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CLEANING FERROUS ARTICLES

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3 Claims. (Cl. 204—18)

This invention relates to improvements in cleaning iron, steel and similar ferrous articles in preparation for subsequent treatment, as, for example, by galvanizing, electroplating, enameling, and the like. Broadly, the object of the invention is the provision of an improved method of removing rust, scale and the like from ferrous articles which is more economical in use and more effective in the removal of such extraneous material than the heretofore customary methods of cleaning such articles. More specifically, the invention aims to provide an improved method of preparing ferrous articles for coating with zinc by electrodeposition, particularly, at relatively high current density with insoluble anodes in a strongly acid zinc electrolyte.

As a preliminary and preparatory step in processes of providing ferrous articles with a protective coating, as, for example, in galvanizing, electrodeposition, enameling, etc., it is necessary that the surface of the ferrous article be thoroughly cleaned and freed from adhering rust, scale, etc. This has heretofore been ordinarily accomplished by immersing the article in a cleaning or pickling solution consisting of dilute sulphuric or hydrochloric acid. The strength of the acid is held down to the point at which the action on the metal itself is not too violent and in recent years it has become the general practice to include in the pickling liquor some organic inhibitor to diminish as much as possible the direct solution of the iron itself. In the case of sulphuric acid such direct solution of iron rapidly increases with increasing concentration, reaching a maximum at an acid strength of about 35% H_2SO_4. In practice, therefore, it is now customary to hold the strength of the sulphuric acid pickling liquor well below this critical acid strength.

While it has long been recognized that concentrated sulphuric acid, say 60% or more H_2SO_4, exerts little, if any, chemical action on iron at ordinary temperatures, such concentrated acid has not, so far as I am aware, been used alone for the pickling of ferrous articles. I have now discovered that concentrated sulphuric acid, particularly when heated to a temperature of 100° C. or more, is an admirable medium for removing rust and scale from iron, steel and similar ferrous articles. Thus, I have found that by using sulphuric acid of a strength of 60% or more the action on iron or steel can be reduced to a minimum or entirely prevented, while the removal of iron oxide, scale, etc. is actually accelerated. Especially good results are obtained, particularly in the case of scale containing combined water, such as rust, soap, lime-scale etc., by using concentrated sulphuric acid of a strength of 80% or more and raising the temperature above the boiling point of water. I find that under such conditions the sulphuric acid abstracts the combined water from the scale which falls as a powder, and, at the same time, the high temperature prevents or minimizes the adsorption of hydrogen at the surface of the ferrous article with consequent danger of embrittlement.

Based on these discoveries, the present invention, in its broad aspect, involves immersing the ferrous article, in preparation for its subsequent treatment, in a solution of sulphuric acid of a concentration of 60% or more H_2SO_4, and preferably at a temperature of 100° C. or more, for a sufficient time interval to effect the removal of extraneous surface material without substantial solution of the metal itself. The invention is particularly applicable to the cleaning of ferrous articles in preparation for zinc coating by electrodeposition from a strongly acid electrolyte. The strongly acid spent electrolyte from the electrodepositing operation (after appropriate concentration by evaporation, by the addition of highly concentrated sulphuric acid, or by other appropriate means) provides a convenient and economical source of sulphuric acid for the cleaning operation.

In practicing the invention, the ferrous article is immersed for the requisite time in the concentrated and preferably hot sulphuric acid pickling liquor. It is my preferred practice to maintain the sulphuric acid concentration of the pickling liquor around 80% or more, and to heat the liquor to a temperature of from 100 to 180° C., preferably in the neighborhood of 150° C. However, entirely satisfactory results are obtained in practice by immersion of the ferrous article in a liquor containing 60–66% sulphuric acid at a temperature of about 70° C. for 12 to 16 hours, say overnight. The stronger the acid concentration and the higher the temperature, the shorter is the required time of treatment. The action of the concentrated sulphuric acid is primarily that of a dehydrating agent, in that it abstracts water from the extraneous matter adhering to the surface of the ferrous article, thereby so disintgerating such matter and weakening the bond between it and the ferrous surface that rust, scale etc. fall from the article and accumulate in a finely divided state on the bottom of the pickling tank or vat.

The pickling liquor may be a concentrated solution of sulphuric acid, or may be made up in whole or in part of strongly acid spent electrolyte after appropriate concentration of its acid content. Since the spent pickling or cleaning liquor may be advantageously and economically utilized in the regeneration of strongly acid zinc electrolyte, the invention is of particular advantage in conjunction with the electrodeposition of zinc from such an electrolyte with

insoluble anodes at relatively high current density. Thus, the spent pickling liquor, after appropriate dilution if necessary, may be used in leaching oxidized zinciferous material to form or regenerate a strongly acid zinc sulphate electrolyte.

The present invention is particularly applicable in coating ferrous articles with zinc by the processes of electrodeposition described in the U. S. patents of U. C. Tainton No. 1,210,017, December 26, 1916 and No. 1,247,179, November 20, 1917, and in his copending patent application Serial No. 597,622, filed March 8, 1932. In those processes a relatively high current density of 50 or more amperes per square foot, preferably 500–600 amperes per square foot, is employed in conjunction with insoluble anodes and a zinc sulphate electrolyte containing 10% or more of free sulphuric acid. Preferably, the zinc electrolyte contains 20 to 30% of free sulphuric acid, and the spent electrolyte contains 30% or more of free sulphuric acid. In the application of the present invention to such processes of zinc electrodeposition, the strongly acid spent electrolyte is admirably adapted as the source of the concentrated pickling liquor. The spent electrolyte may be delivered directly to the pickling vat where the requisite concentration of the sulphuric acid is maintained by the evaporation of water at the prevailing temperature in excess of 100° C. If desired, the spent electrolyte may be separately concentrated with respect to its sulphuric acid content before it is delivered to the pickling vat. Or, very highly concentrated sulphuric acid, such as oleum or fuming acid, may be added to the spent electrolyte to appropriately raise its sulphuric acid content, or may be added to the pickling vat to establish and maintain the contemplated high sulphuric acid content thereof.

It is desirable to wash the article thoroughly with a large volume of water after its removal from the hot concentrated sulphuric acid pickling liquor. This prevents any secondary acid attack which might occur if only a small quantity of water were used for the washing, thereby tending to form weak acid on the surface of the article and so cause solution of the iron and hydrogen occlusion. In certain cases, however, the washing can be dispensed with and the article after draining passed direct to the zinc plating, or galvanizing or other contemplated operation.

Practice of the invention results in the following special advantages:

1. The concentrated sulphuric acid is a practically universal cleaner and removes not only metallic scale, but also grease, soap, lime, etc. which would otherwise have to be made the subject of special cleaning steps.

2. The action of the acid is substantially confined to the scale and other extraneous surface material, and very little of the actual metal surface is dissolved.

3. Such iron as is dissolved by the acid is relatively insoluble in the concentrated sulphuric acid liquor and is precipitated as finely divided iron sulphate which settles to the bottom of the pickling vat from whence it may be readily removed. This makes it easy to dispose of the material removed from the surface of the ferrous article.

4. No electrolytic or equivalent supplementary action is necessary to effect the required cleaning of the ferrous article; the dehydrating action of the concentrated sulphuric acid being complete in itself for the purpose.

The actual consumption of sulphuric acid in the cleaning operation of the invention is relatively slight, and such small amount of acid as is consumed is converted into finely divided solid material which accumulates on the bottom of the pickling vat, from whence it can be conveniently removed as desired. The dehydrating action of the concentrated acid tends, of course, to decrease its acid concentration, but ample compensation for this effect is readily made in practice as hereinbefore described. The pickling liquor may thus be maintained at the desired acid concentration substantially without contamination and used almost indefinitely. Moreover, no spent pickling liquor is provided with the attendant problem of its disposal.

We claim:

1. The process of removing rust and scale from the surface of ferrous articles, which comprises immersing the article in a solution of sulphuric acid of a concentration of 60% or more H_2SO_4 at a temperature of 100° C. or more in the absence of an imposed electric current for a sufficient time interval to effect the removal of extraneous surface material, including rust and scale, without substantial solution of the metal itself, and washing thoroughly with a sufficiently large volume of water to prevent a substantial degree of secondary action of the sulphuric acid upon the ferrous article, and electrodepositing zinc upon such cleaned article.

2. The process of removing rust and scale from the surface of ferrous articles, which comprises immersing the article in a solution of sulphuric acid of a concentration of 80% or more H_2SO_4 at a temperature in excess of 100° C. in the absence of an imposed electric current for a sufficient time interval to effect the removal of extraneous surface material, including rust and scale without substantial solution of the metal itself, and washing thoroughly with a sufficiently large volume of water to prevent a substantial degree of secondary action of the sulphuric acid upon the ferrous article, and electrodepositing zinc upon such cleaned article.

3. In a process of coating ferrous material with zinc, the steps of subjecting successive portions of the material to cleaning by the action of a liquor containing at least 60% sulphuric acid in the absence of an imposed electric current, immediately washing the so treated portions of the material with water in a sufficiently large volume to prevent a substantial degree of secondary action of the sulphuric acid on the ferrous material, subjecting the washed material to electrodeposition at relatively high current density with insoluble anodes in a strongly acid zinc electrolyte, concentrating the spent electrolyte from the electrodeposition operation to produce a solution containing at least 60% sulphuric acid, and using this concentrated solution for the cleaning step.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, lines 36 and 37, claim 1, strike out the comma and words ", and electrodepositing zinc upon such cleaned article"; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 2nd day of March, A. D. 1937.

(Seal)

Henry Van Arsdale
Acting Commissioner of Patents.