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ELECTROCHEMICAL PROCESS FOR REMOVING SCALE AND OXIDE FROM THE SURFACE OF STAINLESS STEEL

Thomas E. Dunn, Bridgeport, Conn., assignor to The Bullard Company, a corporation of Connecticut

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The prime object of the present invention is to provide a safe, sure, rapid and economical method of cleaning chrome alloy steels. The process concerns itself chiefly with the removal of the exceedingly tenacious and adherent scale, such as is formed during annealing and heat treatment. It will be understood that the word scale is used in its broad sense and includes oxides or other undesirable oxide-like surface foreign matter.

Another object is to provide a method which effectively uses electrolytic reactions in the removal of such surface foreign matter as will interfere with subsequent processing, such as cold or breakdown rolling, drawing, or forming.

Another object is to provide a method step which attacks, selectively dissolves and renders more readily removable the hard deleterious scale or oxide so that it may be removed by any one of several subsequent method steps.

A further object is to provide a process of the character set forth which utilizes the characteristic benefits of the phenomenon of throwing power in that the reactions are controlled automatically whereby the concentration of the reaction is automatically shifted over the work surface.

In general, it is the object of the invention to provide an efficient and effective process which will avoid the inherent disadvantages of the many existing cleaning methods, such as pickling, with hydrochloric, sulphuric, or nitric acids, or with combinations of these acids, or by making the work anode in an acid electrolyte, which methods take considerable time, are very hard to control, and may pit, etch, or otherwise spoil the surface or destroy the luster of the steel.

Broadly stated, the process includes a scale or oxide attacking step which is characterized by anodic treatment of the work in an alkaline bath, in the presence of metal ions, and under the influence of the phenomenon of throwing power. The foreign matter is, thereby, transformed to a substance which in some instances may be removed by washing and/or brushing, or which may be removed by a subsequent treatment, where the work is cathode, in either an alkaline or acid electrolyte. This second step is preferably accompanied by the protection of the cleaned surface with a protective film which may be left on permanently, be removed by immersion of the work in an acid solution or may be removed by subjecting the work to the action of the process described in my Patent No. 1,867,527.

As a preferred illustration of one commercially successful way of carrying out the scale or oxide softening step, I make the work anode in an aqueous electrolyte, which for each gallon of solution may contain:

6 oz. tri-sodium phosphate—$Na_3PO_4.12H_2O$
3 oz. sodium carbonate—Na_2CO_3
3 oz. sodium hydroxide—NaOH

Obviously, equivalents may be substituted and proportions varied. The tri-sodium phosphate is preferably maintained in a proportion equal to or in excess of the other constituents. However, the sodium carbonate may be omitted and the sodium hydroxide increased or vice-versa in varying proportions.

The active metallic ions may be introduced in the bath by the use of metallic salts; such metals as lead, tin, zinc and cadmium are preferably selected. However, the invention is not confined to any of the metals illustratively mentioned. While the free metal ions may be introduced by adding to the bath salts of such metals, I prefer for the sake of economy and control to introduce such ions by preliminarily suspending from the anode bus bar a temporary anode of the metal selected which will, under the influence of applied current, corrode and give off such ions. As a commercial practice, I prefer to use cathodes of the selected metal which, while the bath is idle, will replenish the metal ion content.

To a large extent, the effectiveness of this step of the process is found to be a result of the presence in the electrolyte of the metallic ions. While the electro-chemical reactions involved in such processes are very complex and not wholly understood, it is assumed that, in the case of lead, for instance, the metallic ions in solution form sodium plumbate (Na_2PbO_3) which combines with water to form sodium hydroxide (NaOH) and lead peroxide (PbO_2). The latter deposits on the work surface and acts as a strong catalyst favoring oxidation of metals such as chromium, manganese, tungsten, vanadium and molybdenum which are present in the scale and converting these into soluble chromates, manganates, tungstates, etc., thereby rendering the scale loose and porous. Iron oxide forms no such soluble compound. Concurrently therewith, there is formed on the work surface relatively insoluble phosphates such as iron phosphates which increase the electrical circuit resistance at that point and thus throw the intensity of the current action to other portions of the work surface. This so-called throwing characteristic causes a progressive electro-chemical action which insures

thorough and efficient treatment of all portions of the work surface.

The bath is preferably maintained at 160° to 190° F. I prefer to use a current density of 30 to 60 amperes per square foot of surface, which is usually obtainable at a pressure of 3 to 6 volts, and a time element of from 2 to 5 minutes (on heavy scales it may take a longer time element). Before the steel is put into this electrolyte, the scale is adherent, blue, steel grey, or reddish-orange in color, but when the steel comes from this bath, the scale has been transformed into a relatively loose, porous brown residue, the scale on the surface of the alloy steel having been made porous and loosely adherent by the selective dissolution of the chromium, manganese, tungsten, vanadium or molybdenum, forming soluble alkaline salts, such as chromates, tungstates, etc. The insoluble iron oxides and phosphates remain behind and in some instances may be readily rinsed and brushed off, leaving the steel with a cleaned surface.

Should the residue remaining after the anodic step resist economical removal by brushing and rinsing, I find that it may be effectively removed by making the work cathode in the same or an identical alkaline bath with a current density of from 30 to 60 amperes per square foot of surface and a time element of from 2 to 5 minutes. Obviously, this may be accomplished by a reversal of current which operation will change the cathodes to anodes thus causing them to replenish the metallic ion concentration. In this second step, the brown residue on the steel is blasted off at the cathode by the action of hydrogen and the cleaned steel is protected with a film derived from the lead or equivalent metal ions in solution. This step also partakes of the advantages of the phenomenon of throwing power, the reaction being a direct electro-deposit of a microscopically thin film of closely adherent metal such as lead. This step is especially effective in cleaning a variety of stainless steel, such as is commonly known as KA_2 (18 chrome 8 nickel), and heavy rough rolled sections of straight chrome steels.

I have also found that my acid process containing soluble metallic anodes, as covered by Patent No. 1,776,671, can be used as a second step by making the alloy steel the cathode. This will remove the residual foreign matter by an excess of hydrogen and the steel surface will be protected by a metallic film.

Where subsequent operations such as drawing and forming, are necessary, I have found that allowing the protective metal film, such as lead, to remain on the steel, after either of the cathodic treatments, aids in lubricating tools, such as drawing and forming dies.

After the cathodic treatment, the steel may be rinsed and placed for a minute or two in a nitric acid bath to dissolve the film and render the completely cleaned surface entirely passive. I have also found that after the second or cathodic bath, the metallic coating can be safely removed from the surface of the stainless steel by placing in a defilming bath as outlined in my Patent No. 1,867,527.

Having described my new process for cleaning scale or oxide from chrome alloy steel and from articles made therefrom, what I claim is:

1. A process for the removal of scale from chromium alloyed steels which includes the step of subjecting the steel to anodic treatment in a phosphate alkaline electrolyte containing metal ions, the alkaline constituents of the electrolyte being such as to attack portions of the scale and the metallic ions being such as to combine to form a catalyst favoring such attack.

2. A process for the removal of scale from chromium alloyed steels which includes the step of subjecting the steel to anodic treatment in a phosphate alkaline electrolyte containing ions of such metals as lead, tin, zinc, or cadmium, the alkaline constituents of the electrolyte being such as to attack portions of the scale, and the metallic ions being such as to combine to form a catalyst favoring such attack.

3. A process for the removal of scale from chromium alloyed steels which includes the step of subjecting the steel to anodic treatment in an alkaline electrolyte containing tri-sodium phosphate and electro-chemically active metallic ions, the alkaline constituents of the electrolyte being such as to attack portions of the scale, and the tri-sodium phosphate and the metallic ions being such as to combine to form a catalyst favoring such attack.

4. A process for the removal of scale from chromium alloyed steels which includes the step of subjecting the steel to anodic treatment in an alkaline electrolyte containing ions of such metals as lead, tin, zinc, or cadmium, and the tri-sodium phosphate and metallic ions, the alkaline constituents of the electrolyte being such as to attack portions of the scale, and the tri-sodium phosphate and the metallic ions being such as to combine to form a catalyst favoring such attack.

5. A process for the removal of scale from chromium alloyed steel which includes the step of subjecting the steel to anodic treatment in an alkaline electrolyte containing tri-sodium phosphate and lead ions whereby the lead ions will combine to form lead peroxide to act as a catalyst assisting the alkaline constituents of the bath in the selective oxidation of such metals as chromium, manganese, tungsten, vandium, molybdenum.

THOMAS E. DUNN.