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PICKLING SOLUTION AND METHOD

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This invention relates to the chemical treatment of metals to remove scale and similar surface impurities therefrom, and has to do particularly with pickling solutions for cleaning alloys of the type commonly referred to as "stainless steel," which contain iron, nickel and chromium as essential ingredients.

An object of the invention is to provide a pickling solution that is unusually effective in removing scale from stainless steels, including the austenitic stainless steels.

Another object is to provide a pickling solution that retains its effectiveness well during use.

Another object is to provide a pickling solution that can be readily regenerated and maintained in serviceable condition during extended use.

Another object is to provide a method of regenerating a pickling solution to maintain it in highly efficient condition.

Numerous pickling solutions for the cleaning of stainless steel are in use, but to the best of my knowledge the prior-known solutions have usually been limited to two essential ingredients; thus some of them consist of mixtures of nitric and hydrochloric acid, others consist of mixtures of nitric acid and hydrofluoric acid; and still others comprise an acid such as nitric or sulfuric in combination with an alkali salt which is usually a nitrate or a halide.

An exception to this general rule is the solution disclosed in United States patent to Urban No. 2,172,041 which contains hydrofluoric acid with an oxidizing reagent such as chromic acid, potassium chromate, potassium dichromate or potassium permanganate, and may contain sulfuric acid.

In accordance with the present invention, I have discovered that a superior pickling solution for cleaning stainless steels consists of a mixture of three acids, preferably sulfuric acid, nitric acid and hydrofluoric acid, the original solution being preferably built to the following prescription:

By volume:

	Per cent
Commercial concentrated sulfuric acid	7 to 10
Commercial concentrated nitric acid	12 to 15
Commercial (50% to 60% HF) hydrofluoric acid	1.5 to 2.0
Water	remainder

When the solution is used to pickle stainless steel, iron is dissolved, mostly in the ferric form. Analyses of the iron content is made frequently, and after each analysis sufficient hydrofluoric acid is added to bring the molal ratio of total fluoride to total iron to a value of 5.9 to 1 or 6.0 to 1. Analyses and adjustment of the fluoride content should be made frequently enough to prevent the molal ratio of total fluoride to total iron falling below 5.0 to 1 and preferably not below 5.5 to 1. These ratios are for difficult work. If annealing conditions have produced an easily removed scale on the work, a molal ratio as low as 2 to 1 will remove most of the scale.

Additions of hydrofluoric acid should be continued, to maintain the fluoride to iron ratio as specified, until the total iron content of the solution reaches approximately 2% by weight, at which time the hydrofluoric acid content will total about 7% by volume. Thereafter further additions of hydrofluoric acid should be discontinued. However, the solution can continue to be used until the iron content reaches from 5% to 6%, when the solution should be discarded. At that time the molal ratio of total fluoride to total iron will have decreased to about 2 to 1.

As the solution is used, its nitrate content decreases, and nitric acid should be added from time to time to keep the total nitrate content at least 9% by weight, as determined by analysis, until the iron content reaches 2%. Thereafter the nitrate content should be allowed to decrease, only sufficient nitric acid being added thereafter to keep the nitrate content at a percentage value determined by the following formula:

Nitrate content (in percentage by weight of total solution) $=9-\frac{5}{3}x$ (iron content in excess of 2%)

As the solution is used, the total acid titre decreases, and sulfuric acid should be added to keep the total acid titre at least as great as it was in the original solution.

Air should be bubbled through the solution (hereinafter referred to as "air scrubbing") to maintain its activity. The action of the solution on the metal reduces some of the nitrate to nitrite and the air scrubs some of the nitrite out as oxide of nitrogen and oxidizes the rest of the nitrite back to nitrate.

The solution described differs essentially from the prior-known solutions containing mixtures of nitric acid and hydrofluoric acid, by the addition of the sulfuric acid, which is a non-oxidizing, non-halide mineral acid and permits a substantial increase in the total acidity of the solution independent of any variation in the content of the

oxidizing agent or the fluoride content. Because of this fact the solution is not only more effective but retains its effectiveness after a greater amount of use and makes possible a specific system of analytic control and continued regeneration of the solution. Furthermore, my solution has the advantage over that disclosed in the Urban Patent 2,172,041 in that it employs nitric acid as the oxidizing agent. As employed in my solution, nitric acid has the advantage that its reduction products may be eliminated by volatilization or reoxidization (facilitated by air scrubbing), thereby preventing the usual slowing down of the action which results from an accumulation of reduction products.

My solution, in addition to removing the scale, induces a passive surface condition on the metal. The mechanism by which the passivity is induced is not fully understood, but it may be demonstrated that stainless steels are less active chemically after treatment in my solution. Evidence of this condition is shown by inertness of the metal, after treatment, toward dilute acidic copper sulfate solution, and its inability to hold an electroplate. This passive surface condition seems to be due, in part, at least, to the high oxidation potential of the solution.

I find that substantial economies in operation can be effected by maintaining several pickling solutions of different ages and successively moving the metal being pickled from the older to the newer solutions. Thus the work can first be immersed in a solution containing more than 2% iron and having a molal ratio of total fluoride to total iron content of less than 5.5 to 1 until most of the scale is removed and action ceases. The work can then be transferred to a newer solution with less than 2% iron, and having a molal ratio of total fluoride to total iron of from 5.5 to 1 to 5.9 to 1, in which all remaining scale will be quickly removed.

Experience indicates that the descaling of austenitic chromium nickel steels in my solution is a purely electrolytic phenomenon. Thus it may be assumed that the scale and the metal in immediate contact with it is electronegative with respect to any metal more remote from the scale, when immersed in acid solutions. This may be due to the tendency of magnetic oxide of iron and ferric oxide to depolarize hydrogen electrodes. At any rate it is observed that the presence of a high oxidation potential in the solution aids this depolarization. It has also been observed that the presence of free halide ions in aqueous solution depolarizes ferrous alloy anodes. This action unquestionably contributes to the formation of the electrolytic cell, which experimental evidence indicates is responsible for the descaling action.

The electrolytic solution of the metal undercuts the scale, thereby separating it from the metal being pickled. When the surface is clean, there is no more scale to form cathodes, and no excess metal is dissolved. This results in large savings of both acid and metal, and is an important feature of my invention.

The following explanation of the half reactions involved in the electrolytic action will aid in reaching an understanding of the operation of my solution:

The fundamental reaction at the cathode (the scale) is the evolution of nascent hydrogen, which is immediately oxidized in my solution by the oxidizing agents therein, which include dissolved air, nitrate, and ferric iron. This immediate oxidation depolarizes the cathode and speeds up the pickling reaction.

In accordance with mass action concepts, the accumulated reduction products, ferrous iron and nitrite ions, decrease the oxidation potential of the solution and will eventually slow down or stop the pickling action. This has been determined by making oxidation potential measurements and observing actual pickling operations. However, in practice, these reduction products are reoxidized to their original condition by the atmospheric oxygen in the air bubbled through the solution. The air scrubs out some of the nitrite as oxide of nitrogen and oxidizes the rest of the nitrite and all of the ferrous iron to nitrate and ferric iron respectively. Actual measurements have shown that such scrubbing action can raise the oxidation potential as much as 0.10 volt. A solution that has been paralyzed can be restored to effective condition by the air scrubbing.

The fundamental half reaction at the anode (the alloy itself as distinct from the scale) is the solution of the various metals present in the alloy. This half reaction is helped by moderate concentrations of free halide ions, which seem to depolarize this electrode, and by low concentrations of free ferric or ferrous ions.

Although a chloride ion might be used, it seems to be a too effective depolarizing agent and prevents effective operation of the passivation mechanism, and sometimes results in destructive pitting of the material being pickled. The fluoride ion seems to function effectively as a depolarizing agent and does not as frequently cause damaged work.

Good cathode conditions are induced by the presence of moderately low, well buffered, pH values. Because of difficulties in measuring pH values in fluoride-containing solutions of high acidity, no quantitative pH data are presented. However, it has been discovered that a satisfactory buffering action is obtained by having a high concentration of mineral acid. As already indicated, optimum operating conditions are obtained in solutions containing initially 7–10% by volume of commercial concentrated sulfuric acid, although any quantity in the range from 5–20% by volume will give satisfactory results.

It is particularly to be noted that the nitric and hydrofluoric acids contribute to the total acidity, but that their acidity alone is insufficient for most effective operation.

As the solution is used, the acidity must be maintained by additions of sufficient mineral acid (preferably sulfuric) to keep the total acid titre from decreasing materially. Sufficient acid may be added to increase the total acid content to as high as 30% (by volume), but experience does not indicate that any advantage is gained by so doing.

As indicated, it is necessary that the solution provide a sufficient quantity of nitric acid as an oxidizing agent to provide rapid and effective depolarization of the products of the cathodic half reaction, and provide sufficient oxidizing effect for maximum passivation effect on the cleaned surface. When the solution is first mixed, the nitric acid content of the solution should be from 3–20% by volume. Solutions containing more than 12% nitric acid are unnecessarily expensive, but concentrations up to 30% by volume can be used. Also, the starting concentration can be as low as 4% by volume, and starting solutions containing from 7–10% by

volume are useful where the demands are not severe. As the ferric iron content builds up, it provides a strong buffering action on the oxidation potential, and a lower (4–5%) nitric acid content can be tolerated.

It is undesirable to have the molal ratio of total fluoride to total iron greater than 6 to 1, except in fresh solutions containing not more than 2% hydrofluoric acid (by volume) because it invariably results in damaged work. Much of the scale can be removed from all work and all of the scale can be removed from some work, with solutions containing molal ratios of total fluorides to total iron of less than 5 to 1. However such solutions will not remove all of the scale from all work, whereas my preferred solution will. Also, as has been previously indicated, by using more than one solution and placing the work first in an old solution and then in a newer solution, low ratio solutions may be used to break the scale, after which it is cleaned up in a newer solution of higher fluoride ratio.

It has been found that when the sulfuric acid content is much lower than 7% (by volume) the pickling is slower and less effective. However sulfuric contents as low as 3% have been used effectively with higher original nitric acid content than those recommended.

Phosphoric acid may be substituted for part or all of the sulfuric acid with only a slightly detrimental effect upon the solution performance.

It should be noted that alkali nitrates and fluorides may be substituted for the nitric and the hydrofluoric acids, respectively, if the sulfuric acid content is increased accordingly. As long as the alkali metal concentration stays below 2 or 3% no detrimental effect on the pickling is noted, and in some instances acceptable work is produced with much higher alkali metal contents. However the substitution of the alkali nitrates and fluorides for the corresponding acids serves little useful purpose and is not recommended.

For some types of scale, such as those produced in highly reducing atmospheres, organic wetting agents are desirable in the pickling solution to facilitate the penetration of the scale and wetting of the underlying metal. A very small quantity of almost any commercial wetting agent, which is not destroyed by the oxidizing agents in the solution, is useful. The effectiveness of the wetting agent seems to depend solely upon the lowering of the surface tension. However, it is inadvisable to employ wetting agents when they are not needed, since they seem to hinder the passivation mechanism.

It has been mentioned that the iron content of the pickling solution increases with use. As would be expected, some nickel and chromium are also dissolved, but they have been found to have no important effect upon the operation of the solution, and can be disregarded.

For the purpose of explaining the invention, certain specific solutions and procedures have been described in detail. However, it is to be understood that various departures from the exact procedures described can be made while utilizing the advantages of the invention, and it is to be limited only as set forth in the appended claims.

I claim:

1. A pickling solution for removing scale from stainless steels, comprising a water solution containing, by volume: from 3 to 30% of a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid; from 4 to 30% nitric acid; and from 1 to 2% hydrofluoric acid.

2. A pickling solution for removing scale from stainless steels, comprising a water solution containing: from 3 to 30% by volume of a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid; from 4 to 30% by volume of nitric acid; up to 2%, by weight, dissolved iron; and fluoride in amount to make the molal ratio of total fluoride to total iron between 5 to 1 and 6 to 1.

3. A pickling solution for removing scale from stainless steels, comprising a water solution containing: from 3 to 30% by volume of a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid; from 4 to 30% by volume of nitric acid; dissolved iron between 2% and 6% by weight, and fluoride content of approximately 4 to 5% by weight.

4. A pickling solution for removing scale from stainless steels, comprising a water solution containing: from 3 to 30% by volume of a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid; from 1 to 8% by volume of hydrofluoric acid; dissolved iron less than 2% by weight; and a nitrate content of approximately 9% by weight.

5. A pickling solution for removing scale from stainless steels, comprising a water solution containing: from 3 to 30% by volume of a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid; from 1 to 8% by volume of hydrofluoric acid; dissolved iron between 2% and 6% by weight; and a percentage nitrate content, by weight, equal to 9—⅔ of the iron content in excess of 2%.

6. A method of regenerating a pickling solution for removing scale from stainless steels and comprising a water solution containing by volume: from 3 to 30% of a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid; from 4 to 30% nitric acid; and from 1 to 8% hydrofluoric acid; said method of regeneration comprising aerating said solution.

7. A method of removing scale from iron, nickel, chromium alloys of the stainless steel type, which comprises successively immersing the alloy in first and second pickling solutions, respectively, each solution comprising a water solution containing, by volume: from 3 to 30% of a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid; from 4 to 30% nitric acid; and from 1 to 8% hydrofluoric acid; together with dissolved iron from the alloy previously treated; in which said second solution is fresher than the first and contains less dissolved iron.

8. A method of maintaining a pickling bath for stainless steel, said bath containing as essential ingredients nitrate and fluoride ions in a solution acidified by a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid, together with increasing amounts of dissolved iron at least up to 2% by weight; said method comprising replenishing the supply of fluoride ions from time to time in amounts sufficient to maintain the molal ratio of total fluoride to total iron between 5 to 1 and 6 to 1.

9. A method of maintaining a pickling bath for stainless steel, said bath containing as essential ingredients nitrate and fluoride ions in a solution acidified by a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid, together with increasing amounts of

dissolved iron at least up to 2% by weight; said method comprising adding fluoride ions from time to time in amounts sufficient to maintain the molal ratio of total fluoride to total iron between 5 to 1 and 6 to 1 until the iron content by weight increases to 2%, and thereafter maintaining the fluoride content substantially constant.

10. A method of maintaining a pickling bath for stainless steel, said bath containing as essential ingredients nitrate and fluoride ions in a solution acidified by a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid, together with increasing amounts of dissolved iron up to 2% by weight; said method comprising adding nitrate ions to the bath from time to time in amounts sufficient to maintain the total nitrate content in excess of approximately 9% by weight.

11. A method of maintaining a pickling bath for stainless steel, said bath containing as essential ingredients nitrate and fluoride ions in a solution acidified by a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid, together with increasing amounts of dissolved iron from the pickled steel, said method comprising maintaining the total nitrate content at approximately 9%, by weight, until the dissolved iron reaches approximately 2%, by weight, and thereafter adding nitrate in amounts to maintain the percentage by weight in excess of 9—⅓ of the iron content in excess of 2%.

12. A method of maintaining a pickling bath for stainless steel, said bath containing as essential ingredients nitrate and fluoride ions in an acid solution, together with increasing amounts of dissolved iron from the pickled steel; which comprises adding a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid in sufficient amounts to maintain the total acid titre approximately equal to that of a new iron-free solution containing, by volume, 7 to 10% commercial concentrated sulfuric acid, 12 to 15% commercial concentrated nitric acid, and 1.5 to 2.0% hydrofluoric acid of strength 50–60% HF.

13. A method of maintaining a pickling bath for stainless steel, said bath containing as essential ingredients nitrate and fluoride ions in a solution acidified by a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid, together with increasing amounts of dissolved iron from the pickled steel, said method comprising adding fluoride ions from time to time in amounts sufficient to maintain the molal ratio of total fluoride to total iron between 5 to 1 and 6 to 1, and adding a nitrate as necessary to maintaining the nitrate content approximately 9%, by weight, at least until the iron content of the solution reaches 2%, by weight.

14. A method of maintaining a pickling bath for stainless steel, said bath containing as essential ingredients nitrate and fluoride ions in a solution acidified by a mineral acid selected from the group consisting of sulfuric acid and phosphoric acid, together with increasing amounts of dissolved iron from the pickled steel, said method comprising adding fluoride from time to time in amounts sufficient to maintain the molal ratio of total fluoride to total iron between 5 to 1 and 6 to 1, and adding a nitrate as necessary to maintain the nitrate content, by weight, at approximately 9% until the iron content reaches approximately 2%, by weight, and thereafter maintaining the fluoride content substantially constant while maintaining the percentage by weight of nitrate in excess of 9—⅓ of the iron content in excess of 2% by weight, while the iron content increases from approximately 2% by weight to approximately 6% by weight.

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