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STEEL PICKLING PROCESS

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This invention relates to the cleaning of metal surfaces, and more particularly, to the cleaning of wrought stainless steel surfaces by the use of a specific pickling solution.

Particularly in the fabrication of stainless steel hub caps, trim rings and the like, where appearance is an essential feature, there is often encountered a certain amount of difficulty in perfecting the cleaning of the stainless steel surfaces, for example, to remove oxides therefrom. The pickling of certain ferrous metal materials is, of course, old; but the pickling procedures heretofore used in the art have left something to be desired in connection with the cleaning of wrought stainless steel, and particularly, a specific type of wrought stainless steel known as "chrome-manganese" steel. The difficulty here apparently resides in the peculiar nature and extent of oxide formation which takes place in connection with certain of the metals other than iron which are present in these stainless steels. In general, the stainless steels have very high resistance to corrosion, but the oxides formed from certain of the metals present in stainless steel are equally resistant to chemical action in many cases and can be removed from the stainless steel surface only with difficulty.

The instant invention is based upon the discovery of a particular type of pickling solution for steels of this type which operates under specific conditions to obtain unusually superior results. This pickling solution not only accomplishes "pickling" (viz: the removal of the undesirable metal oxides, carbonates etc.) but it also has the unusual property of rendering the stainless steel passive, so that as soon as the undesirable oxide, etc., have been removed from the surface of the metal further chemical action will not take place.

It is, therefore, an important object of the instant invention to provide an improved stainless steel pickling process.

It is a further object of the instant invention to provide an improved method of pickling wrought stainless steel, that comprises the step of immersing the steel in an aqueous pickling solution of 5–20 weight percent sulfuric acid and 5–20 weight percent nitric acid at a temperature of 120–180° F.

Still another important object of the instant invention is to provide an improved method for the pickling of wrought stainless "chrome-manganese" austenitic steel containing 0.05–0.15% C, 16–18% Mn and 14–16% Cr, that comprises the step of immersing the steel in an aqueous pickling solution of 10–15 weight percent sulfuric acid and 10 weight percent nitric acid at a temperature of 140–160° F.

Other objects, features and advantages of the invention will become apparent to those skilled in the art from the following detailed disclosure of preferred embodiments thereof.

The instant invention consists of an improved method of pickling wrought stainless steel, that comprises the step of immersing the steel in an aqueous pickling solution of 10–15 weight percent sulfuric acid and 8–12 weight percent nitric acid at a temperature of 140–160° F.

Wrought stainless steels are a well known class of materials including austenitic, martensitic and ferritic steels, all of which contain a substantial amount of chromium (at least about 11% and preferably 12–25%). Wrought austenitic stainless steels are characterized by the presence of nickel or manganese and chromium therein in a total amount of at least 23% (and not more than about 50%), the Cr content being at least about 14–16% and the Ni and/or Mn content being at least about 7%. Preferred austenic steels for use in the invention are A1S1 type No. 301 (0.08–0.2% C; 16–18% Cr; 6–8% Ni; and max. 2% Mn) and "chrome-manganese" steel (0.05–0.15% C; 16–18% Mn; and 14–16% Cr). The martensitic steels have 11–18% chromium and up to about 1.25–2.5% nickel, an example being A1S1 type No. 431 (max. 0.2% C; 15–17% Cr; and 1.25–2.5% Ni). The ferritic steels have about 11–27% chromium, an example of a particularly preferred steel for use in the invention being A1S1 type No. 430 (max. 0.12% C and 14–18% Cr).

Most preferably the steel used is in sheet form (18–22 gauge) and it is formed into sheet-like articles such as hub caps, wheel covers, etc. The steel which has been found to be most preferred for use in the instant invention is the above identified "chrome-manganese" steel, although the other steel above identified may also be treated with distinct advantage by the use of the instant pickling solution.

Although the precise physical and chemical phenomenon which takes place during the instant pickling operation cannot be fully understood, is believed that the extremely active chemical combination of sulphuric acid and nitric acid results in effective removal of even the most chemically inert oxides, and this removal takes place down to the bare metal surface. As soon as the bare metal surface is reached, however, it is believed that the nitric acid (coupled with the unique inertness of the stainless steel per se) dominates the chemical activity so as to render the steel surface passive or inert toward corrosive action by the instant strong acid concentration.

The amount of sulfuric acid which may be used in the instant aqueous pickling solution may range from a minimum effective amount for cooperation with the nitric acid (namely, about 5%) to a maximum effective amount, which is about 20% of the total weight of the aqueous solution. (As used herein, the terms "parts" and "percent" mean percent by weight, unless otherwise designated.) Preferably, the amount of sulphuric acid used is about 10–15%.

The amount of nitric acid which may be used in the instant pickling solution ranges from about the minimum effective amount for cooperation with the sulfuric acid (which is about 5%) to the maximum amount which may be used (which is about 20%). Preferably, the nitric acid is used in a concentration of about 8–12%, and most preferably about 10%. It has been found that it is preferable to use the same or slightly more sulphuric acid than the amount of nitric acid; and the preferred ratio of sulphuric acid to nitric acid by weight is within the range of about 1:1 to about 3:2. The remainder of the solution is, of course, water, although the invention does not preclude the use of various other pickling solution additives such as stabilizers, etc. The essence of the instant invention, as far as materials used are concerned, resides in the particular cooperation between the sulphuric acid and nitric acid with respect to the pickling of certain stainless steels.

The concentrations of these two ingredients used in the solution are important and also the temperature used for carrying out the pickling operation is important. It has been found that the temperature used should range from a minimum of about 120° F. to a maximum of

about 180° F. The temperature used, of course, controls to a substantial extent the rate of the pickling action, but it is also found that particularly important to employ temperatures at least within the aforementioned operative range in order to accomplish effective pickling of the superior nature here obtained. Most preferably, the pickling temperature is within the range of 140–160° F., whereat ideal pickling operation is obtained.

As hereinbefore mentioned, the "chrome-manganese" stainless steel is preferred for use in the instant invention. This is apparently the case because certain of the oxides of manganese, chromium or complex mixtures thereof, which are characteristic for this particular steel, have been found to cause a great deal of difficulty in the pickling operations heretofore employed. For that matter, the pickling of all of the stainless steels has presented a number of problems; but is believed that the particular chemical combination of oxides or the like undesirable surface chemicals combined with the specific metal or metallurgical characteristics at the bare metal surface (including the carbon content and the metallurgical character of the carbon present) have made the pickling of "chrome-manganese" steel most difficult.

The invention may be demonstrated using a piece of 20 gauge sheet material which has been formed into a wheel cover, this material being the wrought stainless "chrome-manganese" austenitic steel hereinbefore described and having been subjected to one or more heat treating operations so as to obtain a slight but noticeable oxide formation or "scale" on the surface thereof. A solution of 12½% sulphuric acid-10% nitric acid in water, which is maintained at 150° F. is employed as a pickling bath and the steel piece is immersed therein. Active removal of the oxides and other undesirable surface materials commences immediately and after a short period of time all reaction appears to cease. The piece is then removed and washed and examined; and it is noted that the surface impurities have been removed completely, but the metal surface is not corroded by the pickling bath. If dilute concentrations of the acids, such as 1% of each, are used little or no oxide removal takes place. If the nitric acid is used alone very little pickling action occurs; and if the sulphuric acid is used alone corrosion of the metal will be noticed in certain locations. As previously indicated, effective action may be obtained using the nitric acid and the sulphuric acid each within the range of about 5–20 weight per cent; but a much more effective corrosion action is obtained using about 10–15 weight per cent of sulphuric acid and about 8–12 weight per cent of nitric acid. Also, if the temperature is reduced below 140° F., to about 120° F., for example, the pickling action is still noticeable, but much more effective pickling action is obtained using temperatures within the range of 140–160° F. Increasing the temperatures to about 180° F. is a generally undesirable practice because of the tendency to release volatile matter from the pickling bath.

The pickling of other wrought stainless steel is carried out by the use of the same procedure, for example, using the hereinbefore described AISI type No. 301, 431 and 430, respectively, and it is found in each case that very satisfactory pickling of these metals is accomplished.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of the present invention.

I claim as my invention:

1. A method of pickling wrought stainless steel, that comprises the step of immersing the steel in a bath consisting of an aqueous pickling solution of 5–20 weight per cent sulfuric acid and 5–20 weight per cent nitric acid at a temperature of 120–180° F.

2. A method of pickling wrought stainless steel, that comprises the step of immersing the steel in a bath consisting of an aqueous pickling solution of 5–20 weight per cent sulfuric acid and 5–20 weight per cent nitric acid at a temperature of 140–160° F.

3. A method of pickling wrought stainless steel, that comprises the step of immersing the steel in a bath consisting of an aqueous pickling solution of 5–20 weight per cent sulfuric acid and 8–12 weight per cent nitric acid at a temperature of 120–180° F.

4. A method of pickling wrought stainless steel, that comprises the step of immersing the steel in a bath consisting of an aqueous pickling solution of 10–15 weight per cent sulfuric acid and 5–20 weight per cent nitric acid at a temperature of 120–180° F.

5. A method of pickling wrought stainless steel, that comprises the step of immersing the steel in a bath consisting of an aqueous pickling solution of 10–15 weight per cent sulfuric acid and 8–12 weight per cent nitric acid at a temperature of 140–160° F.

6. A method of pickling wrought stainless "chrome-manganese" austenitic steel containing 0.05–0.15% C, 16–18% Mn and 14–16% Cr, that comprises the step of immersing the steel in a bath consisting of an aqueous pickling solution of 10–15 weight per cent sulfuric acid and 8–12 weight per cent nitric acid at a temperature of 140–160° F.

7. A method of pickling wrought stainless "chrome-manganese" austenitic steel containing 0.05–0.15% C, 16–18% Mn and 14–16% Cr, that comprises the step of immersing the steel in a bath consisting of an aqueous pickling solution of 10–15 weight per cent sulfuric acid and 5–20 weight per cent nitric acid at a temperature of 120–180° F.

8. A method of pickling wrought stainless "chrome-manganese" austenitic steel containing 0.05–0.15% C, 16–18% Mn and 14–16% Cr, that comprises the step of immersing the steel in a bath consisting of an aqueous pickling solution of 5–20 weight per cent sulfuric acid and 8–12 weight per cent nitric acid at a temperature of 120–180° F.

9. A method of pickling wrought stainless "chrome-manganese" austenitic steel containing 0.05–0.15% C, 16–18% Mn and 14–16% Cr, that comprises the step of immersing the steel in a bath consisting of an aqueous pickling solution of 5–20 weight per cent sulfuric acid and 5–20 weight per cent nitric acid at a temperature of 140–160° F.

10. A method of pickling wrought stainless "chrome-manganese" austenitic steel containing 0.05–0.15% C, 16–18% Mn and 14–16% Cr, that comprises the step of immersing the steel in a bath consisting of an aqueous pickling solution of 10–15 weight per cent sulfuric acid and 10 weight per cent nitric acid at a temperature of 140–160° F.

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