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ELECTROCHEMICAL PROCESS FOR ANODIC COATING OF METAL SURFACES

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This invention relates to an electrochemical process for forming a surface coating on metals. More particularly, this invention relates to an electrochemical process for forming in a very short time a surface coating on titanium alloys using an aqueous electrolyte solution consisting essentially of an alkali and a chelating agent.

A method of coating metals to increase corrosion resistance of the metal and to promote adhesion of paint, varnish, lacquer, and other organic finishes to the metal is well known. The latter method comprises the steps of dipping zinc, cadmium, and galvanized steel into chromic acid solution containing sulfuric acid or sulfate plus nitric acid to form a chromate coating. This method has not proved successful in coating iron and steel. Another method of dipping aluminum in chromate or dichromate solution containing phosphate and fluoride, or spraying the said solution on aluminum to produce a chromate coating in a short time is known in the prior art. Electrochemical methods for coating steel surfaces in an extremely short time in dichromate solution containing phosphoric acid, or in chromic acid solution containing boric acid, borate or phosphoric acid have already been patented. A process for forming a chromate coating on metals such as steel, aluminum, magnesium, zinc and copper by applying to the surface of the metal a film of an aqueous solution of chromic acid containing a reducing agent and then drying the film on the metal by heating has been developed. In spite of these attempts, a process for forming a highly corrosive-resistant coating as described according to the teachings of this invention has not yet been presented.

Another well known method for coating the surfaces of metals is taught in the patent to Kitamura, No. 2,998,361. The latter invention teaches the use of aromatic sulfonic acid or sulfonate containing a hydroxyl radical as an additional agent to provide the catalytic driving force according to the subject patent. As taught in the Kitamura patent, sulfonic acids or sulfonates are used because their chemical structure makes possible the easy formation of chelating compounds with metal ions. The formation of such compounds with metal ions is effective in the film formation of oxides of chromium upon a metal surface. The acids or salts used in the subject patent are the aromatic sulfonic acids containing hydroxyl radical or water-soluble salts of such acids having a chemical structure which, as noted above, easily forms chelate compounds with metal ions. The Kitamura patent, however, discloses the use of chelating complexes in combination with an acid, and for coating metals other than titanium.

Another patent to McGraw and Stockdale, No. 3,075,896, directs its invention toward a process for finishing an article made of titanium. In general, the latter patent teaches a process wherein the titanium article is immersed in an acidic or alkaline bath of a character that will not attack titanium. Similarly, the patent to Slomin, No. 2,934,480, proposes to electrolytically coat titanium using an alkaline electrolyte. Relative to the latter two patents, experience shows that the resulting anodic coating is relatively thin, and does not promote adequate bonding or strength with structural adhesives. An endeavor to produce thicker coatings using the methods of the latter disclosed prior art by increasing the alkaline concentration and using a higher current density simply results

in formation of a partially non-adherent (powdery) coating.

A feature of this invention produces an oxide coating differing from conventional oxide coatings formed on metal surfaces according to methods taught in the prior art in the following ways: (1) a thicker coating is produced, having inherently better corrosion and abrasion resistance; and (2) the coated surface possesses a different, more uniform electrical charge or potential. This favorable surface possesses the important characteristic of promoting exceptional wetting or bonding with structural adhesives and organic finishes. By enabling better wetting of the titanium surface, applied film adhesives and coatings adhere to the titanium with minimum loss of film adhesion or strength of bond to the surface from moisture and other contaminants working between coating and metal during exposure to corrosive environments.

In particular, the unique feature of this invention provides for an anodic coating process incorporating the use of a chelating agent in an aqueous anodizing solution consisting of an electrolyte containing an alkali. It is believed that a chelating agent complexes metal ions which otherwise, without such complex ion formation, impede coating formation, cause formation of a non-adherent coating, or leaves an electric charge which resists wetting of the surface by adhesives or finishes. Measurement of surface potential of an oxide-coated metal indicates that an oxide coating formed upon a metal surface by a process using an alkali-aqueous electrolyte solution in combination with a chelating agent according to the teachings of this invention is fundamentally different from that produced using a simple alkaline electrolyte solution, or an acidic solution containing a chelate. Further evidence of this difference is the very unusual behavior of the anodizing process according to the teachings of this invention compared with anodic coating processes taught by prior art. Typically during a metal anodizing process, the electrical current density decreases, or at most stabilizes with time. This is natural since oxide films are much less conductive than bare metal. Usually the current must flow to the base metal through pores in the insulative coating formed. With the process of the instant invention, however, even though the finished coating is thicker and more insulative than conventional coatings, the current density cure is reversed from that experienced with other processes, viz., during anodizing the electrical current density increase 30% to 300% at a fixed voltage, depending on the alloy involved, anodizing time, etc. This paradox is believed due to the ionic chelate complexes which form at the surface or in the coating's pores, thereby causing the solution to become actually more electrically conductive.

It is an object of this invention to form in a relatively short time a relatively thick protective oxide coating upon a metal which is highly corrosive resistant.

Another object of this invention is to form in a very short time a relatively thick oxide coating upon a metal so as to develop an excellent base for organic coating and to improve the adhesion of paint, varnish, lacquer, adhesive, and other organic finishes.

The process for forming a suitable coating on metals and in particular on alloys of metals from the group consisting of titanium, zirconium, hafnium, and thorium according to the teachings of this invention depends on concentration of the alkaline aqueous electrolyte solution and the concentration of the chelating agent which in part comprises the aqueous solution, the temperature at which the electrolyte solution is maintained during the anodizing process, and the current density at which the anodizing process is performed.

Of the operating conditions, the temperature of the electrolyte solution has a marked effect upon film for-

mation. Adhesion of organic finishes to such a film coating is much better on films produced with the anodizing solution at higher temperatures. The corrosion resistant property of the oxide film gradually increases in general with increasing cathodic current density. Above a certain current density, however, this relationship does not continue to apply, i.e., appreciable gain is not obtained. Adhesion of organic finishes on the film produced is superior at a certain current density to that formed at other densities. Generally, the period of treating time for forming the oxide film does not affect the adhesion between the filmed surfaces and organic coatings; however, generally the corrosion resistance of the film is greater for longer treating periods than for shorter periods.

Referring to a particular solution composition, the optimum concentration of the electrolyte solution according to the teachings of this invention includes approximately 8% by weight of an alkali metal hydroxide, and 3% by weight of an alkali metal gluconate or water soluble salt of gluconic acid which serves as the chelating agent. Other chelating agents are usable providing they are compatible with an alkaline solution and are capable of forming titanium chelation compounds. For example, two chelating agents which will form chelate complexes with titanium ions but with less effectiveness than alkali metal gluconate are: nitrilotriacetic acid trisodium salt, and ethylene diamine tetra-acetic acid. Lesser or greater concentrations of the active ingredients can be used. With too great a reduction in concentration, however, higher anodizing voltages are required and the resulting coatings are less uniform. The practical minimum concentrations are 2% by weight alkali hydroxide and 1% by weight alkali metal gluconate or other suitable chelating agent.

The anodizing process according to the teachings of this invention must be performed with the solution maintained within a temperature range of 150° F. to 212° F., and preferably within the range 190° F. to 205° F. Too low an operating temperature results in larger voltage requirements and irregular coating formation. The solution itself will boil above 215° F. The property of the film coating shows considerable differences over 10° F. changes.

The support or rack which holds the part should be of a metal similar to that which is to be anodized, at least the submerged portion of the support. The use of a dissimilar metal as a support will disturb the normal voltage current relationship, wherein the dissimilar metal will dissipate current from the part to be anodized. In an anodic process, the metal upon which a coating is to be disposed, of course, is the anode. The metal which forms the electrically opposing cathode is preferably of steel in all cases regardless of the metal undergoing treatment for low cost considerations as well as simplicity of design; the tank in which the solution is disposed constitutes the cathode.

After cleaning and pickling the metal part to be anodized according to the usual commercial practices, the subject part and its rack or support is electrically connected to a direct current power source as the anode. Voltage is gradually applied between the submerged part and the opposing cathode, until the current density attains a value of 10 to 120 amperes per square foot of part surface area. The oxide coating thickness will be proportional to this current density. For optimum use in bonding to structural adhesives, the appropriate range will be 40 to 60 amperes per square foot though higher current densities also give good results. After attaining the desired current density, the voltage must usually be reduced to maintain a fixed current. An anodizing time of 20 to 40 minutes is convenient, depending on coating thickness desired.

As an example, to maintain a current density of 50 amperes per square foot for 30 minutes, the voltage will initially be increased gradually to a value of about 13 to 14 volts. As the current thereafter tends to slowly climb upward, it is maintained at the desired value of 50 amperes by decreasing the voltage to a final value of about 7 to 8 volts. The power is then shut off, and the anodized part is rinsed and dried according to commercial practices.

Variations are possible in the anodizing cycle. For example, when a precise coating thickness is not required, the voltage can be set at a value of about 8 to 12 volts and the current allowed to increase naturally. The final current may be two to three times its starting value, depending on the length of cycle used. The final coating thickness will be in proportion to the coulombs of electricity passed per square foot. Adjustments to limit current density may be needed to avoid exceeding the amperage capacity of the available power source.

The proper procedure for this invention is to use the minimum current density for the most economical operation, which produces an adequate coating correlating favorably with the application to which the coating is put. While the coating herein described is particularly noteworthy in producing good bonding and strength with adhesives and finishes, as noted above, the following additional applications are realize: (1) The anodic coating will offer good resistance to corrosion and abrasion, depending on the severity of the environment. Titanium is recognized to be naturally corrosion resistant to many environments because of its natural oxide film, and with the oxide film provided by this process, approximately 60 microinches thick, the versatility to resist corrosion will be greatly increased. (2) The anodic coating according to the teachings of this invention will provide an insulative barrier when a titanium or other metal part is used in contact with another metal. For example, such bimetallic contact is known to result in severe galvanic corrosion of one of the metals in certain environments. An organic finish is usually used as a barrier against this, but the anodic coating will sever that purpose unassisted in some applications. (3) Anodic coatings on titanium have been found to be of utility in reducing the adverse galling characteristics of bare titanium when working against itself or other metals. The anodic coating according to this invention provides a similar or superior anti-galling characteristic, particularly when advantage is taken of its good bonding properties with organic films, such as dry film lubricants. It is to be understood that although titanium is singled out particularly in the above discussion, this invention effectively provides a definite technological advance in coating metals of the group consisting of titanium, zirconium, hafnium and thorium.

It is intended that all matter contained in the foregoing description shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. A method of forming a protective coating on a metal surface of metals from the group consisting of titanium, zirconium, hafnium and thorium which comprises subjecting as anode an article having a metal surface characteristic of said group to electrolysis in an aqueous solution consisting essentially of two to eight percent by weight of an alkali metal hydroxide and one to three percent by weight of an alkali metal gluconate.

2. A method of forming a protective coating on a metal surface of metals from the group consisting of titanium, zirconium, hafnium and thorium which comprises subjecting as anode an article having a metal surface characteristic of said group to electrolysis in an aqueous solution consisting essentially of two to eight percent by weight of an alkali metal hydroxide and one to three percent by weight of a water soluble salt of gluconic acid.

3. A method of forming a protective coating on a metal surface of metals from the group consisting of titanium, zirconium, hafnium and thorium which comprises subjecting as anode an article having a metal surface charac-

teristic of said group to electrolysis in an aqueous solution consisting essentially of two to eight percent by weight of an alkali metal hydroxide and one to three percent by weight of an alkali metal gluconate at a current density of 10 to 120 amperes per square foot of anode surface area.

4. A method of forming a protective coating on a metal surface of metals from the group consisting of titanium, zirconium, hafnium and thorium which comprises subjecting as anode an article having a metal surface characteristic of said group to electrolysis in an aqueous solution consisting essentially of two to eight percent by weight of an alkali metal hydroxide and one to three percent by weight of an alkali metal gluconate at a solution temperature of the range 150° F. to 212° F.

5. A method of forming a protective coating on a metal surface of metals from the group consisting of titanium, zirconium, hafnium and thorium which comprises subjecting as anode an article having a metal surface characteristic of said group to electrolysis in an aqueous solution consisting essentially of two to eight percent by weight of an alkali metal hydroxide and one to three percent by weight of a water-soluble salt of gluconic acid at a current density of ten to 120 amperes per square foot of anode area and at a solution temperature in the range of 150° to 212° F.

6. A method of forming a protective coating on a metal surface of metals from the group consisting of titanium, zirconium, hafnium and thorium which comprises subjecting as anode an article having a metal surface characteristic of said group to electrolysis in an aqueous solution consisting essentially of two to eight percent by weight of an alkali metal hydroxide and one to three percent by weight of an alkali metal gluconate at a current density of 10 to 120 amperes per square foot of anode surface area and at a solution temperature in the range of 150° F. to 212° F.

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