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ANODIC CLEANING PROCESS

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My invention relates to an anodic cleaning process and an article produced thereby.

It is the object of my invention to provide a cleaning process which produces a passified etched metal surface suitable for subsequent electroplating steps so as to produce a bonded electroplated coat thereon that is permanent, dense and of fine grained structure.

It is my particular practical object to provide for the plating of wire by electro-galvanizing by providing metal in such a state that it can be electrogalvanized instead of hot galvanized.

It is a further object to provide an article which is first passified and etched, then depassified without destroying the etching, and then plated with the plating bonded thereon.

It is a further object to provide a process in which the metal surface is passified and optionally thereafter depassified and plated either after the passifying or passifying and depassifying.

In particular it is my object to provide an anodic cleaning process in which the article to be treated, such as wire, is so cleaned that it may be thereafter immediately plated, preferably electroplated.

It is my object to provide a process of anodic cleaning in which the article to be cleaned is the anode and is subjected in a relatively weak acid bath such as nitric acid to a current of very high density, that is, high amperage, which results in passifying the surface of the metal and in some cases etching it. The passified metal can thereafter be directly plated, or, optionally, a second step of depassifying by immersion in a concentrated solution of hydrochloric acid may be employed, thereafter causing the electroplating immediately to take place.

It is my object to so treat the metal in the first step, which is a base metal, that it will act like a Noble metal and not be subject to attack by acids, will not rust, and will not dissolve anodically in ordinary plating solutions, and the Noble metal will not displace copper from a copper sulphate solution.

It is my object to provide such a metal that is preferably so etched that the resulting electroplating results in a bond of the plated metal to the base metal so that a smooth, hard, permanently bonded coat that is almost impossible of being detached is formed on the base metal.

It is my object, by applying a suitable current density materially above anything heretofore practiced and considered necessary, to thereby bring about an abrupt change in the action of the anode, which in this case is the wire or other article being treated in the acid solution. This condition depends upon the time and the amount of the current density, although I prefer a very short interval of time and a very high current density.

Upon a suitable time interval having elapsed, bubbles appear on the surface of the anode metal being treated and escape from the surface of the metal. The region of the bubbling is very small when it first appears and thereafter spreads over the entire anode surface, the rate of spreading being controlled by the regulation of the current. Ordinarily, however, the bubbling will spread almost instantaneously over the immersed anode. This is accomplished by a fundamental change in the property of the metal surface which I have called passivation. While it is related to, it is not identical with passivity caused by treating metal with oxidizing agents.

It is my object to provide such a treatment that there is no deposition of any fine black film or other discoloring films or oxides on the steel or other metal being treated so that it is not necessary to wipe off any such accumulations. The result of my treatment is to provide a clean surface which is ready for immediate plating or for depassivation and plating as hereinafter specified.

It is my object to eliminate the objectionable accumulations of anode black or acid black heretofore accompanying other types of treatment of metal when treated as anodes in an acid bath.

In the practical use of my process I pass the material to be treated, such as a steel wire, through a bath of nitric acid. The concentration of the acid is 0.1 to 15.0 per cent by weight of pure nitric acid. The steel wire is made the anode in this bath of nitric acid and a current density of from 70 to 500 amperes per square foot is applied so that bubbling is secured on the surface of the wire. It is possible to use a current density of as low as 70 amperes per square foot if sufficient time be allowed, as for instance, several minutes, but in practice higher current densities of from 200 to 300 amperes per square foot produce bubbling in a second or less and are preferred. A better result is secured by this nearly instantaneous production of the bubbling and the application of the higher amperages. The result is that no fine thin black film is left on the steel as in the case of low current densities and medium current densities.

The action of this treatment results in passivation of the wire surface and in the production of a wire surface that is clean so as to furnish a basis for a strong adhesion of the electroplated coating. The time of treatment is from 2 to 30 seconds. The etching is of a peculiar type, readily distinguishable under the microscope from the condition of the steel when using other processes and other current densities. This process of cleaning completely removes the surface and imbedded impurities that adhere with extraordinary tenacity to the wire as a result of the drawing of the drawn wire.

For instance, electrodeposited zinc deposited

on the wire cleaned by my process will adhere to the wire even though the wire is deformed so severely as to fracture the steel. The zinc coating is free from fractures, flaking and breaks. It will be understood that the wire has been treated with the usual preliminary treatments, such as lead annealing, which is optional, an alkaline cleaner, and pickling, accompanied by suitable rinses.

The result of this anodic cleaning is the passivation of the wire so that it has the characteristics of a Noble metal in that it is not attacked by acids, will not rust, and does not dissolve anodically in the ordinary plating solutions, and the Noble metal will not displace copper from a copper sulphate solution.

It is possible to use for the solution in this anodic cleaning process of mine other oxidizing agents such as chromic acid, chromates, permanganates, chlorates, etc., but I prefer the nitric acid for this cleaning process as the best of the oxidizing agents.

It should be clearly understood that the passivity of the steel is not identical with that caused by dipping steel in strong nitric acid. There is little or no solution of iron and the acid will not give an appreciable test for iron in ordinary analytical tests. The anode surface of the metal so treated by my process is radically altered in addition to its conversion to a noble character. Many impurities which may have been present in the surface and may not be metallic in character, are entirely removed. A fresh, clean etched surface is left which is especially suitable for receiving electrodeposits. The result is an absolutely clean surface having a peculiar etching, with a reduction of embrittlement and with an excellent surface for the supporting of an electrodeposit.

I find that by the addition of another step I can still further improve this process, or rather, make it more certain under some conditions. For this purpose I pass the metal, such as wire, through a cold water rinse and thereafter immediately introduce it, from .5 to 15.0 seconds in an acid dip employing any one of the common pickling acids. I have found concentrated hydrochloric acid one of the best of the acids for this purpose. Its concentration ranges from 5 to 38 percent of dry hydrogen chloride in water.

This treatment, I believe, brings about a depassivation of the wire. I have found that under some circumstances it is desirable to pass an electric current through the bath or to add suitable salts or other agents to control the action of the bath. After this treatment, a cold water rinse may be provided and immediately before any oxidation can take place, the metal is passed into the electroplating bath. One of the characteristics of my product of my process is that satisfactory deposits in the electroplating bath may be obtained with extraordinary high current densities on the wire running up to 2,000 amperes per square foot or higher. The weight of the coating can be controlled according to the time of plating and current density used.

The result of this process is a markedly superior degree of adhesion of the plated coating to the wire, and a metallic coating which is ductile, attractive in appearance, and serviceable.

The solution first mentioned for anodic cleaning can be operated at room temperatures but it should be operated with current densities sufficiently great so that there is a steady, quiet bubbling around the wire. Below the proper current densities, masses of brown scum are thrown off so that cleaning is not satisfactory.

It will be understood that I desire to comprehend within my invention such modifications as may be necessary to adapt it to varying conditions and uses.

Having thus fully described my invention, what I claim as new and desire to secure by Letters Patent, is:

1. In a process of anodic cleaning, treating a work piece as an anode, subjecting it to a high current density of between 200 to 300 amperes per square foot to secure a passivation of the surface while submerging it in an oxidizing electrolyte of nitric acid so that bubbles appear on the surface of the work piece; and thereafter bringing about depassivation of the surface by an acid treatment.

2. In a process of anodic cleaning, submerging a work piece as an anode and subjecting it to a high current density of above 200 amperes per square foot in a nitric acid electrolyte with an acid concentration of 0.1 to 15.0 per cent by weight of pure nitric acid so as to bring about bubbling on the work piece; rinsing the work piece; and submerging the work piece in a solution of hydrochloric acid of from 5 to 38 per cent concentration of dry hydrogen chloride and water.

3. In a process of anodic cleaning, submerging a work piece as an anode and subjecting it to a high current density of from 200 to 300 amperes per square foot immediately upon immersion in an electrolyte of weak nitric acid for a sufficient time to cause a copious evolution of gas adjacent the surface of the work piece.

4. In a process of anodic cleaning, submerging a work piece as an anode and subjecting it to a high current density of from 200 to 300 amperes per square foot immediately upon immersion in an electrolyte for a sufficient time to cause a copious evolution of gas adjacent the surface of the work piece of weak nitric acid, said acid being of a concentration between 0.1 to 15.0 per cent by weight of nitric acid.

5. In a process of anodic cleaning, treating a work piece as an anode, subjecting it to a high current density of between 200 to 300 amperes per square foot to secure a passivation of the surface while submerging it in an oxidizing electrolyte of nitric acid, so that bubbles appear on the surface of the work piece; and thereafter bringing about depassivation of the surface by an acid treatment, rinsing the work piece and electroplating the same immediately thereafter.

6. In a process of anodic cleaning, submerging a work piece as an anode and subjecting it to a high current density of from 200 to 300 amperes per square foot immediately upon immersion in an electrolyte of weak nitric acid for a sufficient time to cause a copious evolution of gas adjacent the surface of the work piece, rinsing the work piece and immediately thereafter submerging the work piece in an electroplating solution.

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