damage the metal. The advantage of such a procedure lies in the increased life of the relatively expensive ferric sulfate-hydrofluoric acid bath at the expense of a comparatively cheap sulfuric acid solution and in the marked reduction in time of pickling frequently attained.

We have also found that the present invention may be used advantageously in the known process of pickling stainless steels electrolytically. The steel is suspended from the anode in a bath

containing a suitable electrolyte, such as dilute mineral acid, and the electrolytic pickling carried out in the usual manner, after which it is possible to give it a bright silvery, metallic appearance by immersion in any of the baths forming the subject of the instant invention (e. g., a 5% ferric fluoride solution or a 15% ferric sulfate-5.7% hydrofluoric acid mixture).

In preparing a solution containing ferric sulfate and hydrofluoric acid, the following procedure has been found to be satisfactory. The ferric sulfate is added to the water in an amount sufficient to make the desired strength of solution. Heat is applied and the temperature is maintained at 80-90° C. until with agitation the chemical is completely dissolved. Then the temperature is lowered to the constant point at which the steel is to be pickled. Finally the hydrofluoric acid is added and the bath is ready for use. Commercial ferric sulfate containing about 90% $\text{Fe}_2(\text{SO}_4)_3$ may be used and the hydrofluoric acid may be the commercial product containing 30% or more HF.

In the pickling operation, the stainless steel is kept immersed in the ferric sulfate-hydrofluoric acid bath until the scale drops from the steel or becomes sufficiently loosened to be easily and completely removed by a light brushing under water or by a forceful stream of water.

The foregoing description has been directed more particularly to the use of solutions containing ferric sulfate and hydrofluoric acid in pickling stainless steel because this combination of chemicals seems to be the most satisfactory from a consideration of cost, results and other factors. However, the other previously mentioned combinations of ferric salts with acids or with fluoride salts or with fluoride salts and acid may be employed in a similar manner and they constitute a part of the present invention.

The following are examples of successful application of these other combinations at 60° C. on an annealed stainless steel of the 18-8 composition, no preliminary pickle in sulfuric acid having been given. All percentage figures are on the basis of 100% chemicals.

Composition of the Bath	Time of Immersion for Satisfactory Scale Removal
15% Ferric Sulfate, 5% Sulfuric Acid	1 hour.
5% Ferric Fluoride, 2% Sulfuric Acid	10 minutes.
4% Ferric Fluoride, 5% Sulfuric Acid	Do.
15% Ferric Fluoride, 5% Sulfuric Acid	5 minutes.
8.5% Ferric Fluoride, 11% Sulfuric Acid	Do.
15% Ferric Fluoride, 15% Sulfuric Acid	Do.
5% Ferric Fluoride, 1% Hydrofluoric Acid	35 minutes.
5% Ferric Fluoride, 2.3% Hydrofluoric Acid	20 minutes.
8.5% Ferric Fluoride, 5.7% Hydrofluoric Acid	Do.
5% Ferric Sulfate, 4.2% Sodium Fluoride, 4.9% Sulfuric Acid	10 minutes.
15% Ferric Sulfate, 10.5% Sodium Fluoride, 12.3% Sulfuric Acid	5 minutes.
5% Ferric Sulfate, 3.9% Calcium Fluoride, 4.9% Sulfuric Acid	10 minutes.
15% Ferric Sulfate, 9.8% Calcium Fluoride, 12.3% Sulfuric Acid	5 minutes.
15% Ferric Sulfate, 5% Sodium Hydrogen Fluoride	Do.

It should be kept in mind that the above combinations and percentages are merely exemplary, and that it is possible to vary the percentage of each substance or mixture of substances employed without detracting appreciably from the benefits of this invention. For example, ferric fluoride and sulfuric acid may be used together in amounts varying from .5 to 20% ferric fluoride and from .7 to 25% sulfuric acid, while ferric

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fluoride alone is suitable in amounts varying from 5 to 35%. Ferric fluoride and hydrofluoric acid may be used together in amounts varying from .5 to 20% of ferric fluoride and .3 to 10% of hydrofluoric acid; ferric sulfate, sodium fluoride, and sulfuric acid may be used in amounts varying from 1 to 30% ferric sulfate, .6 to 25% sodium fluoride, and .7 to 25 sulfuric acid, and if calcium fluoride is substituted for sodium fluoride in the last mentioned mixture, the calcium fluoride may be used in amounts varying from 1 to 30%. Where sodium hydrogen fluoride is used as the acidifying agent together with ferric sulfate, the latter salt may be present in amounts varying from 1 to 30%, while from .6 to 20% of the sodium hydrogen fluoride may be used.

It will be understood that this invention is applicable to stainless steels other than the 18% chromium-8% nickel alloy of iron specifically referred to. For example, satisfactory results are obtained when it is applied to steel alloys containing chromium, nickel and iron; chromium and iron; and chromium, nickel, molybdenum and iron in varying quantities, whether or not they also contain small, variable quantities of common stabilizing elements or impurities such as columbium, titanium, zirconium, selenium, tungsten, copper, silver, carbon, silicon, sulfur or phosphorus.

It is to be understood that although specific temperatures have been stated herein and the time required for the treatment has been indicated, these vary with the nature and condition of the article being pickled, age of the bath and other factors. Although only the preferred forms of the invention have been presented in the foregoing description, it will be apparent to those skilled in the art that numerous modifications may be made therein without departure from the spirit of the invention or the scope of the appended claims.

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This application is a division of our co-pending application, Serial No. 340,772, filed June 15, 1940, now Patent No. 2,408,424, issued October 1, 1946, which is a continuation-in-part of application Serial No. 140,988, filed May 5, 1937.

What we claim is:

1. An aqueous acid reacting non-electrolytic pickling bath for stainless steels consisting essentially of water and active pickling agents consisting of a non-oxidizing mineral acid and ferric fluoride, said mineral acid being present in the bath in an amount varying between 0.7 and 25% and said fluoride being present in an amount varying between 0.5 and 20%, said bath being substantially free of nitric acid.

2. The method of pickling stainless steels which comprises immersing them in an aqueous acid reacting non-electrolytic pickling bath consisting essentially of water and active pickling agents consisting of a non-oxidizing mineral acid and ferric fluoride, said mineral acid being present in the bath in an amount varying between 0.7 and 25% and said fluoride being present in an amount varying between 0.5 and 20%, said bath being substantially free of nitric acid.

JOHN J. HEALY, Jr.

MAURICE H. TAYLOR.

FURIO A. ABBIATI.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,824,932	Schermer	Sept. 29, 1931
2,115,005	Blaut et al.	Apr. 26, 1938

FOREIGN PATENTS

Number	Country	Date
8,236	Great Britain	1896