METHODS OF PICKLING FERROUS METALS

Patrick Costelloe, Chester, and Albert Edward Jackson, Gwernafaidl Mold, England, assignors to John Summers & Sons Limited, Deeside, England, a British company

No Drawing. Filed May 27, 1968, Ser. No. 732,059
Claims priority, application Great Britain, June 8, 1967, 26,585/67
Int. Cl. C32g 1/02

U.S. Cl. 134—3
5 Claims

United States Patent Office
Patented Feb. 23, 1971

3,565,688

This invention concerns a method of pickling ferrous metal.

Ferrous metal, such as, for example, mild steel, which has been subjected to manufacturing processes at high temperatures becomes coated with a layer of surface contamination, mainly metal oxides. This contamination must be removed before any subsequent treatment can be applied to the metal surface.

The contamination is often removed by "pickling" the metal in an acid pickling bath, the acid generally being a dilute solution of sulphuric or hydrochloric or phosphoric acid or, very occasionally, dilute nitric acid.

Pickling ferrous metal in dilute nitric acid has hitherto been unsatisfactory because the quality of the pickled surface, while initially good, quickly deteriorates as the quantity of metal pickled in a given quantity of acid is increased.

We have found that this is because a dilute nitric acid pickling solution is unstable, the products of a reaction between the dilute nitric acid and the iron poisoning the solution. When a solution has become poisoned, the rate of dissolution of iron from the pickled surface decreases and the pickled surface becomes dirty and uneven. The addition of concentrated nitric acid to such a poisoned solution makes little improvement to the quality of the pickled surface.

We think that dilute nitric acid attacks iron by two reactions. The first or desirable reaction which produces a good quality pickled surface, yields ammonium nitrate and ferrous nitrate.

The second or undesirable reaction is more complex.

We think that the iron liberates nitrous acid and oxides of nitrogen from the nitric acid. The nitrous acid and oxides of nitrogen tend to remain near the surface of the metal, and react further with the iron. The products of this reaction also tend to remain near the surface of the metal and are thought to promote the aforementioned second or undesirable reaction and inhibit the first or desirable reaction. If the undesirable reaction is allowed to continue, the quality of the pickled surface produced will quickly deteriorate.

We have found that if the undesirable reaction can be inhibited in its early stages, that is before the nitrous acid and oxides of nitrogen can attack the iron then the quality of the pickled surface produced can be maintained.

Our invention therefore comprises a method of pickling ferrous metal comprising treating said ferrous metal with a solution containing dilute nitric acid, said solution containing urea to inhibit the accumulation of nitrous acid and oxides of nitrogen in the solution.

Preferably, the concentration of the nitric acid in the solution does not exceed 5% by weight.

Preferably the urea is present in a concentration of 25 grams of urea per litre of solution.

Preferably the pickling is effected at a temperature not exceeding 20° C.

Preferably the solution is agitated.

The invention also comprises ferrous metal when pickled by the method set forth above.

Merely by way of example, the invention will be described with reference to the following experimental results.

We have added urea to a dilute nitric acid pickling solution and have found that the undesirable reaction is markedly inhibited. In particular, urea destroys nitrous acid by reacting with it to give nitrogen, carbon dioxide and water.

We have also found that the undesirable reaction is further inhibited by maintaining the temperature of the solution approximately in the range 17–20° C. Agitation of the solution by means, for example, of pumping has also been found to inhibit the undesirable reaction.

We have found that the most suitable concentration of nitric acid in the solution is 5% by weight, although acceptable pickling quality is obtained at acid concentrations up to 15% by weight. A higher concentration is unsuitable, since urea is insoluble in cold dilute nitric acid and the concentration above 15% by weight, and thus cannot in this case inhibit the undesirable reaction. The only significant difference in performance between a relatively low and a relatively high acid concentration is that the latter removes iron from the pickled surface at a faster rate.

We have found that 25 gm. urea per litre of dilute nitric acid is a suitable concentration.

The following tabulated results show the effects of adding urea to the pickling solution.

<table>
<thead>
<tr>
<th>Table 1. —% w/w. NITRIC ACID WITHOUT UREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of Acid, 100 galls</td>
</tr>
<tr>
<td>Kg.</td>
</tr>
<tr>
<td>0.9</td>
</tr>
<tr>
<td>0.9</td>
</tr>
<tr>
<td>0.9</td>
</tr>
<tr>
<td>0.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. —% w/w. NITRIC ACID CONTAINING 25 GMS./LITRE UREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of Acid, 100 galls</td>
</tr>
<tr>
<td>Kg.</td>
</tr>
<tr>
<td>0.9</td>
</tr>
<tr>
<td>0.9</td>
</tr>
<tr>
<td>0.9</td>
</tr>
<tr>
<td>0.9</td>
</tr>
</tbody>
</table>
The quality of the pickling produced by the solution containing urea was acceptable after 60,000 square feet of surface has been processed. There was no reason to suppose that the solution would produce an unacceptable pickled surface until the quantity of dissolved salts caused crystallisation. Although the above tabulated results refer to mild steel, it will be appreciated that the invention is applicable to the pickling of many other steels and other ferrous metals.

Pickling ferrous metals according to our invention may have the following advantages.

1. The metal surface can be deeply and uniformly etched without the application of an electric current.
2. The rate of dissolution of iron is high without the application of current.
3. The acid can be used cold and the products of dissolution are very soluble in cold acid.
4. No hydrogen is introduced into the metal during pickling.
5. The pickled surface is to some extent inhibited against rusting.

We claim:

1. A method of pickling ferrous metal comprising treating said ferrous metal with an aqueous solution consisting of nitric acid and urea, said nitric acid not exceeding 15% by weight, said urea being present in amounts sufficient to inhibit the accumulation of nitrous acid and oxides of nitrogen in the solution, said treatment being carried out at a temperature not exceeding 20° C., thereby preventing said nitrous acid and oxides of nitrogen from reacting with said ferrous metal.
2. The method of claim 1 in which the concentration of the nitric acid in the solution is 5% by weight.
3. A method as claimed in claim 1 in which the urea is present in a concentration of 25 grams of urea per litre of solution.
4. The method of claim 1 in which the pickling is carried out at a temperature in the range of 17 to 20° C.
5. A method as claimed in claim 1 wherein the solution is agitated.

References Cited

UNITED STATES PATENTS
2,368,955 2/1945 Weesner et al. .......... 134—3X
2,915,420 12/1959 Hardy .................. 134—3
3,228,816 1/1966 Kendall ................. 134—41X
3,280,038 10/1966 Morris .................. 134—41
3,479,293 11/1969 Bellinger et al. ......... 252—79.4

FOREIGN PATENTS
458,163 12/1936 Great Britain .......... 252—148

JOSEPH COVRONEK, Primary Examiner
J. T. ZATARGA, Assistant Examiner
U.S. Cl. X.R.
134—41