ALKALINE DESMUTTING COMPOSITION FOR FERROUS METALS

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5 Claims

ABSTRACT OF THE DISCLOSURE

An aqueous alkaline ferricyanide composition is disclosed for removing smut formed on the surface of ferrous metals by common surface treatments such as pickling, cleaning, descaling and etching.

This invention pertains to a composition for and a method of removing smut formations produced on the surface of ferrous metals and alloys, which smut results inherently during many common surface-conditioning treatments such as pickling, descaling, satinizing and the like to which such metals are subjected. The invention is particularly directed to compositions which, when dissolved in water, are useful in the foregoing manner and which are alkaline in character rather than acidic as heretofore more commonly used.

Most acid treatments such as pickling, descaling, satinizing or etching leave a smut on the surface of ferrous metals and alloys. The composition of this smut varies and depends largely on two factors; namely, the nature of the ferrous metal or alloy, and the composition of the acid treatment bath. The amount of smut depends mainly on the degree of attack by the acid on the surface of the metal. The smut may consist of carbon, graphite, carbides, nitrides, sulfides, phosphides, oxides, etc., of the constituent elements. Whatever the composition of the smut, its removal by means of prior desmutting technologies has left room for improvement in many respects. Prior treatments include the use of acids such as hydrochloric or hydrofluoric, or mixtures of these or other acids. While relatively smut-free surfaces can be obtained using such acids, the acids attack most ferrous metals and alloys very rapidly, and accurate control or buffering of the action is difficult. There is, moreover, a tendency of most ferrous surfaces to rust very rapidly after being subjected to acid treatments, in many cases involving only a very few minutes. The use of hydrochloric acid causes the surface to be pitted and hydrogen embrittlement is apt to occur. Also hydrogen gas is formed and evolved in the process and constitutes a hazard unless care is taken to see that there is proper ventilation.

Some use has been made of electrolytic cleaning or desmutting of metals, using a highly alkaline electrolyte medium in which the parts to be cleaned are immersed, as in a barrel or on racks while being advanced through a tank, during which a direct current voltage is impressed between the parts and electrodes placed in the solution. The desmutting action in this case is accomplished primarily by gas evolution from the surface of the parts being cleaned, being more in the nature of mechanical operation and the smut is deposited as an insoluble sludge or cake in the cleaning tank and must be removed periodically.

In another known procedure, sodium or potassium permanganate with sodium or potassium hydroxide in solution has been used. While this system eliminates most of the problems encountered with acid baths, the main objection to permanganate baths is that an insoluble manganese dioxide is the end product of the reaction. Thus there is generally a film of manganese dioxide left on the surface of the part, but more importantly the necessary operating conditions of temperature and immersion time are high, thereby increasing the operating cost.

It is accordingly a principal object of the present invention to provide an improved composition and process for removing smut from ferrous metals and alloys, whereby the problems and disadvantages of the prior technologies are overcome or substantially reduced. This objective is accomplished by means of an aqueous alkaline composition as hereinafter described, in which the articles are immersed to effect removal of smut from the surfaces thereof. The new compositions offer the advantages of lower operating cost by reducing the concentrations necessary as well as the temperature and immersion time required for satisfactory smut removal. The new compositions do not attack the base metal, or result in pitting or hydrogen embrittlement in its surface, and do not encounter the previously mentioned hydrogen evolution problems. Moreover, no insoluble reaction products are formed. When the desmutting composition is spent, since it has negligible toxicity and is non-slugging, there is no waste disposal problem. Finally, the new compositions have substantial effect in retarding rusting of the clean surface of the metal.

In brief, the new compositions consist of aqueous solutions of a ferricyanide ion in alkaline medium. Either sodium or potassium ferricyanide may be used to provide the ferricyanide ions, while the alkaline medium is best provided by sodium, potassium or lithium hydroxide. The ratio of ferricyanide to hydroxide ion is not critical. The concentration of ferricyanide ion, in order to be effective, should be at least one quarter ounce per gallon of water, and may be anything up to the limit of solubility of the selected ferricyanide compound in the resulting solution. The concentration of hydroxide present is likewise not critical but should be sufficient to make the solution definitely alkaline so that the pH is on the order of 13. A particularly effective composition comprises about four ounces per gallon of water of combined potassium ferricyanide and sodium hydroxide in which the weight ratio of the hydroxide to ferricyanide is about one and one-half to one.

For many types of smut removal, solution temperatures as low as ambient are sufficient, but in that case the immersion time will ordinarily be relatively long. Optimum combinations of temperatures and times to effectively remove the smut will vary, depending on the metal and type of acid treatment employed but in general temperatures of 100° F. to boiling and immersion times of five seconds to five minutes cover the bulk of the practical applications. In short, operating variables such as concentration, temperature and time of immersion should be varied within the limits indicated, depending on the nature and amount of the smut.

Typical examples are given below for the removal of various types of smut produced on several different ferrous articles.

EXAMPLE I

A mild steel panel measuring 3" x 4" was immersed in an aqueous solution at room temperature for 10 minutes containing 25% by volume hydrochloric acid. This produced a heavy smut on the surface of the panel. The panel was rinsed in cold running water and immersed in a desmutting solution containing four ounces of alkaline potassium ferricyanide per gallon as described above. The desmutting solution in this case was maintained at 120° F. All smut was removed from the surface of the panel within 30 seconds, resulting in a clean, bright surface on the panel. The panel was rinsed in cold running water and was immediately ready for further processing.
such as plating, phosphating, painting, etc. The dried panel when stored for substantial period of time in ordinary ambient room temperature and humidity conditions showed remarkably improved characteristics in respect to resistance to rusting. Whereas such a panel does not show rust for up to as much as two weeks, a similar panel employing a conventional acid desmutter will rust in a matter of minutes under identical conditions.

EXAMPLE II

Again a mild steel panel the same as that in Example I was processed in an acid solution, this time containing 25% by volume of sulfuric acid in place of the hydrochloric acid. A heavy dark smut was produced on the surface. Again the panel was rinsed and subjected to immersion in the same desmutting solution as described in Example I. A clean, bright and smut-free surface was obtained within 30 seconds as before.

EXAMPLE III

Another mild steel panel of the same type was processed in nitric acid solution instead of hydrochloric. A heavy dark smut was produced on the surface. Again the panel was rinsed in water and subjected to desmutting in the solution described in Example I. A clean, bright and smut-free surface was obtained within 30 seconds.

EXAMPLE IV

A stainless steel, Type 434, panel was etched for 10 minutes at 120° F. in an aqueous solution comprising 10% by volume of hydrochloric, 5% by volume of nitric acid and 25% by volume of phosphoric acid. The panel was rinsed in cold running water and was found to be completely covered by a heavy black smut. A desmutting solution was prepared containing 1 ounce per gallon of alkaline ferricyanide and maintained at a temperature of 140° F. The smutted panel was immersed in this solution for 30 seconds and then rinsed in cold running water. A clean, bright and smut-free surface was obtained.

EXAMPLE V

Parts composed of spring steel were pickled for three minutes in an acid mixture of the same composition and under the same conditions as that given in Example IV above. The parts were rinsed in cold running water and then immersed for 1 minute in a solution containing 4 ounces per gallon of alkaline ferricyanide at 150° F. After rinsing in cold running water, the surface of the parts was brownish due to a light ferric hydroxide layer. This was easily removed by a quick dip in water (15 seconds) in a 25% by volume hydrochloric acid solution at room temperature. The parts were then rinsed in cold running water and presented a clean, bright and smut-free surface.

EXAMPLE VI

Short lengths of cast iron pipe and elbows were pickled in an acid mixture of the same composition as that given in Example IV for 15 minutes at room temperature and rinsed in cold running water. The surface so obtained was heavily smutted with a black smut. The pieces were then immersed for 2 minutes at 160° F. in a 4 ounce per gallon solution of alkaline ferricyanide. Again the pieces were rinsed in cold running water and immersed in a 25% by volume hydrochloric acid solution at room temperature for 15 seconds to remove the ferric hydroxide layer. They were then rinsed in cold running water. The surfaces obtained were clean and smut-free.

The new desmutting compositions have been found to be especially effective in preventing blushing or hazing of nickel or other metal deposits plated onto the base ferrous metal, and to ensure good adhesion of such deposits. Whereas the specific examples above used potassium ferricyanide and sodium hydroxide, the anions are relatively unimportant so long as they do not render the compounds insoluble. These particular compounds are selected because of their availability and cost, but sodium ferricyanide and either potassium or lithium hydroxide will work as well.

What is claimed is:

1. The method of desmutting the surface of a ferrous metal article which comprises immersing the article in an aqueous solution which consists essentially, in addition to water, of a first member selected from the group consisting of sodium, potassium and lithium hydroxide, and a second member of the group consisting of sodium and potassium ferricyanide; said ferricyanide being present in said composition to provide from about one-quarter ounce per gallon of water to the limit of its solubility in solution, and said hydroxide being present in an amount sufficient to render the solution alkaline, at solution temperatures ranging from ambient room temperature to boiling, and maintaining said articles in said composition until the smut has been removed, removing and then rinsing them in water.

2. The method as defined in claim 1, wherein the solution pH is equal to about one and one-half times the weight of the ferricyanide.

3. The method of claim 1 wherein the solution pH is about 13.

4. The method of claim 1 wherein in the aqueous solution the concentration of the ferricyanide is about 1.6 ounces per gallon and that of the hydroxide is about 2.4 ounces per gallon.

5. The method as defined in claim 1, wherein the articles are immersed for periods of from about five seconds to five minutes.

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