

Sept. 19, 1972

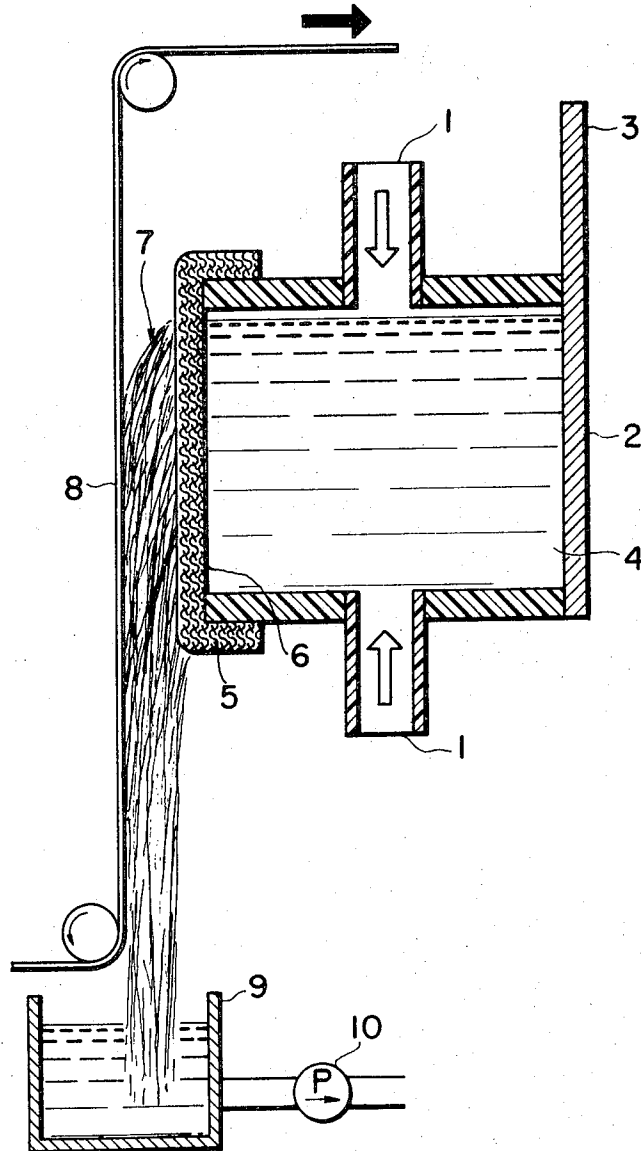
TAKESHI HAMABE ET AL  
CONTINUOUS ANODIC OXIDATION METHOD FOR ALUMINUM  
AND ALLOYS THEREOF

3,692,640

Filed Sept. 14, 1970

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FIG. 1



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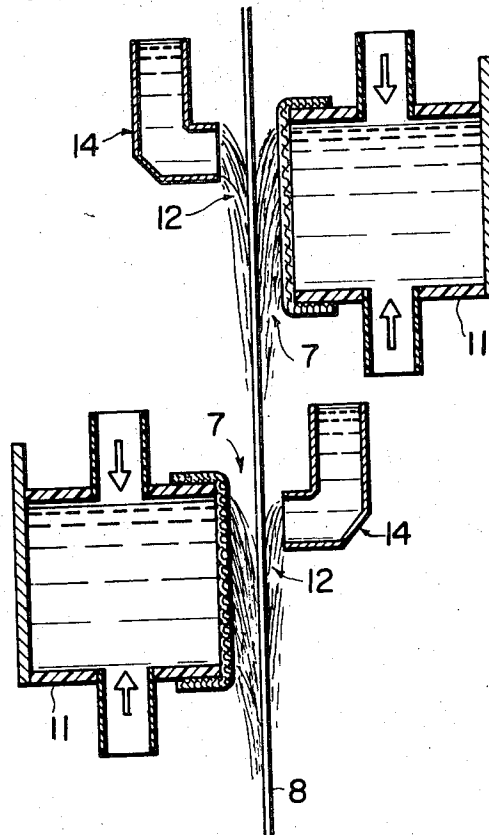
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FIG. 2



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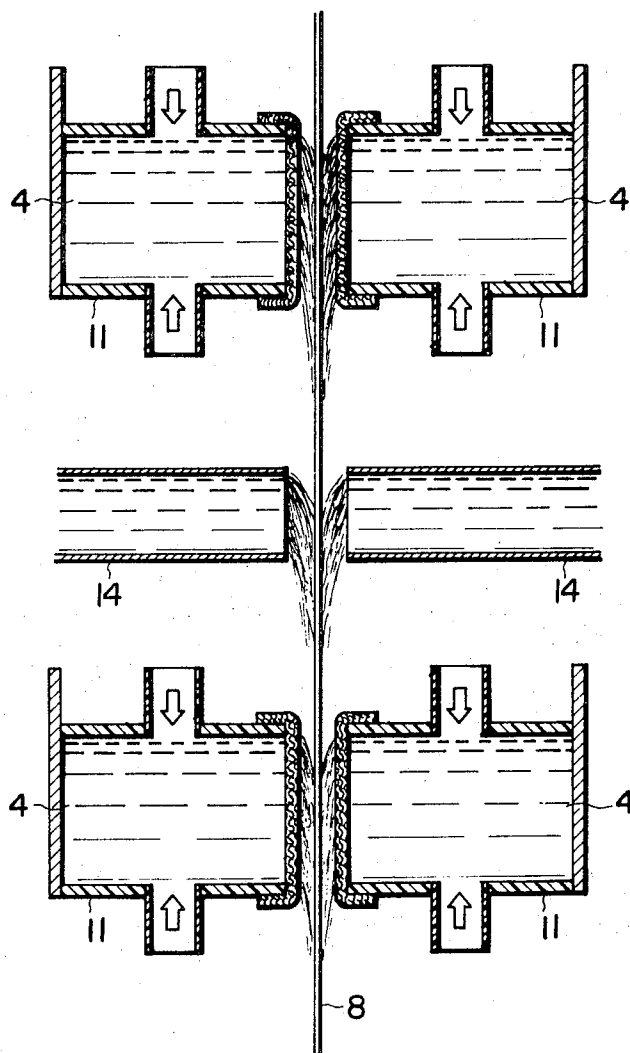
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FIG. 3



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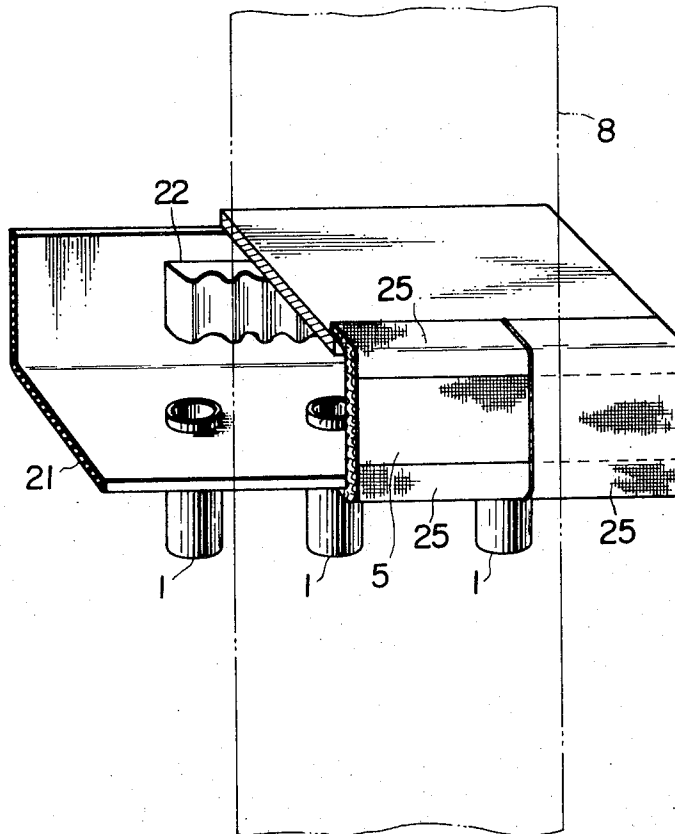
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FIG. 4



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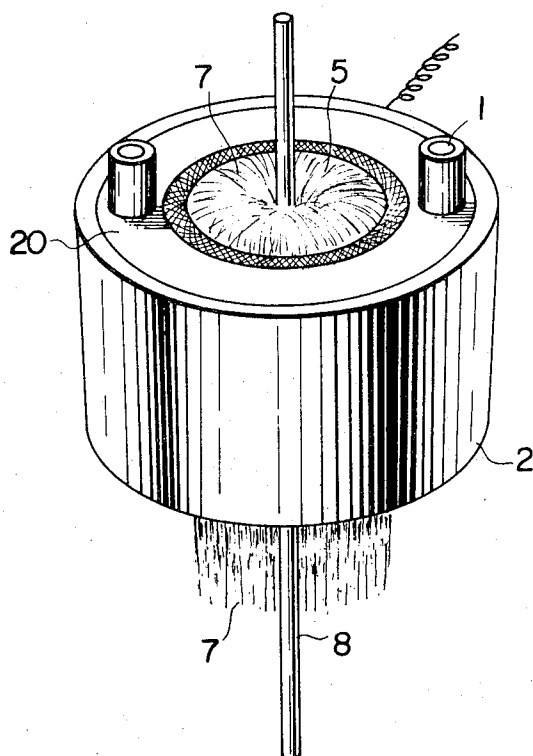
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FIG. 5



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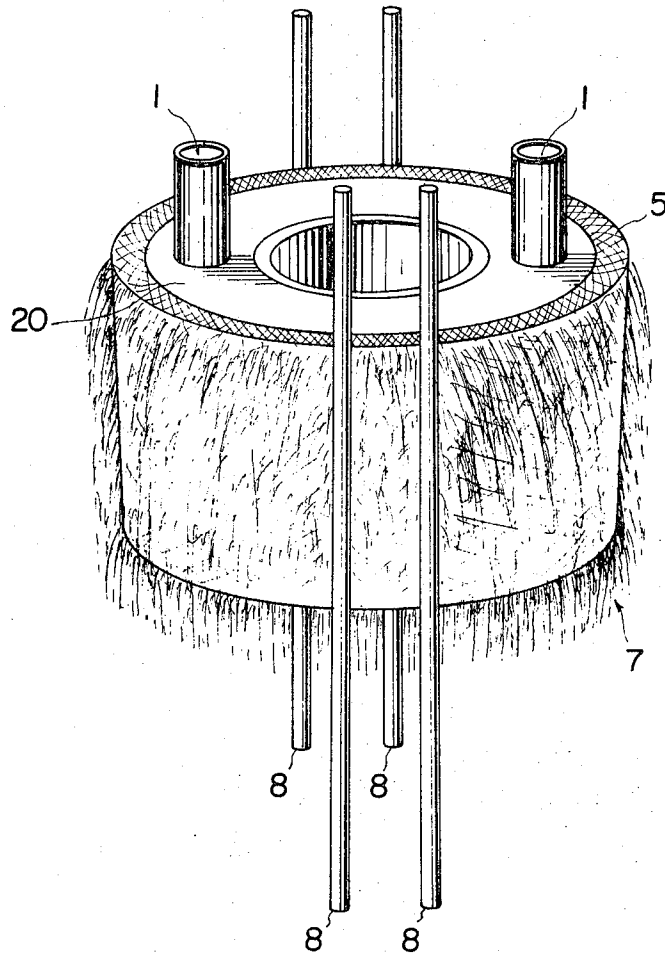
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FIG. 6



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## CONTINUOUS ANODIC OXIDATION METHOD FOR ALUMINUM AND ALLOYS THEREOF

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44/112,251; Dec. 9, 1969, 44/99,659, 44/  
99,660; Dec. 11, 1969 (utility model), 44/  
118,210, 44/118,203

Int. Cl. B01k 3/00; C23b 9/02

U.S. Cl. 204—28

7 Claims

### ABSTRACT OF THE DISCLOSURE

A method of continuously forming an oxide film on aluminum and alloys thereof by anodic oxidation without resorting to a conventional process using an electrolytic cell, and an apparatus for practicing the method which is compact in size and is capable of not only high current density treatment and high speed treatment but also various types of electrolysis.

The present invention relates to a method and apparatus for continuously oxidizing by anodic oxidation the surface of elongate articles consisting of aluminum or an aluminum alloy (hereinafter referred to as aluminum as a whole), i.e. aluminum foils, aluminum strips, aluminum wires, etc.

Anodic oxidation of aluminum has heretofore been conducted at a low current density of several amperes per 1 dm.<sup>2</sup>. At such a degree of current density, the occurrence of the so-called yellowing of film and non-uniform current distribution can be prevented simply by proper temperature control and sufficient stirring of electrolyte. However, the recent tendency in the art of anodic oxidation is towards high current density anodic oxidation with a view to high speed anodic oxidation treatment and the problems of film yellowing and non-uniform current distribution are being highlighted. These problems are difficult subjects which cannot be solved unless the electrode construction and anodic oxidation process are drastically changed. The so-called yellowing of film is caused by the heat which is generated in the process of anodic oxidation, and is closely related to current distribution.

The heat generated in the anodic oxidation is attributed to the heat generated by the reaction between aluminum and oxygen, and the Joule heat generated during the passage of a current through the oxide film, electrolyte, cathode and aluminum. In the ordinary anodic oxidation conducted in an electrolytic cell, the heat generated is substantially entirely transferred to the electrolyte in the electrolytic cell and, therefore, the temperature of the electrolytic system can be maintained constant, by cooling the electrolyte. However, with the current density at which the anodic oxidation is conducted becoming higher and higher, such a method is not capable of sufficiently cooling the electrolysis system and non-uniform temperature distribution will result. At a current density higher than a certain value, yellowing of the film occurs, making it impossible to obtain a normal oxide film. This is because the intensity and uniformity of stirring of the electrolyte undergo a certain limitation.

The present invention consists in an anodic oxidation method which is proposed with a view to obviating the above-described problems, and in which the so-called electrolytic cell with a predetermined quantity of

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electrolyte stored therein, as used heretofore, is not used and hence the electrolytic portion can be sufficiently cooled, providing for a high current density anodic oxidation at high efficiency.

The anodic oxidation method according to the present invention is adapted for continuous oxidation of the entire area of at least one side surface of an elongate article of aluminum, basically by passing the article continuously in opposed relation to a cathode device. The cathode device is composed of a hollow container which is provided with inlet ports for continuously feeding an electrolyte therein and has a cathode therein. One side of the hollow container is open and covered with a liquid-permeable material. The elongate article of aluminum is passed in front of the liquid-permeable material, with a predetermined interval therebetween, or is passed in contact with the same. The space between the liquid-permeable material and the elongate article of aluminum is filled with the electrolyte which has been fed into the hollow container through the inlet ports and uniformized in liquid pressure by the liquid-permeable material during passage therethrough. In this case, the space between the cathode and the liquid-permeable material interior of the cathode device is of course filled with the electrolyte. Therefore, the cathode and the elongate article of aluminum are electrically connected by the electrolyte through the liquid-permeable material. A voltage is impressed on the cathode and the elongate article of aluminum under such condition, whereby the surface of the aluminum is oxidized by anodic oxidation.

The present invention will be described in further detail hereunder with reference to the accompanying drawings, in which:

FIG. 1 is a cross-sectional view illustrating an embodiment of the present invention;

FIG. 2 is a cross-sectional view illustrating another embodiment of the invention;

FIG. 3 is a cross-sectional view illustrating still another embodiment of the invention, in which a plurality of the electrolytic units shown in FIG. 1 and cooling sections are arranged alternately;

FIG. 4 is a perspective view, partially in section, of another form of the cathode device shown in FIG. 1; and

FIGS. 5 and 6 are perspective views of still other forms of the cathode device, which are adapted for the anodic oxidation of aluminum wires, respectively.

Referring first to FIG. 1, there is shown in cross-section an electrolytic unit for practicing the method of this invention. The term "electrolytic unit" as used herein refers to a unit by which anodic oxidation is effected and which includes aluminum to be oxidized, a cathode device and an electrolyte. In the arrangement of FIG. 1 reference numeral 1 designates inlet ports through which the electrolyte is continuously fed into the cathode device by a pump 10 or from a tank (not shown) disposed above said cathode device. Reference numeral 2 designates a cathode-constituting electrode plate and a lead 3 thereof is connected to one terminal of an anodic oxidation power source (not shown). Reference numeral 4 designates the electrolyte filling the interior of the cathode device, and 5 designates a liquid-permeable material constituting one side of the cathode device. The liquid-permeable membrane 5 serves as a discharge port 6 for the electrolyte. Reference numeral 7 indicates the electrolyte discharged from the cathode device through the liquid-permeable material 5, which constantly fills the space formed between an aluminum 8 to be treated and the cathode device. As described above, the cathode device is composed of the inlet ports 1 for the electrolyte, the cathode 2 and the

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liquid-permeable material 5 constituting the discharge port for the electrolyte.

The electrolyte first flows into the cathode device through the inlet ports 1 as indicated by the arrows and then towards the discharge port 6 to be discharged from the cathode device through the liquid-permeable material 5. The aluminum 8 to be treated is continuously passed in front of the liquid-permeable material 5 in the direction of the arrow or in an opposite direction, with a predetermined interval therebetween. Therefore, the electrolyte 7 discharged through the liquid-permeable material 5 flows down along the surface of the aluminum. As a result, a current flows between the cathode and the aluminum through the electrolyte and the surface of the aluminum is oxidized by anodic oxidation. The electrolyte which has been used for the electrolysis reaction while filling the space between the aluminum and the cathode device, immediately flows down into a tank 9 disposed below the liquid-permeable material 5, cooled in said tank and again fed into the cathode device through the pump 10.

The apparatus of FIG. 1 is adapted for anodic oxidation of only one side surface of the aluminum. Where both side surfaces of the aluminum are desired to be oxidized by anodic oxidation, this can be attained simply by providing another apparatus of the same construction on the opposite side of the aluminum.

As will be clearly understood from the foregoing description, since the electrolyte discharged from the cathode device is used for electrolysis while flowing downwardly and the aluminum is moving per se, in no case is the electrolyte allowed to remain stationary at any point on the aluminum. Therefore, the heat generated on the film-forming surface of the aluminum can quickly removed therefrom, and hence yellowing of the film hardly occurs in the method of this invention.

Although many materials are used for the liquid-permeable material which covers the discharge port for electrolyte, an acid-resistant metal screen, an ethylene tetrafluoride fabric or a polypropylene fabric is suitably used. The mesh of the liquid-permeable material is selected case by case within the range of 0.01–1 mm., in relation with the desired rate of discharge of the electrolyte.

By using the cathode device described above, various anodic oxidation methods can be considered, besides the one described above. The first one of these methods is to pour a cooling liquid onto the surface of the aluminum opposite to the surface on which an oxide film is being formed, so as to enhance the cooling effect of the surface being subjected to anodic oxidation. This arrangement is shown in FIG. 2 in cross-section. In FIG. 2, reference numeral 11 designates the cathode devices by which both surfaces are oxidized by anodic oxidation respectively and each of which forms an electrolytic unit together with the aluminum 8 and the electrolyte 7. Reference numeral 12 designates a cooling liquid poured onto the surface of the aluminum opposite to the surface being subjected to anodic oxidation, to cool the electrolytic unit. In this method also, one or a plurality of the cathode devices are provided on one side of the aluminum where only one side of the aluminum is desired to be oxidized, or on each side of the aluminum where both sides of the aluminum are desired to be oxidized. The cooling liquid is poured at each electrolytic unit.

The second method is to provide the electrolytic units and the cooling units alternately for the purposes of enhancing the cooling effect of the electrolytic units and forming cracks in the oxide films formed by anodic oxidation. This arrangement is shown in FIG. 3 in cross-section. In FIG. 3, reference numeral 11 designates the cathode devices, 14 the cooling units for ejecting a cooling liquid against the aluminum 8 to cool the latter, and 4 the electrolyte in the respective cathode devices. The cooling liquid serves, not only to cool the aluminum but also to form cracks in the oxide films formed. Namely, by rapidly cooling the surfaces of the aluminum which is heated to an

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elevating temperature by anodizing reaction, cracks are formed in the oxide films formed thereon, due to thermal stress. In this case, the greater the numbers of the electrolytic units and the cooling units, the greater the number of cracks formed, and oxide films excelling in flexibility can be obtained.

The third method is to create an electrolyte temperature difference between adjacent ones of two or more electrolytic units provided along the direction of travel of the aluminum, for the purpose of forming cracks in the oxide films formed on the surfaces of the aluminum. In the process of electrolysis, a large amount of heat is generated on the surfaces of the aluminum being subjected to electrolysis, and hence the aluminum substrate and the oxide films formed thereon are elevated to a considerably high temperature. If, in this case, a temperature difference is created in the electrolyte in the respective electrolytic units, cracks are formed in the oxide films due to thermal stress. These cracks are useful for improving the flexibility of the oxide films.

On the other hand, the construction and shape of the cathode device are widely variable. FIG. 4 is a perspective view, partially shown in section, of a cathode device which is particularly advantageous in providing a uniform current distribution in the treatment of a band-shaped aluminum. In FIG. 4, reference numeral 22 designates a cathode, 1 inlet ports for feeding the electrolyte into the cathode device therethrough, 5 the liquid-permeable material covering the discharge port of the cathode device, 8 a band-shaped aluminum to be treated, 21 an insulating material constituting a part of the cathode device, and 25 a liquid-permeable material for further enhancing the uniformity of current distribution in both vertical and horizontal directions. The width of the cathode is equal to or smaller than the width of the aluminum to be treated and the vertical length thereof is shorter than the vertical length of the electrolyte discharge port. The front surface of the cathode is corrugated, so as to increase the effective area thereof. On the inside or outside of the liquid-permeable material at the electrolyte discharge port of the cathode device are provided the other liquid-permeable material for contact with the longitudinally spaced edge portions and the opposite edge portions of the aluminum, so as to avoid concentration of current to the longitudinal and transverse edges of the aluminum due to the edge effect of electric current.

FIG. 5 and 6 are perspective views of cathode devices respectively which are most adapted for anodic oxidation of aluminum wires. Referring first to FIG. 5, the cathode device shown in a double-walled cylindrical body having an inner wall consisting of a liquid-permeable material 5 and an outer wall consisting of a metal plate 2 which constitutes a cathode. The inner and outer walls are connected at the upper and lower edges thereof by annular metal plates which serve as cathode, or other material as at 20, so as to define an annular space between the inner and outer walls, and electrolyte inlet ports 1 are provided on the upper annular plate 20. An electrolyte introduced into the cathode device through the inlet ports 1 is ejected towards an aluminum wire 8 to be treated, through the liquid-permeable material 5. Thus, the aluminum wire 8 is oxidized by anodic oxidation, while continuously moving in the direction of the arrow. The electrolyte 7 is continuously ejected through the liquid-permeable material 5 and drops down under gravity, so that the heat is removed from the electrolytic unit highly efficiently. The ring shape of the cathode is advantageous in providing a uniform electric field for the aluminum wire, and makes a great contribution to the improvement in uniformity of the oxide film formed. Turning now to FIG. 6, there is shown a cathode device of the same type as that of FIG. 5 but the inner wall thereof consists of the metal plate or other material and the outer wall thereof consists of the liquid-permeable material. Aluminum wires 8



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are oxidized by anodic oxidation during their passage along the surface of the liquid-permeable material.

Now, the present invention will be further illustrated by way of examples thereof.

#### EXAMPLE 1

Both surfaces of an aluminum strip, having a thickness of 0.3 mm. and a width of 85 mm., were continuously oxidized by anodic oxidation, by the method shown in FIG. 1. The cathode device was provided on each side of the aluminum strip. The height an width of the electrolyte discharge port of the cathode device were 50 mm. and 120 mm. respectively, and the dimensions of the cathode were the same. A stainless steel was used for the cathode and a 0.3 mm. mesh polypropylene fabric for the liquid-permeable material covering the electrolyte discharge port. The interval between the aluminum strip and the cathode was 5 mm. A 30 weight percent sulfuric acid solution was used as electrolyte and the temperature thereof was maintained at 30° C. by a cooling device. The electrolyte was supplied into the cathode device at the rate of 40 l./min. The anodic oxidation was carried out at a current density of 200 a./dm.<sup>2</sup> by continuously conducting a quantity of electricity at the rate of 0.5 ah./dm.<sup>2</sup>. As a result, a uniform oxide film having a thickness of 6.3μ was formed over the entire area of both surfaces of the aluminum strip.

#### EXAMPLE 2

A continuous anodic oxidation was conducted, using the method illustrated in FIG. 2. The aluminum strip, the cathode and the electrolyte used were the same as those mentioned in Example 1. The sulfuric acid solution used as the electrolyte, was concurrently used as the cooling liquid at the same temperature. The cooling liquid discharge port was formed in a rectangular shape so that it may be ejected uniformly against each side of the aluminum strip.

During the anodic oxidation, the direct current was supplied to give a quantity of electricity at the rate of 0.5 ah./dm.<sup>2</sup> and the current density was varied from 200 to 600 a./dm.<sup>2</sup>. An excellent oxide film having a thickness of 6.3μ and a dielectric breakdown voltage of 220 v. A.C. was formed by anodic oxidation in the current density range up to 560 a./dm.<sup>2</sup>.

#### EXAMPLE 3

An anodic oxidation of an aluminum wire having a diameter of 0.6 mm. was carried out continuously, using the cathode device shown in FIG. 5. Lead was used for the cathode and a polypropylene fabric was used for the liquid permeable material at the electrolyte discharge port. The inner diameter of the cathode device was 15 mm. and the outer diameter thereof was 80 mm. An electrolyte consisting of 30 weight percent sulfuric acid solution was supplied to the cathode device by means of a pump, and the temperature thereof was maintained at 30° C. The anodic oxidation was conducted at the supply rate of a quantity of electricity of 0.5 ah./dm.<sup>2</sup> and a current density of 600 a./dm.<sup>2</sup>, and a uniform, excellent oxide film having a thickness of 8μ was obtained.

As may be clearly understood from the foregoing description, when a continuous anodic oxidation of an elongate article of aluminum by the method of this invention, the heat generated at the area of electrolysis incident to the anodic oxidation reaction can be efficiently removed and anodic oxidation can be attained at a high speed. Therefore, the so-called yellowing of the film can be completely avoided, even under electrolysis at a high

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current density. Thus, a high speed electrolysis becomes possible and also the size of the anodic oxidation apparatus can be reduced, since the method of the instant invention does not require a large electrolytic cell.

It is also to be noted that, by practicing the method of this invention, an oxide film of improved flexibility can be obtained because cracks can be formed in the film only by the anodic oxidation treatment.

Thus, the present invention is of great industrial advantage.

What is claimed is:

1. A continuous anodic oxidation method for aluminum, comprising continuously feeding a sulfuric acid solution into a device consisting of a hollow container having a cathode, at least one inlet port, a discharge port, and a liquid-permeable material covering said discharge port, through said inlet port and discharging the same from said discharge port through said liquid-permeable material at a rate of about 0.67 l./cm.<sup>2</sup>/cm.<sup>2</sup>/min.: passing band- or rod-shaped aluminum along the surface of said liquid-permeable material in opposed relation thereof; and impressing a voltage across said cathode and said aluminum at a current density of about 200-600 amps/m.<sup>2</sup> at about 30° C., whereby the surface of said aluminum is oxidized by anodic oxidation.

2. A continuous anodic oxidation method for aluminum according to claim 1 wherein said device is provided on one side of said aluminum band and cooling liquid is poured onto the surface of the aluminum band opposite to the surface of same facing said device.

3. A continuous anodic oxidation method for aluminum according to the method of claim 1 wherein two of said devices are provided, one on each side of said aluminum band at points removed from each other so that said two devices are not opposed to each other.

4. A continuous anodic oxidation method for aluminum, as defined in claim 1, wherein a plurality of said devices and a plurality of cooling liquid pouring devices are arranged alternately on at least one side of the aluminum along the direction of travel of the aluminum.

5. A continuous anodic oxidation method for aluminum, as defined in claim 1, wherein at least one device which discharges the electrolyte at a relatively high temperature and at least one cathode device which discharges the electrolyte at a relatively low temperature are alternately arranged along the direction of travel of the aluminum.

6. A continuous anodic oxidation method for aluminum according to claim 1 wherein said discharge port is in the side of said container and said band- or rod-shaped aluminum is passed vertically along the surface of said liquid-permeable material in opposed relation thereto.

7. A continuous anodic oxidation method according to claim 1 wherein said liquid-permeable material is an acid-resistant metal screen, an ethylene tetrafluoride fabric or a polypropylene fabric having a mesh size of from 0.01 to 1 mm.

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U.S. Cl. X.R.

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