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PICKLING SOLUTION AND METHOD

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My invention relates to the treatment of metal, more particularly the brightening, pickling or de-scaling of metal and to the treating solution employed.

One of the objects of my invention is the provision of a simple, efficient and reliable non-electrolytic method of de-scaling and brightening metal such as stainless steel, the carbon steels, the low alloy steels, titanium and its alloys, aluminum and its alloys, magnesium alloys and, in fact, all metals and alloys which acquire a scale or heat-tint in various processing and fabrication operations.

Another object is the provision of a method of the character indicated whereby heat-scale, heat-tint or other oxide film is removed from the surface of metal, all without etch, pitting, intergranular or other objectionable attack of the surface of the metal itself, with a minimum of metal removal, and without deposit of scum or the like during treatment and with the surface of the metal, following treatment, resistant to further corrosion, rusting or staining as a result of exposure to the atmosphere or to chemical forces and in condition receptive to the application of either electrolytic or non-electrolytic coatings of zinc, aluminum, copper, silver, nickel and the like, or other coatings such as baked and air-dryed paint, enamels and wrinkle finishing, ceramics and porcelains.

A further object is the provision of a metal pickling, de-scaling or brightening bath formed of readily available and comparatively inexpensive materials which are easily and safely handled, which requires a minimum of attention and replacement and which is of long useful life.

Other objects of my invention are obvious in part and in part pointed out in the description which follows.

My invention, therefore, resides in the combination of materials and composition of ingredients and the various operational steps and the relation of each of the same to one or more of the others as described herein and particularly set out in the claims at the end of this specification.

As conducive to a better understanding of certain features of my invention it may be noted at this point that certain metals such as stainless steel, the titanium alloys and the aluminum alloys find application in a host of articles which are used under conditions of oxidizing or corrosive atmosphere. And these metals are particularly suited to such applications because of their inherent tendency to resist corrosive attack, whether by acid base or salt and whether at room temperature or at elevated temperatures. It generally is held that this property of corrosion resistance is had by virtue of a complex oxide film which forms on the surface of the metal itself.

Now in the fabricating and fashioning of the various corrosion resisting metals into the host of articles of ultimate use there frequently is formed on the surface of the metal, as a result of some heating operation perhaps, an undesirable oxide film such as a heat-tint or occasionally an even thicker film in the form of a scale. The formation of a heat-tinted surface and even an objectionable scale commonly is encountered in the conversion of stainless steel ingots and billets into plate, sheet, strip, bars, rods, wire, tubes and the like by hot working methods. The rolling, drawing or piercing temperatures employed commonly give rise to scale formation. And even in the heat treatment of the converted products or in the heat treatment of the ultimate articles of use, as by age-hardening or precipitation-hardening methods, a light heat-tint occasionally is had.

The stainless steels affected in hot working operations or even in heat treating operations ordinarily contain 10% to 35% chromium either with or without nickel, the nickel content ranging up as high as 35%. In such steels other ingredients such as silicon, manganese, copper, aluminum, molybdenum, tungsten, columbium, titanium, sulfur, phosphorus, carbon and nitrogen may be present in minor amounts. In several grades of stainless steel the manganese content may amount to as much as 12%. And in others the silicon content may be as high as 3 or 4%. The copper content, where copper is employed as an essential ingredient, may be as much as 5%. Similarly, the manganese and tungsten contents may amount to as much as 5% for the one and 2% for the other. The titanium and columbian contents seldom exceed about 1%. Sulfur and phosphorus contents may reach .5% where these additions are employed for special purposes. So too the nitrogen content may amount to as much as .6%. And the carbon content may range anywhere from about .03% to .15%. It will be understood, of course, that the remainder of the composition is iron.

Because of the inherent nature of the stainless steels, and of the titanium and aluminum alloys as well, any oxide film, such as a heat-tint or a scale, is very difficult to remove. Now in the prior art it frequently is necessary to resort to treatment in an alkali metal hydride bath as described for example in the Gilbert U.S. Patent 2,448,262, or in a bath composed of alkali metal nitrates and hydroxides in accordance with the method of the Webster and Falter U.S. Patent 2,458,661. And following treatment in these baths of molten salts the metal is immersed in a bath of commercial mineral acid, for example nitric-hydrofluoric acid. In some grades of stainless steel the metal is severely etched, this producing a dull, rough surface. Moreover, in many grades this drastic treatment causes intergranular corrosion. This is especially noticed in the stanless steels of the chromium-nickel type wherein the carbon content appreciably exceeds some .12%. And even in those grades which are not actually etched or pitted there often is found a dirty black smut which is deposited out upon the surface of the steel. This smut generally is said to be a deposit of metal carbides which are actually removed from the surface of the steel.

There, of course, is less difficulty in removing the heat-tint or even scale from the stainless steels of low alloy contents. Even with those grades, however, there is required a treatment in a pickling solution, as for example treatment in a nitric-hydrofluoric acid bath or treatment in a bath comprising nitric acid with soluble fluoride salts and/or soluble chloride salts. Here again, however, certain of these grades of steel are found to severely etch with the resultant formation of a dull rough surface. And certain of the austenitic chromium-nickel steels of substantial carbon content are inclined to suffer through intergranular corrosion.

It will be seen, therefore, that the de-scaling or pickling baths of the prior art are not entirely satisfactory for any substantial number of grades of stainless steel and that considerable care must be used to select a particular bath and method of treatment for the particular grade of steel to be treated. Such a practice is not entirely satisfactory.

One of the objects of the present invention, therefore, is to provide a bath which is adapted to remove the scale from a wide variety of grades of stainless steel and from other metals and alloys as well, such as the carbon steels,

the low alloy steels, the titanium alloys and the aluminum alloys, and pickle and brighten these metals without surface etch, intergranular attack, or other appreciable metal removal.

Referring now more particularly to the practice of my invention I find that excellent pickling and brightening of stainless steel and other alloys is achieved by treating these metals with an aqueous solution of inorganic acid and hydrofluosilicic acid or derivatives of the same. Almost equally good results are had where the metal is treated with an aqueous solution of inorganic acid together with hydrofluoboric acid or derivatives. Ordinarily I prefer a treating solution essentially consisting of one or more of the mineral acids together with hydrofluosilicic acid or its derivatives. I generally prefer to employ a treating bath composed of one or more of phosphoric, sulfuric or nitric acids, with or without acetic acid, together with a derivative of hydrofluosilicic acid such as one or more of the sodium, potassium, ammonium or magnesium silicofluorides. I find, however, that substantially the same desired results are achieved with an aqueous solution of mineral acid together with one or more of the methylamine, dibutylamine, ethylhexylamine, aniline and morpholine silicofluorides. As indicated above good results are had in a treating solution employing mineral acid together with one or more of the borofluorides corresponding to the various silicofluorides. These various compounds yield in solution a silicofluoride ion or a borofluoride ion.

In general I find that excellent results are had where the amount of mineral acid ranges from about 2 to 75% by weight of solution. And the amount of compound yielding the silicofluoride ion, or the borofluoride ion as the case may be, amounts to about .5 to 40%.

A preferred bath contains about 2 to 15% commercial nitric acid, 0 to 60% commercial phosphoric acid, .5 to 40% commercial derivative of hydrofluosilicic acid and remainder water. Actually, certain savings are had by substituting a small amount of sulfuric acid for the nitric acid, but such a modified bath largely is limited in utility to the products with a light scale and where the acid concentration is low. In such a bath phosphoric acid ordinarily is not employed. For the baths of the higher acid concentration phosphoric acid preferably is included because of the buffering effect enjoyed. And I find that phosphate salts conveniently may be employed as a substitute for phosphoric acid.

In accordance with the method of my invention the various metal products to be treated are immersed in a bath of treating solution maintained at a temperature of 125° to about 195° F. At substantially lower temperatures the reaction is much too slow while at substantially higher temperatures there is objectionable loss of active ingredient by evaporation. In general a temperature of around 170° F. is preferred, the bath being conveniently heated by a steam line in order to assure the preferred operating temperature. Immersion in such a bath for a period of one to forty-five minutes is sufficient to remove heat-tint or scale, the time differing largely with the nature of the metal being treated and the initial condition of its surface oxidation.

With the steels of high total alloy content, as for example the straight chromium steels having a chromium content of 25% or more or the austenitic chromium-nickel stainless steels having a total chromium and nickel content amounting to 25% or more, I preferably subject the same to a scale softening treatment in advance of actual de-scaling. Especially is this beneficial in the case of converted products such as plate, sheet, strip, bars, rods, wire and the like in which the conversion is had by hot-working or hot-cold-working methods.

In accordance with the practice of my invention the converted products are first given a scale softening or scale loosening treatment, conveniently referred to as a scale conditioning treatment, by immersion in a molten

bath of sodium hydride or a bath of molten sodium hydroxide and sodium nitrate. The products then are withdrawn from the bath and washed either in a tank of water containing a small amount of acid or washed with a hose. Following this I immerse the products in a bath of nitric acid with or without phosphoric acid and together with a product such as a derivative of hydrofluosilicic acid yielding the silicofluoride ion. Equally good results are had where the converted products are first treated in a bath of molten sodium hydroxide and sodium nitrate followed by water rinse and immersion in an aqueous bath of the nitric acid with or without the phosphoric acid, but containing the hydrofluoboric acid derivative.

Certain savings in the cost of scale removal are achieved in wire and other converted products by subjecting them to a mechanical flexing over rolls to loosen or condition the scale, and then immersing the products in the acid bath containing the derivative of the hydrofluosilicic acid or the hydrofluoboric acid.

While precipitation hardened fabricated articles fashioned of stainless steel generally are free of scale they occasionally have a lightly heat-tinted surface. Ordinarily the heat-tinted articles are cleaned and brightened by immersion immediately in my bath of mineral acid and hydrofluosilicic acid derivative (or hydrofluoboric acid derivative) although I occasionally find benefit in first subjecting the articles to an aqueous bath of 10% sodium hydroxide containing potassium permanganate in small amount followed by treatment in my scale removing bath. Benefit also occasionally is had by preliminary treatment in aqueous sulfuric acid with or without one or more chlorides. Such treatment serves to soften the scale and condition it for easy removal by immersion in the mineral acid bath containing the hydrofluosilicic acid derivative (or hydrofluoboric acid derivative).

I find that stainless steel converted products treated in accordance with my method, and various fabricated stainless steel products so treated as well, have a better surface color with less surface roughening than products and articles treated with the prior art processes. Moreover, I find that my products and articles are singularly free from intergranular attack and that there is minimum of metal removal. Furthermore the products and articles leave the bath in a condition which is less susceptible to atmospheric corrosion, that is rusting or other staining or streaking. And the converted products are in better surface condition for further working or forming, such as deep drawing, drawing into wire and the like, particularly where the scale removal treatment is had in a bath including the phosphoric acid. This I would attribute to the presence of a phosphate coating on the surface of the steel. The various stainless steel products and articles pickled, cleaned or brightened in accordance with my invention are particularly free of any surface pitting, whether the bath has just been newly made or has been in use for some time. This is somewhat surprising because in many of the treating methods of the prior art an old bath is found to pit the metal, this apparently because of the high iron content of the bath. I attribute the freedom from pitting had in the method of my invention to the formation of complex ions, for example iron silicofluorides, which do not have the same adverse effect upon the surface of the metal as the ions found in the used baths of the prior art.

There is a further advantage of the bath of my invention in that evaporation losses are minimized as compared to the known commercial baths employing hydrofluoric acid as a necessary ingredient. Moreover, the ingredients of my bath are much easier to handle than those of the prior art in that the hydrofluosilicic acid derivative is in the form of a dry crystal powder as distinguished from the liquid hydrofluoric acid of the prior art. And there is much less hazard in handling the same as compared with hydrofluoric acid.

As specifically illustrative of the practice of my inven-

tion I give below three examples of treatment in which excellent results are had:

(1) Armco 21–4 N stainless steel (21% chromium, 4% nickel, 9% manganese, .40% nitrogen and remainder iron) exhaust valve steel hot rolled and annealed rod material in 7/16" and 3/8" sizes was subjected to immersion in molten sodium hydride bath for about ten minutes followed by water quenching. The rod was then pickled for seven and a half minutes in a bath consisting of 19% commercial orthophosphoric acid, 7½% commercial nitric acid, 4% magnesium silicofluoride and the remainder water, all percentage figures being by weight, and the bath being held at a temperature of about 170° F. After rinsing in tap water the samples of rod were found to have an excellent clean surface, free of pits and with no undue darkening or etching. Metallographic examination revealed the rod to be without traces of intergranular corrosion.

(2) Further samples of Armco 21–4 N stainless steel exhaust valve rod in the hot rolled and annealed condition were treated in a sodium hydride bath for ten minutes followed by water quenching after which they are pickled for seven and a half minutes at 170° F. in a bath consisting of 5% commercial nitric acid, 2% commercial magnesium silicofluoride and the remainder water, all by weight. An excellent clean bright surface was had which was free from scale and free from undesirable etching. Here again, metallographic examination revealed the surface to be free of intergranular corrosion.

(3) Sample sheets, .060 inch thick, of the Armco 17–7 pH precipitation hardening stainless steel (17% chromium, 7% nickel, 1% aluminum and remainder iron) in the commercially annealed condition were given a 1050° F. precipitation hardening treatment. Close examination showed that the hardened steel samples had a tight thin grey blue scale. This was removed by pickling for five minutes in a bath consisting of 10% commercial phosphoric acid, 7% commercial nitric acid, 4% commercial sodium silicofluoride and remainder water, the bath being maintained at a temperature of about 175° F. A good clean bright surface was produced which showed no evidence of etching. Here it will be noted that no scale conditioning treatment was given and yet excellent results were achieved.

While, as more particularly indicated above, many grades of stainless steel are pickled and brightened with excellent results with my aqueous bath of nitric acid, with or without phosphoric acid, but containing the hydrofluosilicic acid derivative (or derivative of hydrofluoboric acid) I find that all commercial grades of stainless steel are satisfactorily de-scaled, pickled and brightened with my process wherein there first is had a scale conditioning treatment as by scale softening or scale cracking (mechanical flexing over rolls) followed by the treatment in the nitric acid bath, with or without phosphoric acid, and acid derivative. Moreover, the method of my invention satisfactorily removes scale, pickles and brightens other alloy steels such as the silicon steels and the tool steels and certain non-ferrous metals and alloys which are found with extremely refractory oxide coating such as titanium and titanium alloys as well as the magnesium alloys and aluminum alloys.

Thus it will be seen that I have provided in my invention a method and a pickling bath in which the various objects hereinbefore noted together with many practical advantages are successfully achieved. The method is simple, reliable and does not require the necessity for expensive electrical equipment. And the bath is easily prepared and achieves long useful life with a minimum of replacement.

As many possible embodiments may be made of my invention and as many changes may be made in the embodiments hereinbefore set forth it will be understood that all matter herein is to be interpreted as illustrative and not as a limitation.

I claim as my invention:

1. In the brightening, pickling and de-scaling of steel, the art which comprises conditioning any scale on said steel for subsequent removal; and then subjecting the steel to an aqueous treating solution comprising 2% to 75% of at least one of the group consisting of phosphoric, sulfuric and nitric acids, and .5% to 40% of at least one of the group consisting of sodium, potassium, ammonium, and magnesium silicofluorides.

2. In the brightening, pickling, and de-scaling of steel, the art which comprises subjecting the steel to an aqueous treating solution comprising 2% to 15% of at least one of the group consisting of phosphoric, sulfuric and nitric acids, together with .5% to 40% of at least one of the group consisting of sodium, potassium, ammonium and magnesium silicofluorides.

3. In the brightening, pickling and de-scaling of stainless steel of high total alloy content, the art which comprises subjecting the steel to an aqueous treating bath essentially comprising by weight about 7% nitric acid, about 10% phosphoric acid, and about 4% magnesium silicofluoride.

4. In the de-scaling of stainless steel of 25% or more total alloy content, the art which comprises conditioning the metal scale for subsequent removal by immersing the steel in a bath of molten sodium hydride; removing from the bath and washing in water; and then subjecting the steel to an aqueous solution essentially comprising 2% to 15% of at least one inorganic acid and .5% to 40% of at least one compound of the group consisting of derivatives of hydrofluosilicic acid yielding a silico fluoride ion and derivates of hydrofluoboric acid yielding a borofluoride ion.

5. A solution for brightening, pickling and de-scaling steel comprising about 7% nitric acid, about 10% phosphoric acid, about 4% magnesium silicofluoride, and remainder water.

6. An aqueous solution for brightening, pickling and de-scaling steel comprising by weight about 2% to 15% nitric acid, up to about 60% phosphoric acid, and about .5% to 40% magnesium silicofluoride.

7. In the de-scaling of steel, the art which comprises conditioning the metal scale for subsequent removal by immersing the steel in a bath of one of the group consisting of aqueous sodium hydroxide with potassium permanganate, aqueous sulfuric acid, and aqueous sulfuric acid with chlorides; and subjecting the steel to an aqueous solution comprising 2% to 75% of at least one of the group consisting of phosphoric, sulfuric and nitric acids, and .5% to 40% of at least one of the group consisting of sodium, potassium, ammonium and magnesium silicofluorides.

8. In the de-scaling of steel, the art which comprises conditioning the metal scale for subsequent removal by mechanically flexing the steel over rolls; and subjecting the steel to an aqueous treating solution comprising 2% to 75% of at least one of the group consisting of phosphoric, sulfuric and nitric acids, and .5% to 40% of at least one of the group consisting of sodium, potassium, ammonium and magnesium silicofluorides.

References Cited in the file of this patent

UNITED STATES PATENTS

921,350	Bishop	May 11, 1909
2,337,062	Page	Dec. 21, 1943
2,340,328	Jones	Feb. 1, 1944
2,383,800	Johnson	Aug. 28, 1945
2,413,365	McCoy	Dec. 31, 1946
2,422,066	Bacon	June 10, 1947
2,477,181	Holman	July 26, 1949
2,542,779	Neill	Feb. 20, 1951
2,655,481	Clingan	Oct. 13, 1953
2,711,364	Beach	June 21, 1955
2,719,079	Murphy	Sept. 27, 1955