PROCESS FOR DESMUTTING METAL

Edwin W. Goodspeed, Royal Oak and Galillard W. Dell, Detroit, Mich., assignors to Hooker Chemical Corporation, Niagara Falls, N.Y., a corporation of New York

No Drawing. Filed May 17, 1965, Ser. No. 456,547

8 Claims. (Cl. 252—95)

ABSTRACT OF THE DISCLOSURE

A process for removing a carbonaceous smut from a ferrous metal surface wherein the ferrous metal surface containing the carbonaceous smut is treated with an alkaline permanganate solution. Preferably the alkaline permanganate solution contains sodium hydroxide and potassium permanganate and may also contain sodium carbonate, as an optional ingredient. In the overall process, the ferrous metal surface is first contacted with an acid pickling solution, the ferrous metal being maintained in contact with the pickling solution for a period sufficient to form a deposit of carbonaceous smut thereon. Thereafter, the ferrous metal surface is then contacted with the alkaline permanganate solution which is maintained in contact with the surface for a period sufficient to effect substantial removal of the carbonaceous smut which has been formed.

This invention relates to an improved method for treating metal surfaces and more particularly relates to an improved method and composition for treating ferrous metal surfaces to remove carbon smut.

One of the problems frequently encountered in the cleaning of metal surfaces, and particularly ferrous metal surfaces, is that of removing carbonaceous deposits from the metal surface. This smut may be a deposit left after pickling or etching of the metal, due to insoluble alloying elements such as ferric carbide and the like, or it may be carbonaceous deposits from the decompositition of rolling or drawing lubricants during the rolling of the ferrous steel or the forming of shapes, or from subsequent heat treatment. The removal of this carbonaceous smut is important in that the presence of the smut may adversely affect the quality of a coating subsequently applied to the ferrous metal surface, such as a protective or paint base coating, an electro-coating or plating, or the like.

Because of the nature of such carbonaceous smuts, they have, heretofore, been removed only with great difficulty and have, sometimes, required the use of costly and time consuming hand cleaning or scouring operations. In an effort to eliminate these hand cleaning operations, it has been proposed to use electro-cleaning to effect desmutting of the ferrous metal surfaces. Even with this type of cleaning, however, high current densities are required, and the cleaning solution generally must have a high conductivity and is used at high concentrations and elevated temperatures. Moreover, unless the cleaning of the work is to be followed by an electro-plating or other electro-coating operation, the cost of installing the necessary direct current generators or rectifiers, for only an electro-cleaning operation is generally not justified. Accordingly, up to the present time there has not been a completely satisfactory method for desmutting ferrous metal surfaces easily and at a comparatively low cost.

It is, therefore, an object of the present invention to provide an improved method for desmutting ferrous metal surfaces.

Another object of the present invention is to provide an improved method for treating ferrous metal surfaces wherein deposits of a carbonaceous smut are easily and economically removed from the metal surface.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

Pursuant to the above objects, the present invention includes a process for treating ferrous metal surfaces having thereon a carbonaceous smut which comprises, contacting the ferrous metal surface with an alkaline permanganate solution and maintaining the solution in contact with the metal surface for a period of time sufficient to effect a substantial removal of the smut.

More specifically, in the practice of the method of the present invention a ferrous metal surface containing a carbonaceous smut is desmutter by contacting it with an alkaline permanganate solution. This contact is preferably effected by immersing the ferrous metal in the permanganate solution. Although it is preferred to immerse the ferrous metal surface in the alkaline permanganate solution, it is to be appreciated that the solution may be brought into contact with the metal surface in other ways, as for example, by spraying, flowing, or the like. In many instances, however, it has been found that the most economical usage of the permanganate solution is obtained when the metal surface is immersed therein and for this reason primary reference will be made hereinafter to contacting the ferrous metal surface with the alkaline permanganate solution by immersion.

The ferrous metal surface is maintained in contact with the alkaline permanganate solution for a period of time sufficient to effect the substantial removal of the carbonaceous smut from the metal surface. Generally, contact times within the range of about one-half to about 5 minutes have been found to be sufficient, with contact times of from about 1 to 2 minutes being typical. It will be appreciated, however, that in some instances, both shorter and greater contact times may be used. In any case, the time of contact between the alkaline permanganate solution and the ferrous metal surface will be at least sufficient to effect the substantial removal of the carbonaceous smut from the metal surface.

The solution which is to be used as the ferrous metal surface is contacted with the alkaline permanganate solution, e.g., an aqueous solution containing an alkaline permanganate. By "alkaline permanganate," it is intended to refer to the permanganates of lithium, sodium, potassium, cesium, and rubidium. Of these, the potassium permanganate and, accordingly, primary reference will be made hereinafter to this material. The solutions used in desmutting the ferrous metal surfaces will contain the potassium permanganate in an amount at least sufficient to effect the desired removal of the carbonaceous smut from the metal surface. Typically, the potassium permanganate is present in the treating solution in an amount within the range of about 2 to about 40 grams per liter and preferably in an amount within the range of about 3 to about 8 grams per liter. It is to be appreciated, of course, that in some instances, the treating solutions may contain the potassium permanganate in amounts either greater than or lesser than those which have been indicated, provided that the amounts used are sufficient to effect a substantial removal of the smut from the ferrous metal surface without detrimentally affecting the metal surface.

In addition to the alkaline permanganate, the desmutting solutions of the present invention also desirably contain an alkaline metal hydroxide. Although various alkaline metal hydroxides may be used, such as the hydroxides of lithium, sodium, potassium, cesium or rubidium, it has generally been found to be preferable to use sodium hydroxide in the present composition. Typically, the so-
3,380,921

Dium hydroxide is present in an amount within the range of about 5 to about 70 grams per liter with an amount within the range of about 12 to about 30 grams per liter being preferred. It is believed that the alkalinity added to the solution by the sodium hydroxide in some manner increases the effectiveness of the permanganate in removing the smut from the ferrous metal surface treated. Accordingly, in some instances both greater and lesser amounts of the alkali metal hydroxide may be included in the desmutting solution, provided that the amount present is at least sufficient to obtain the desired enhancement of the permanganate in the composition.

In formulating the smut removing solutions of the present invention, the potassium permanganate may be dissolved in water in amounts sufficient to provide an aqueous solution containing the permanganate in the amounts which have been indicated hereinabove. Where it is desired that the desmutting solution also contain an alkali metal hydroxide, a dry composition may be formulated by admixing the potassium permanganate and sodium hydroxide, in amounts sufficient to provide the desired concentration of these components in the aqueous solution, and this dry composition is then admixed with water to form the aqueous desmutting solution. Typically, such a dry composition may contain from about 50 to about 95 parts by weight of sodium hydroxide and from about 5 to about 50 parts by weight of potassium permanganate. Amounts of sodium hydroxide within the range of about 60 to 90 parts by weight and amounts of potassium permanganate within the range of about 10 to about 40 parts by weight are preferred.

In formulating such a dry composition, it may also be desirable to include therein an alkali metal carbonate, such as sodium carbonate. Typically, where the sodium carbonate is included in the dry mixture, it is present in an amount within the range of about 5 to 50 parts by weight with amounts within the range of about 10 to 40 parts by weight being preferred. A specifically preferred composition of this type, for use in formulating the aqueous desmutting composition of the present invention, is one containing about 60 parts by weight sodium hydroxide, about 20-25 parts by weight of potassium permanganate and about 12-20 parts by weight of sodium carbonate.

As has been noted hereinabove, such a dry admixture is combined with water in an amount sufficient to give an aqueous desmutting solution containing the alkali metal hydroxide and alkali metal permanganate in the amounts which have been indicated. Where the admixture also contains an alkali metal carbonate, this component is present in the aqueous solution in an amount within the range of about 2 to about 40 grams per liter and preferably in an amount within the range of about 3 to about 8 grams per liter. A specifically preferred aqueous desmutting solution is one containing about 14-16 grams per liter of sodium hydroxide, about 5-7 grams per liter of potassium permanganate and about 3-5 grams per liter of sodium carbonate.

In the absence of the preferred method of the present invention, a ferrous metal surface containing a carbonaceous smut is immersed in an aqueous desmutting solution, as has been described hereinabove, for a period of about 1 to 2 minutes. As has been previously indicated, contacting techniques, other than immersion, and contact times both greater than and lesser than 1 to 2 minutes may be used in some instances. Preferably, the aqueous desmutting solution is at an elevated temperature above room temperature, i.e., 20 degrees centigrade, temperatures within the range of about 27 to about 85 degrees centigrade being typical with temperatures within the range of about 33 to about 50 degrees centigrade being preferred. Thereafter, the ferrous metal surface is removed from the desmutting solution and, if desired, may be rinsed with water so as to remove any of the desmutting solution which may remain on the surface. This surf

face may then be further treated, as for example by electroplating, by the application of a protective or paint base coating, such as a phosphate coating, and/or by painting.

In an overall process for treating ferrous metal surfaces, utilizing the desmutting method of the present invention, the ferrous metal surface is first pickled, using an acid pickling solution. Such acid pickling solutions are well known to those in the art and may be formulated from various acids, including organic acids; mineral acids, such as sulfuric acid, hydrochloric acid, and phosphoric acid and the like. Typically, the pickling solutions are aqueous solutions of mineral acids, and preferably aqueous solutions of sulfuric acid or hydrochloric acid. The ferrous metal surface is maintained in contact with the acid pickling solution until a carbonaceous smut is formed on the metal surface, times of about 10 to 45 minutes being typical. The metal surface is then removed from the pickling acid and, preferably, rinsed with water so as to remove any of the acid solution which remains on the surface. Thereafter, the ferrous metal surface is contracted, preferably by immersion, with an aqueous alkaline permanganate solution, preferably containing about 15 grams per liter sodium hydroxide, 5 grams per liter potassium permanganate, and 5 grams per liter sodium carbonate, which solution is preferably at a temperature within the range of about 35 to 50 degrees centigrade, for a period of about one to two minutes or until the carbonaceous smut has been substantially removed from the ferrous metal surface. The ferrous metal surface is then ready for any of the aforesaid coating treatments.

It has been found that the ferrous metal surface, upon removal from the permanganate desmutting solution contains a brown film, probably of manganese dioxide. Although such a film is generally not detrimental to subsequent phosphatizing applications, if it is desired, this film may be removed by subjecting the surface to a short or so-called "flash" pickle in an acid pickling solution. Where such a pickle is used, the pickling solution is preferably the same as that which has previously been used, e.g., a mineral acid pickle such as sulfuric acid or hydrochloric acid. When using this pickling step, the ferrous metal surface is maintained in contact with the pickling solution for a period of time sufficient only to remove the manganese dioxide film from the ferrous metal surface, but not sufficient to develop a new deposit of carbonaceous smut on the metal surface. Pickling times of up to about 2 minutes are typical, with pickling times within the range of from a few seconds up to about 1 minute being preferred. After removal from this flash pickle, the ferrous metal surface, preferably after water rinsing to remove any remaining pickling solution, is then ready for subsequent coating steps, such as electroplating, application of a protective or paint base coating such as a phosphate coating, and/or painting and the like.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. It is to be understood that these examples are given for illustrative purposes only and it is not intended that they will limit the scope of the invention. In these examples, unless otherwise indicated, temperatures are in degrees centigrade and parts are by weight.

**EXAMPLE 1**

A dry composition containing 60 parts of sodium hydroxide, 20 parts of sodium carbonate and 20 parts of potassium permanganate was dissolved in water in an amount of about 25 grams per liter, to provide an aqueous solution containing about 5 grams per liter potassium permanganate, 5 grams per liter of sodium carbonate and 15 grams per liter of sodium hydroxide. This solution was then heated to a temperature of about 45 degrees centigrade and a cold rolled steel panel having a heavy de-
The deposit of carbonaceous smut on the surface was immersed in the hot solution for about 2 minutes. The panel was then removed from the aqueous solution, rinsed with water, given a flash pickle for about 45 seconds in H₂SO₄ rinsed again with water and then tested while wet for the presence of smut by wiping with a clean white cloth. Upon examination, the cloth showed only a faint trace of gray, indicating substantially complete removal of the smut from the metal surface.

**EXAMPLE 2**

The procedure of Example 1 was repeated with the exception that the aqueous solution in which the cold rolled steel panel was immersed contained only 5 grams per liter potassium permanganate and 5 grams per liter sodium hydroxide. This solution was formulated by dissolving in water a dry composition containing 50 parts of potassium permanganate and 50 parts sodium hydroxide. After testing the treated panel, as in Example 1, examination of the cloth showed only faint traces of gray, again indicating substantially complete removal of the smut.

**EXAMPLE 3**

The procedure of Example 1 was repeated with the exception that the aqueous desmutting solution contained only 5 grams per liter potassium permanganate and 15 grams per liter of sodium hydroxide. This solution was formulated by dissolving in water a dry composition containing about 75 parts of sodium hydroxide and 25 parts of potassium permanganate. Testing of the treated panel as in the previous examples again indicated substantially complete removal of the smut.

**EXAMPLE 4**

A cold rolled steel panel was immersed at 77 degrees centigrade in an aqueous solution of sulfuric acid, which solution contained 15% by weight H₂SO₄, for a period of 30 minutes. At the end of this time, the panel was removed from the acid solution and was found to have a deposit of the carbonaceous smut on the surface. This panel was then immersed in an aqueous solution containing about 6 grams per liter of potassium permanganate, 3 grams per liter sodium carbonate and 15 grams per liter sodium hydroxide. This solution was at a temperature of about 45 degrees centigrade and the panel was maintained in the solution for about 2 minutes. After this time, the panel was removed from the desmutting solution. The surface of the panel was covered with a brown manganese dioxide coating. The panel was then immersed for about 30 seconds in a sulfuric acid pickling solution. Upon removing the panel from this solution, the brown manganese dioxide coating was found to be completely removed. The panel was then tested for the presence of smut in the same manner as previously described. The testing cloth showed only a faint trace of gray, indicating that substantially all of the smut had been removed from the surface.

The preceding example was repeated using a hydrochloric acid pickling solution and a desmutting solution containing sodium permanganate, potassium hydroxide and potassium carbonate and comparable results were obtained.

**EXAMPLE 5**

The procedure of Example 1 was repeated with the exception that after the panel was removed from the permanganate solution it was rinsed in water and then coated by immersing in a conventional aqueous acid zinc phosphate coating solution, which solution contained about 11 grams/liter of zinc, about 27 grams/liter of NO₃⁻, and about 17 grams/liter of PO₄³⁻. The brown manganese oxide coating was removed in the phosphate solution and there was obtained an excellent, adherent zinc phosphate-containing coating on the panel.

While there have been described various embodiments of the invention, the compositions and methods described are not intended to be understood as limiting the scope of the invention, as it is realized that changes therewithin are possible and it is further intended that each element cited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A process for treating a ferrous metal surface which comprises contacting the ferrous metal surface with an inorganic mineral acid pickling solution, maintaining the acid pickling solution in contact with the ferrous metal surface for a period of time sufficient to form a deposit of a carbonaceous smut on the metal surface, thereafter, removing the ferrous metal surface from contact with the acid pickling solution, contacting the ferrous metal surface containing the deposit of carbonaceous smut with an alkaline permanganate solution and containing from about 2 to 40 grams per liter of an alkali metal permanganate and about 5 to 70 grams per liter of an alkali metal hydroxide, buffer the permanganate solution in contact with the metal surface for a period of time sufficient to effect substantial removal of the carbonaceous smut from the ferrous metal surface.

2. The method as claimed in claim 1 wherein the alkali metal permanganate is potassium permanganate, the alkali metal hydroxide is sodium hydroxide.

3. The method as claimed in claim 1 wherein there is also present in the aqueous solution an alkali metal carbonate in an amount within the range of about 2 to about 40 grams per liter.

4. A ferrous metal surface treated in accordance with the procedure of claim 1.

5. The method as claimed in claim 2 wherein the potassium permanganate is present in the solution in an amount within the range of about 3 to about 8 grams per liter and the sodium hydroxide is present in the solution in an amount within the range of about 12 to about 30 grams per liter.

6. The method as claimed in claim 3 wherein the alkali metal carbonate is sodium carbonate and wherein the sodium carbonate is present in an amount within the range of about 3 to about 8 grams per liter.

7. The method as claimed in claim 6 wherein after removal from contact with the permanganate containing solution the ferrous metal surface is contacted with a second inorganic mineral acid pickling solution.

8. A ferrous metal surface treated in accordance with the procedure of claim 7.

References Cited

**UNITED STATES PATENTS**

1,899,734 2/1933 Stockan 252--103
3,000,829 9/1961 Arden 252--103
3,080,323 3/1963 Newman 252--103
3,085,917 4/1963 Netzlet et al. 252--103 XR
3,210,284 10/1965 Duvall 252--103 XR

LEON D. ROSDOH, Primary Examiner.
M. WEINBLATT, Assistant Examiner.