

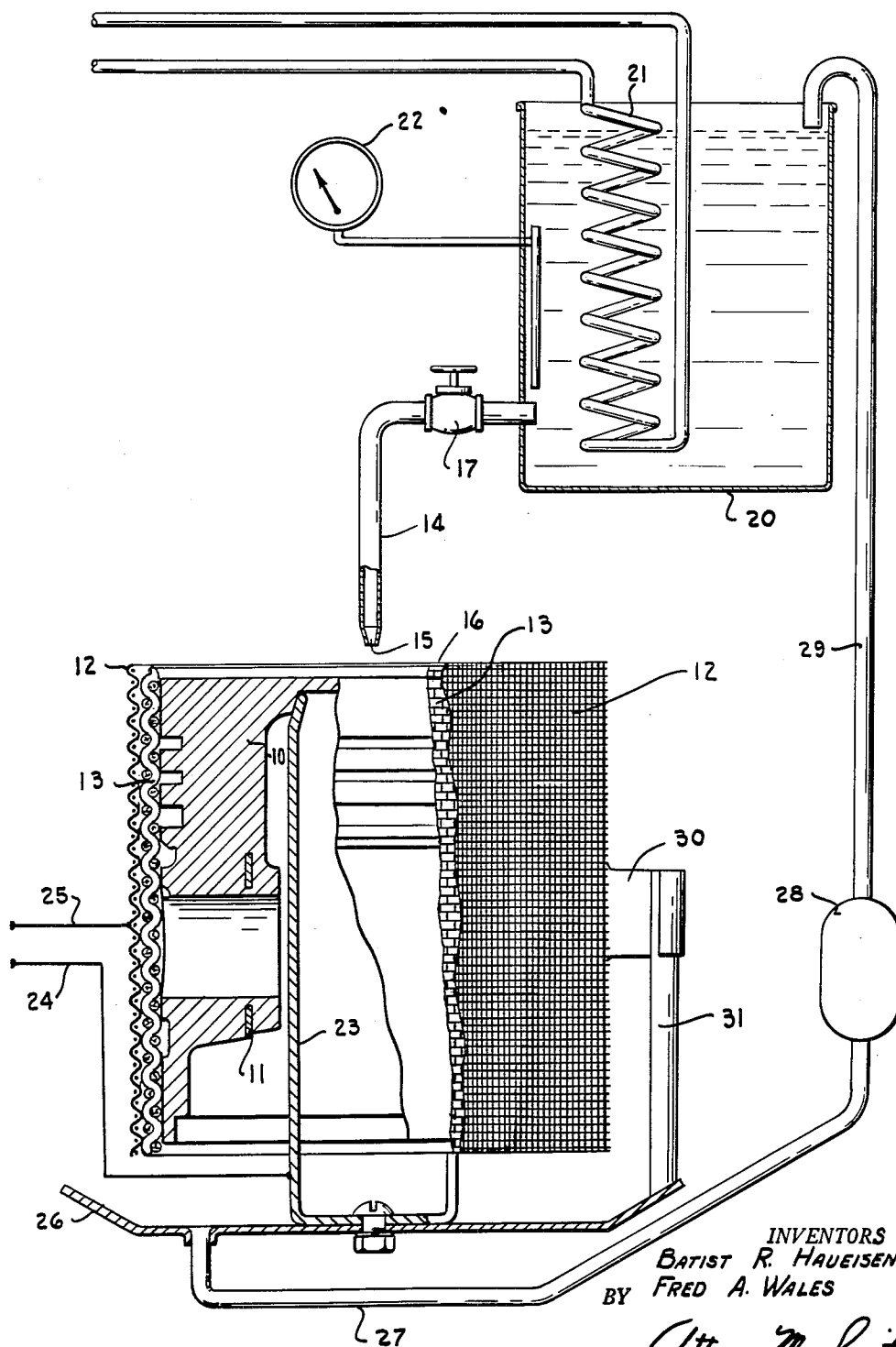
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METHOD OF COATING METAL SURFACES

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METHOD OF COATING METAL SURFACES

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The present invention relates to the method of and apparatus for forming coatings, known to those skilled in the art as "oxide coatings" on aluminum and aluminum alloys or articles formed therefrom.

Such "oxide coatings" are commonly recognized as being formed chiefly of Al_2O_3 , SO_3 , and H_2O . Such coatings have been formed by processes heretofore known in the art by passing an electric current through the aluminum, aluminum alloy or article formed therefrom as the anode in an electrolytic cell in which an acid, such as dilute sulfuric acid is used as the electrolyte. In using such prior processes the electrolyte was employed as a fluid bath in which the aluminum, aluminum alloy or article formed therefrom was suspended or submerged during the passage of the electric current therethrough. In the development of composite metal articles, such for example, as steel strut aluminum and aluminum alloy pistons, the presence of such steel struts in the pistons made such processes unsatisfactory due to the destructive action of the acid electrolyte on the ferrous metal struts of the piston and due to the high current density required because of the absence of the electrolytic valve action in such ferrous metal portions.

In forming such coatings it is difficult on a commercial scale basis to regulate the temperature of the electrolyte within the rather narrow limits which produce the optimum quality of oxide coating. Also, the evolution of gas at the interfaces of the electrolytic bath and the surfaces being subjected to treatment presents practical difficulties in achieving the best results.

The process and apparatus of the present invention therefore has as a principal object the provision of an oxide coating on selected portions of an aluminum or aluminum alloy surface or an article formed therefrom to provide a dense, fine grained oxide coating on such selected portions of said surfaces without subjecting any non-aluminum components thereof to the action of the electrolyte.

A further object of the present invention is to provide a process and apparatus for producing a protective coating on selected surfaces of aluminum, aluminum alloys, or articles formed therefrom, in those instances in which it is not commercially feasible to immerse the surfaces in an electrolyte bath.

A further object of the present invention is to provide a process for the production of a protective coating on the aluminum or aluminum alloy surfaces of articles formed of composite metallic structures and in which the maintenance of electrolyte temperatures can be achieved within the relatively close limits required to produce oxide coatings of optimum quality and at a cost of operation and equipment which is substantially reduced over prior art operations and equipment, the present invention also providing a ready means for dissipating the gases evolved during the formation of the coating thereby producing superior coatings at substantially reduced costs.

It is a further object of the present invention to provide a method and apparatus for forming oxide coatings on

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aluminum or aluminum alloy constituents of a composite metal article in which provision is made for providing a uniform flow of an acid electrolyte maintained at a substantially constant temperature within pre-fixed limits, over the surfaces on which the oxide coating is to be formed while diverting the flow of such electrolyte from other surfaces of the article which would be deleteriously affected by the said electrolyte.

It is a further object of the present invention to provide a process for forming an oxide coating on an aluminum or aluminum alloy surface in which provision is made for the accurate control of the temperature of the electrolyte and for the discharge of gases formed during the treatment, thus producing oxide coatings having superior characteristics of strength and uniformity.

Other objects of the present invention will appear in the following description and appended claims.

One preferred form of apparatus embodying the present invention is shown by way of example in the accompanying schematic drawing forming a part of this specification, in which the figure is a diagrammatic view showing one form of application of the method and apparatus of the present invention to the formation of an oxide coating on the top and side portions of a composite bi-metallic piston.

It is to be understood, however, that while the use of the method and apparatus of the present invention for treating bi-metallic pistons is a preferred embodiment of the invention that this use is described solely by way of example and not of limitation as the invention is not limited in its application to the details of construction and arrangement of parts illustrated in the accompanying drawings since the invention is capable of other embodiments and of being practiced or carried out in various ways and with various other articles. Also, it is to be understood that the phraseology or terminology employed herein is for the purpose of description only and not of limitation.

Referring to the drawing, there is illustrated by way of example a bi-metallic piston 10 in which the body of the piston is formed of an aluminum alloy while the internal strut structure indicated by the numeral 11 is formed of steel or other ferrous metal alloys. It will be apparent that the immersion of such a piston in an electrolyte bath using an acid such as dilute sulfuric acid as the electrolyte would have a very deleterious effect on the steel or ferrous alloy strut. Due to the fact that ferrous metals do not possess the electrolytic valve action of aluminum or an aluminum alloy, a high current density would also be created in any electrolytic bath so used and such oxide coating as might be produced on the aluminum or aluminum alloy constituents of the piston would be very inferior and produced under such conditions that the process would be very expensive to operate. Prior attempts to solve the problem by masking or blocking off the non-aluminum portions have not been satisfactory either from the standpoint of costs or of results obtained.

We have discovered that these and other difficulties may be overcome and submersion of the piston in the electrolyte may be avoided by using the process and apparatus of the present invention which will now be described.

We have discovered that if the side wall portions of the piston 10 are enclosed in a porous cathode shell 12, preferably formed of perforated or woven electrically conductive metals such as copper or aluminum or alloys thereof, provided with a liner 13 formed of any suitable dielectric materials which are inert to the electrolyte applied, that such a liner will act to distribute the liquid electrolyte uniformly over the contacting side surfaces of piston 10 which are to be treated for the formation of the

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oxide coating. The porous shell 12 and the liner 13 are preferably carried by a bracket 30 which is supported by and hinged to a supporting member 31. Any other suitable form of support for said shell and liner may be provided. As indicated in the drawing, the electrolyte is supplied through a feed tube 14 the orifice 15 of which is such a size as to provide a constant flow of electrolyte discharged on the surface of the piston head 16 forming a part of the piston 10. The amount of electrolyte supplied through the feed tube 14 is regulated by the valve 17 to provide such an amount of electrolyte to the piston head 16 that its top surface will be flooded and the excess thereof will be fed through the liner 13 and distributed by it over the adjacent side walls of the piston 10.

Electrolyte is supplied to the feed tube 14 from an electrolyte supply tank 20 in which the temperature of the electrolyte is regulated by the immersed cooling coils 21, the temperatures of which are controlled by any suitable type of conventional heat exchange apparatus (not shown) whose action is controlled by an conventional type of control thermostat indicated by the numeral 22.

The piston 10 is electrically connected as the anode of an electrolytic cell through contact with the internal piston support 23 which is electrically connected as at 24 with the positive side of a direct electric current source (not shown) which is provided with any suitable type of means for controlling the current density. The porous cathode shell 12 is electrically connected as at 25 with the negative side of the said direct electric current source. The electric current flows through the liner 13, the electrolyte and the piston 10 and builds up the desired oxide coating on all surfaces wetted by the electrolyte. In the particular embodiment here shown, this includes the top and side surfaces of the piston 10. It is to be understood, however, that the electrolyte can be supplied directly to the liner 13 engaging the side surfaces of the piston and thus form an oxide coating on the piston side wall surfaces only.

The electrolyte flows downwardly by gravity through the liner 13 and is caught in the drainage trough 26 from which it flows by gravity through the conduit 27 to the circulating pump 28 from which it is discharged into the tank 30 through the open discharge line 29.

Regular concentration control tests can be run on the electrolyte in the tank 20 and suitable steps taken to maintain the electrolyte at the desired concentrations. The temperature of the electrolyte in the tank can be regulated readily as above described and thus both the concentrations and temperatures of the electrolyte are at all times under the control of the operator to maintain any predetermined set of optimum conditions to produce an oxide coating having the desired characteristics.

In a preferred operation of the method, a very satisfactory coating was produced on a high silicon alloy aluminum steel-strut piston having a treated surface area of .41 sq. ft. under the following conditions:

Electrolyte concentration	20% H ₂ SO ₄ .
Flow rate	approx. 4 gal. per hr.
Voltage at cell	approx. 15.
Current density	approx. 13 amps. per sq. ft.
Temperature	approx. 72° F.
Time	approx. 20 minutes.
Thickness of coating	approx. .0003".

From tests run to determine the preferred range of limits on such general types of pistons we have determined that the following ranges of conditions will produce commercially satisfactory results:

Electrolyte—from approx. 10% to approx. 25% H ₂ SO ₄ concentration
Voltage at cell—from approx. 6 to approx. 20
Current density—from approx. 7.5 amps. to approx. 17.5 amps. per sq. ft.
Temperature—from approx. 60° F. to approx. 90° F.
Time—from approx. 10 min. to approx. 40 min.
Thickness of coating—approx. .0002" to approx. .0004"

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The selection of the particular operating factors within said ranges for any given alloy can be made readily by one skilled in this art. The actual voltages employed will depend upon the time of treatment, nature of the alloy, temperature of the electrolyte, thickness of the liner 13, and desired thickness of the film to be produced.

We have found that the addition of from approximately 1% to approximately 5% by weight of oxalic acid to the electrolyte permits the operation of the process at increased temperatures without impairing the desired properties of the produced oxide coating.

It will be seen that the supply of the electrolyte as a constantly flowing stream will continually wash and wet the surfaces being treated. This is accomplished without contact between the electrolyte and the non-aluminum portions of the piston. This action flushes off the surfaces and constantly carries off the gas bubbles evolved at the interface between the electrolyte and the surface to be coated. The gas can work its way out through the liner 13 and the perforate cathode shell 12. The flowing electrolyte also cools the surface being coated and thus controls the temperature of the reaction from which the oxide coating is formed.

The liner 13 should be formed of materials possessing the following properties:

1. Be unaffected by H₂SO₄ in the concentrations and under the conditions employed.
2. Be readily wet by the electrolyte.
3. Be dense enough or have sufficient number of fibers per unit area to permit adequate ionic conduction by way of their surface liquid.
4. Be of such texture that it conforms to the contours of the anode and the cathode.
5. Be loose or permeable enough to permit electrochemically generated H₂ and O₂ to escape from the active surfaces to the top or from the perforated cathode.
6. Be loose or porous to permit a generous rate of flow of electrolyte from top to bottom so that desired temperature can be maintained.
7. Be mechanically rugged so that operations of loading and unloading the cell will not damage it.

A preferred material for use in forming the liner 13 is woven, knitted or loose fibers of synthetic polymeric amides, such as nylon. The material may be used either in the form of a single extruded filament woven or knitted into a liner sleeve, or as separate fibers spun into a thread and then woven or knitted to form a liner sleeve, or it may be used as matted fibers. If desired, other materials such, for example, as glass fibers or the like may be employed. In employing loose or matted fibers, it is preferable to enclose them in an envelope formed of such knitted or woven materials.

Even in a conventional anodizing tank with a large volume of electrolyte, the formed anodic film will be defective if there is not a vigorous flow of the solution at the anode-electrolyte interface. The quantity of heat generated by the formation of the aluminum hydrate or oxide is very large. Conduction and convection cannot properly dissipate it in a still solution.

We have found that the use of nylon threads or similar materials possessing constant dielectric properties and which are passive electrically in the process may be so knitted or woven so as to provide a stationary non-slipping sleeve or liner which will engage the surfaces to be treated without permitting relative movement between them. In addition, it is possible to knit or weave such materials in any desired mesh which will act as a distributing member to distribute a substantially uniform thickness of electrolyte film over the entire surface.

Any desired size or shape may be given to the liner 13 and the porous cathode shell 12 to accommodate any size or shape of article to be treated by the process. While a woven, knitted or matted material appears presently to possess the most desirable characteristics for use as the liner 13, it is contemplated that a series of

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bristles or separate filaments mounted as a brush in a metal back may be employed as the shell 12 and liner 13. Such a brush type of shell and liner would facilitate the handling of the articles into and out of the shell and would provide a substantially uniform distribution of the electrolyte over the surfaces to be treated.

This feature of a constant dielectric liner 13 inert to the electrolyte employed provides a very satisfactory oxide coating on the aluminum or aluminum alloy portion of the piston and eliminates the destruction of the steel or ferrous metal parts by oxidation in the electrolyte. It has also been found that the process makes more effective use of the electrolyte employed since there is no opportunity for contamination of an entire bath, and each of the articles can be supplied with a definite and predetermined amount of electrolyte at a constant and predetermined concentration. It has been found that the present method and apparatus assures a more uniform coating of the articles than is the case where a group of articles is placed in an electrolytic bath and current is passed through the entire group of articles and the bath.

Having thus described our invention, we claim:

1. In the method of selectively forming a corrosion resistant coating on the exterior surfaces of the aluminum alloy portions of a composite aluminum steel strut internal combustion engine piston, the steps of placing said piston upright in a tubular porous shell supported in a vertical position and having an absorbent liner therein in contact with the sides of said piston, flooding the top of said piston with an acid electrolyte in regulated amounts and allowing the electrolyte to flow downwardly through said absorbent liner, connecting said porous shell as the cathode and said piston as the anode and passing an

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electric current therebetween so as to form said coating on the surfaces of said piston which are wet with said electrolyte, and providing circulating means for said electrolyte including means to maintain said electrolyte at a predetermined acid concentration and temperature.

2. The method as claimed in claim 1 and further characterized in that the said absorbent liner comprises a dielectric plastic material.

3. The method as claimed in claim 2 and further characterized in that the said dielectric plastic material is a synthetic polymeric amide.

4. The method as claimed in claim 3 and further characterized in that the electrolyte comprises a sulfuric acid solution in which the acid content comprises from approximately 10% to approximately 25% by weight of said solution and said solution is maintained at a temperature within the limits of from approximately 60° F.-90° F.

5. The method as claimed in claim 4 and further characterized in that the said direct electric current is maintained at a current density of approximately 13 amperes per square foot of surface to be coated under a potential of approximately 15 volts.

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