July 13, 1971 K. AIHARA 3,592,754

APPARATUS FOR THE ANODIC OXIDATION OF A PLURALITY OF ALUMINUM WORKPIECES

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FIG. 1

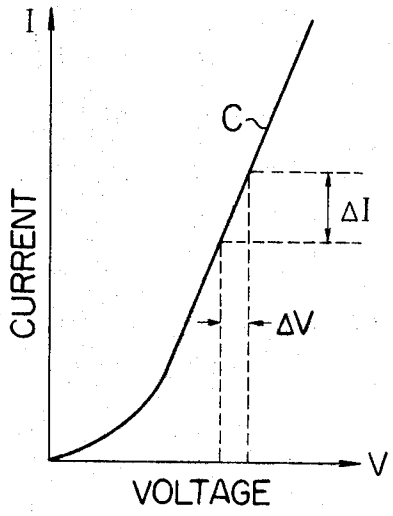


FIG. 2

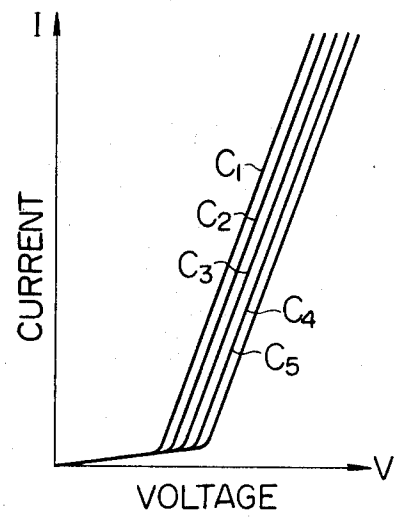


FIG. 3

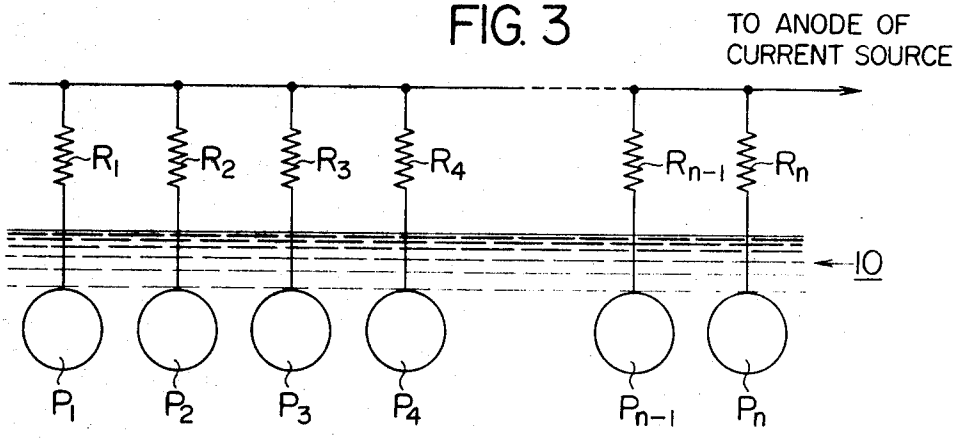
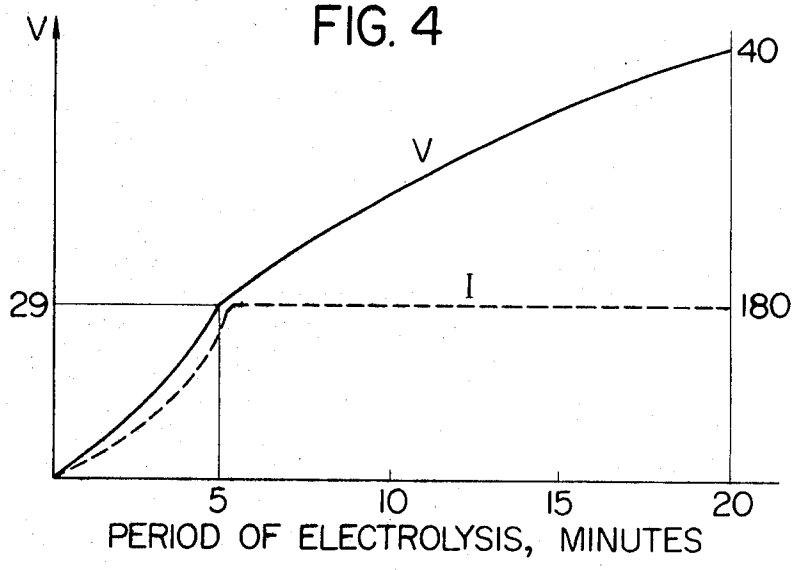


FIG. 4



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FIG. 6

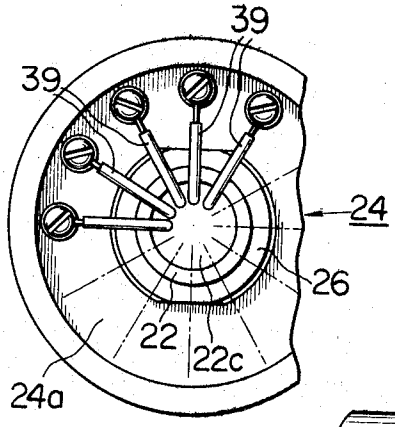


FIG. 5

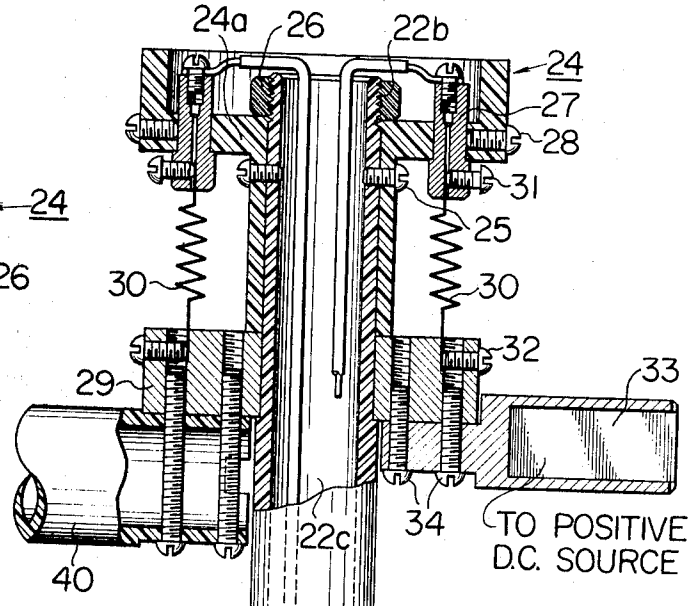


FIG. 7

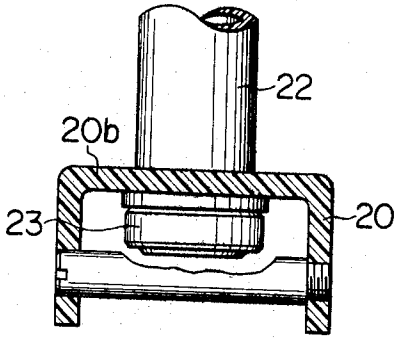
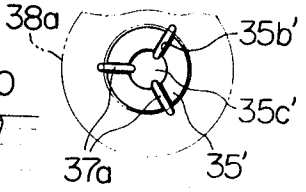


FIG. 10



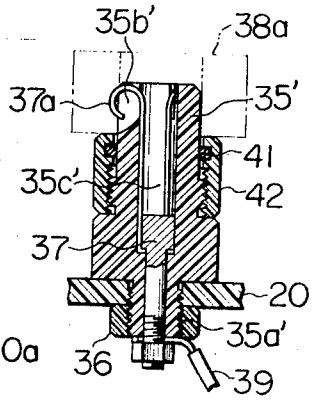
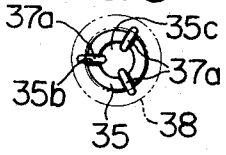


FIG. 9

FIG. 8



United States Patent Office 3,592,754 Patented July 13, 1971

3,592,754

APPARATUS FOR THE ANODIC OXIDATION OF A PLURALITY OF ALUMINUM WORKPIECES

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Filed Oct. 28, 1968, Ser. No. 770,959
Int. Cl. C23b 5/70; B01k 3/00
U.S. Cl. 204—297 6 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a process for the mass-productive formation of hard oxide coating on a number of aluminum stocks through anodic oxidation technique, wherein said stocks immersed in an electrolytic acid bath and connected electrically in parallel to the anodic side of an electrolytic current source. The process is characterized by that said stocks are connected to the anode through the intermediary of respective resistors. The resistance values of these resistors are preferably so selected that a voltage drop, in the order of say amounting to 1–2 volts will take place in the anodic current path.

This invention relates to a process for the mass-productive formation of oxide coating on a plurality of aluminum stocks through anodic oxidation technique.

The term "aluminum" as used herein throughout the present specification is intended to cover various conventional aluminum alloys containing at least one of the following alloying elements: Cu, Si, Mg, Ni, Cr and the like.

Various and profound studies and experiments have hitherto been carried out by those skilled in the art in the anodic oxidation technique for the purpose of formation of hard and abrasive-resistant oxide coating on aluminum stocks. Experience has shown, however, that it is highly difficult to produce a unified quality coating on each of a large number of, say, several hundreds aluminum stocks set up in an electrolytic bath and in a single operational step. when reliance is made exclusively on the prior art. Thus, considerable specks or the like surface defects are generally found on the treated products.

It is therefore the main object of the invention to provide an improved process for the anodic formation of abrasive-resistant coating on a large number of aluminum stocks on an industrial scale, yet with substantially equal quality of the oxide coating.

A further object is to provide a process of the kind above referred to, capable of suppressing conventionally appearing voltage and current deviations from the corresponding design or mean values.

Still further object is to provide a process of the kind above referred to which is highly economical in its operation and maintenance.

These and further objects, features and advantages of the invention will become more apparent from the following detailed description of the invention by reference to the accompanying drawings which constitute part of this specification, as well as several preferred numerical examples to be given only for illustrating purpose.

It should be however stressly understood that a preferred embodiment shown and several numerical examples to be given are only for illustrating purpose as hinted above

and various changes and modifications may easily occur to those skilled in the art upon read through the following detailed description of the invention. These changes and modifications should be included within the true spirit and scope of the invention so far as they fall within the scope of the appended claims.

In the drawings:

FIG. 1 is a diagram, the scales being taken at random, showing a generalized relationship between the electrolytic voltage and the electrolytic current, as appearing in the course of anodized electrolytic formation of oxide layer on aluminum stocks.

FIG. 2 is an explanatory diagram, illustrative of frequently encountered voltage deviations appearing in the course of anodic treatment of a number of aluminum stocks connected electrically in parallel to the anode of an electrolytic device for the anodizing formation of oxide coatings on said stocks.

FIG. 3 is a schematic view of an arrangement for the anodizing electrolytic formation of oxide coatings on a number of aluminium stocks in accordance with the new teaching proposed by the present invention.

FIG. 4 is an explanatory diagram, showing the relationship among voltage, current and treating period in a preferred embodiment case of the inventive process.

FIG. 5 is a partially broken-away and partially sectional view of a part of a device in its side elevation, showing an electrolytic current distributor mechanism embodying the principles of the invention.

FIG. 6 is a simplified and partial top plan view of the mechanism shown in FIG. 5, showing however its essential parts only.

FIG. 7 is a partial vertical sectional view of the mechanism shown in FIG. 5, the section being taken substantially along the section line 7–7′ shown therein.

FIG. 8 is a top plan view of a stock holder unit shown in FIG. 5.

FIG. 9 is a longitudinal sectional view of a modified stock holder unit from that shown in FIGS. 5 and 8.

FIG. 10 is a top plan view of the modified holder unit shown in FIG. 9.

Referring now to FIG. 1 of the accompany drawings, which illustrates a current voltage curve as appearing in the electrolytic process treating a single aluminum stock for anodized oxide coating. It is a relatively easy matter to anodizingly coat the single aluminum stock as judged from the sole current-voltage curve C, on account of easy adjustment of voltage and current conditions for obtaining optical coating results by carefully observing the anodizingly processing step as it goes.

Considerable and various difficulties will be encountered however when it is tried to coat in the similar way a number of aluminum stocks by a single electrolytic process by connecting them electrically in parallel with each other to the anodic electrode. More specifically, in this case, a plurality of current-voltage curves as shown by way of example at C_1, C_2 . . . C_5 in FIG. 2 may be observed, thus appearing considerable and frequent deviations from the design or predetermined optimum value, as caused by unavoidable minor discrepancy in the physical configuration as well as chemical nature and properties of each of the treating aluminum stocks, even if most careful and ideal pretreatment should have been performed thereon for exposing the true metallic or alloy

surface by removing occasionally and previously formed oxides, hydroxides and the like.

When observing precisely the specific electrolytic process in the above sense relative to respective aluminum stock, variously deviating voltage-current curves as shown in FIG. 2 as hinted briefly above will be observed when a number of similar stocks are subjected to an anodizingly coating process in an electrolytic bath. Although in this figure only five characteristics curves are representatively shown, it may be well defined that a corresponding number of deviating curves are observed to that of the treating stocks. According to our experience, it is further observed under the electrolytic conditions a remarkable concentration tendency in the course of current distribution among the treating stocks on such one of the stocks which shows a most sharpe slope $\Delta I/\Delta V$ (see. also FIG. 1) of said current-increasing characteristic curve rising suddenly from a predetermined lower voltage level as shown.

This kind of current concentrations of random nature as observed over the whole number of treating stocks will be more remarkable with larger value of said slope or gradient. In the practical anodizing oxide coating process, this current concentration will give rise to "bursts" which means burnt specks on the coated products caused by the current surge, or at least uneven coating of the desired oxide. It was therefore practically impossible to operate the anodizingly coating process by applying a high voltage or a heavy current to the stocks so as to finish the process within a short period, without sacrificing the desirous equal quality of the oxide coatings on the stocks. It was therefore the conventional mode of the anodizing coating process to impress a lower voltage upon and supply a weak current to the treating stocks when the number thereof amounts to ten or more numerous one and frequent and careful adjustments of voltage and/or current must be made during the whole progress of the anodizing process.

When relying upon the novel teachings proposed by the invention, however, these drawbacks can be effectively obviated as will become more clear as the description proceeds, and a large number of, such as, for instance, one hundred or more number of aluminum stocks may be well treated simultaneously and within a remarkably short period so as to provide even-quality oxide coatings thereon at a highly improved operating efficiency.

The present invention in its broadest sense resides in an anodizing hard oxide coating process on a plurality of aluminum stocks immersed in an electrolytic acid bath and connected electrically in parallel to the anodic pole of an electrolytic current source, said process being characterized by that said stocks are connected so through the intermediary of respective resistors.

In FIG. 3, these stocks are only schematically shown at P_1, P_2, P_3 . . . P_{n-1} and P_n, and the resistors at R_1, R_2 R_3 . . . R_{n-1} and R_n, respectively, the electrolytic bath being shown generally and schematically at **10**.

In the course of the anodizing coating process wherein the novel teachings according to this invention has been employed, even when a current increment ΔI should be applied on one of the treating aluminum stocks in advance of current application on all other stocks, the voltage will be reduced at that instant moment by the amount of $\Delta I \cdot R$, if R stands for the electric resistance value of each of said resistors, whereby the leading current is automatically checked. This automatic current control is applicable naturally to all the treating stocks which are therefore subjected almost instantly to the initiation of a current passage commonly at a predetermined electrolytic current or voltage value. Thanks to this automatic and mutually affecting control action, all the treating stocks are subjected to a smooth and even anodizing and oxidizing operation, in spite of unavoidable minor uneven surface and material conditions of the stocks. Since otherwise encountered current surges can be effectively avoided in this way, the prescribed voltage and current necessary for carrying out the electrolytic process can be attained within a short period, while insuring the uniformity of the hard oxide coating on the stocks.

It is preferable to adopt the said resistance value R to be at least several times, such as three times, of the resistance value as measured between the work pieces and the cathodic electrode through the electrolytic bath. As a safety measure, the value of resistor R may be so selected that the voltage drop across the resistor amounts to 1–2 volts.

FIGS. 5–8 show a preferred embodiment apparatus adapted for carrying out the inventive process.

In FIG. 5, numeral **20** represents a stationary supporting member, only partly shown, which is dipped in an acid bath **10**, the free liquid surface of which is shown at **21**. A hollow tubular pillar **22** made of a plastic material as shown is formed at its root with male threaded part **22***a* passing through a plain opening **20***a* formed through the upper and horizontal web **20***b* of said supporting member **20** having preferably a channel-shaped cross-section as shown in FIG. 7, and fixedly attached thereto by means of a nut **23** screwed onto said threaded part **22***a*.

Normally, the number of pillars **22** are plural so as to cover all the number of stocks under anodizing treatment, although not shown. This will naturally be applied to the number of supporting members **20**.

A flanged sleeve **24**, made of a plastic material as shown, is fixedly attached to the upper end of said tubular pillar **22** by means of a plurality of set screws **25** and a fixing nut **26**, the latter being threaded on male threaded top end **22***b* of the pillar. A plurality of, herein twelve, shouldered terminal pieces **27** are fixedly mounted, in a radial arrangement, on the shell flange at **24***a* of said flanged sleeve **24**, by means of respective set screws **28**.

Conductor ring **29** is fixedly and concentrically mounted on the pillar **22** at an intermediate level between its upper and lower ends, yet above the free liquid level **21** of the electrolytic bath **10**. As shown, each of the terminal pieces **27** is connected through resistor **30** only schematically shown. For assuring this electrical connection, there are provided a plurality of set screws **31** and **32**. To the conductor ring **29**, a bus bar **33** preferably made of copper is fixedly attached by means of a plurality of fixing screws **34**. The bus bar is electrically connected through either a constant current device or constant voltage device, not shown because of its very popularity, to the positive side of a D.C. source, again not shown.

The supporting member **20** has a channel cross-section as was referred to above and carries detachably a plurality of, herein twelve, work piece supports formed into sleeves **35** having male threaded parts **35***a* on which a fixing nut **36** is screwed. These supporters **35** are arranged in a row and only one of said supporters is shown only for simplicity.

Each of said supporters **35** has a conductive and springy core **37** formed with a plurality of radially arranged spring arms **37***a* which have looped top ends emerging from their respective receiving slots **35***b* for providing a frictional grip to the working pieces. As will be seen the working piece is a cylindrical member **38**, in this case, as shown by a representatively and phantom manner.

Each of the terminal pieces **27** is connected through an insulated wire conductor **39** to said conductive core piece **37**, said conductor passing through the interior hollow space **22***c*. Therefore, it will be seen that a positive current passage can be established from the D.C. current source through the constant current control device, bus bar **33**, conductor ring **29**, resistors **30**, terminal pieces **27**, wire conductors **39**, core pieces **37** to the respective works pieces **38**.

The negative side of said D.C. source is connected to a cathodic electrode formed as conventionally into a plate and dipped in the electrolytic bath, although not shown from its very popularity.

Hollow handle piece **40** made of a plastic material is attached firmly to said conductor ring **29** for easily handling of the pillar assembly for mounting and detaching thereof to and from the supporting member **20.**

Although not shown, the work piece is not limited to a cylinder or sleeve. When it is desired to process a pin or bar work piece, it is sufficient to insert it into the open interior space **35***c* of the sleeve-shaped supporter **35** so as to be elastically gripped by spring arms **37***a*. Of course, the supporter assembly **35–37** may be properly modified so as better to grip any work piece and to feed the anodizing current thereto in a more convenient way.

Somewhat modified work piece supporter is shown in FIGS. 9 and 10. In this case the supporter **35'** formed equally into a hollow sleeve receives threadedly a nut member **42** fitted with a sealing ring **41.** By employing this modified kind of supporter assembly a ring-shaped work piece schematically shown at **38***a* in a phantom way can advantageously be treated. Although not shown, there is provided a large number of the supporters for anodizingly treating a corresponding number of work pieces **38***a*.

In the following, several preferred numerical examples will be given for better understanding of the inventive process.

EXAMPLE 1

An electrolytic bath shown at **10** described in the foregoing was employed and kept at —3° C. The bath contained an acid electrolytic aqueous solution comprising: H_2SO_4 17 wt. percent and glycerin 5 wt. percent. The current capacity was 200 amperes. 180 aluminum stocks of 99.7% purity were charged on respective work piece supporters as at **35.** The current density was adjusted to 4 amperes per cubic decimeters by properly adjusting the constant current device of the known design.

The electrolytic current amounted to 4 amperes per stock. As the resistor R, a carbon film-coated one, 1 ohm, was employed. The processing course is illustrated in FIG. 4. As shown, the voltage reached 29 volts within 5 minutes and finally amounted to 40 volts. The overall electrolytic duration term was for 20 minutes as equally shown. The thickness of the oxide coating was amounted to 30 microns. Upon investigated, every coating was of an equal thickness. No bursts were found.

EXAMPLE 2

As the electrolytic bath, that explained in the foregoing was employed. Each of the stocks, 200 pieces, was of an aluminum alloy containing Si: 0.4% and Mg: 0.7%. The electrolytic surface area of the stock was measured to 0.2 cubic decimeter. The electrolytic current was set to 1 ampere per stock. The electrolytic current density, as measured on the anodized piece as before, amounted to 5 amperes per decimeter.

The electrolytic acid bath liquid contained H_2SO_4: 15 wt. percent and glycerine 5% and kept at —3° C.

The initially rising temperature was 29 volts as before and the overall treating period extended for 15 minutes. The final voltage was measured to 40 volts.

In this way, an even oxide coating, 30 microns thick, was formed which is excellent in its sticking performance and has a superior surface condition. No bursts. The resistance value of the resistor R amounted to 2 ohms.

EXAMPLE 3

The electrolytic device was similar to that described hereinbefore. The acid bath solution contained H_2SO_4: 17% and glycerine 5%. The bath temperature was kept at —1° C. The stock was of an aluminum alloy containing Mg: 2:5 wt. percent and Cr: 0.25%. The electrolytic surface of the stock was measured to 1 cubic decimeter. 40 equal size stocks were treated. The resistor R was 2 ohms. The electrolytic current density measured at the anodized stock amounted to 5 amperes per cubic decimeter. Current passed was set to 5 amperes throughout the processing period. The initially rising voltage was 29 volts. The electrolysis extended for 15 minutes. The final voltage 42 volts.

In this way, superior oxide coating, 30 microns thick, was obtained for all 40 treated stocks. No bursts. Sticking was tight.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What I claim is:

1. An apparatus useful for the anodic oxidation of a plurality of aluminum workpieces comprising an electrolytic tank adapted to contain an acid electrolytic bath, a plurality of stationary hollow non-conductive supporting members vertically disposed in said tank and attached to a support in the lower portion of said tank, a direct current source, a plurality of workpiece supports disposed around each of said hollow non-conductive supporting members and attached to said support, each of said workpiece supports being electrically connected to the positive terminal of said direct current source through a resistor by means of an insulated conductor disposed in the interior of said hollow non-conductive support, and a cathodic electrode electrically connected to the negative terminal of said direct current source, wherein each of said stationary hollow non-conductive supporting members is a hollow plastic tube, wherein an electrically conductive terminal is attached to the uppermost portion of said plastic tube, and wherein an electrically conductive ring is disposed around said plastic tube at a position intermediate the uppermost end of said tube and the point where said tube enters the surface of said bath, said conductive ring being connected to the positive terminal of said direct current source through a bus bar electrically connected to said conductive ring, and wherein a resistor is disposed and electrically connected between said conductive ring and said terminal, and wherein a flexible insulated conductor is electrically connected between said terminal and said workpiece supports through the interior of said hollow plastic tube, and wherein said workpiece supports are arranged on a channel mounted on the lowermost portion of said hollow tube at that end of said hollow tube which is supported in the bottom of said tank.

2. An apparatus as in claim **1**, wherein each of said workpiece supports has a conductive and flexible core which is electrically connected to said insulated conductor and which is adapted to bias against a workpiece which is being supported, thereby providing electrical contact to said workpiece and firmly holding said workpiece in place during the anodic operation.

3. An apparatus as in claim **2**, wherein twelve workpiece supports are disposed on a channel mounted on the lowermost portion of said hollow plastic tube, an equivalent number of resistors being present intermediate the conductive ring and the conductive terminal at the uppermost portion of said hollow plastic tube.

4. An apparatus as in claim **2**, wherein the value of each of said resistors is at least several times the resistance value as measured between the workpieces being supported on said workpiece supports and said cathodic electrode through the electrolytic bath at the initial stage of the anodic oxidation operation.

5. An apparatus as in claim **4**, wherein the value of each of said resistors is the resistance value as measured between the workpieces supported on said workpiece supports and said cathodic electrode disposed in

said electrolytic bath at the last stage of the anodic oxidation operation.

6. An apparatus as in claim 4, wherein the value of each of said resistors is such that the voltage drop across each of said resistors varies between one and two volts during the stationary anodic oxidation operation.

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U.S. Cl. X.R.

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