

[54] **PROCESS FOR CONTINUOUSLY
ANODIZING ALUMINUM**

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[58] **Field of Search** 204/28, 211, 267, 269,
204/58, 42

[56] **References Cited**

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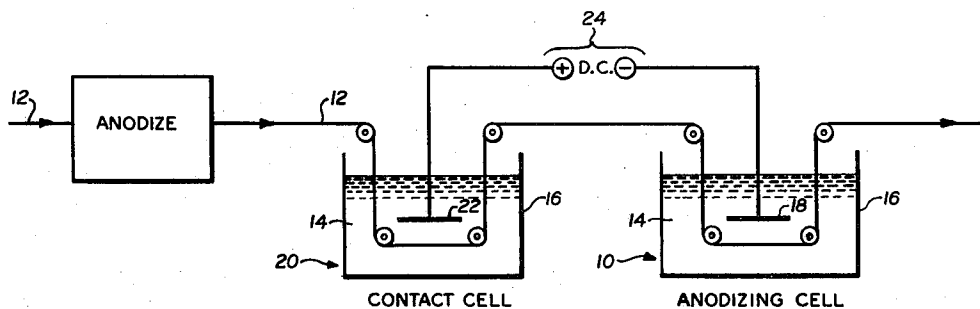
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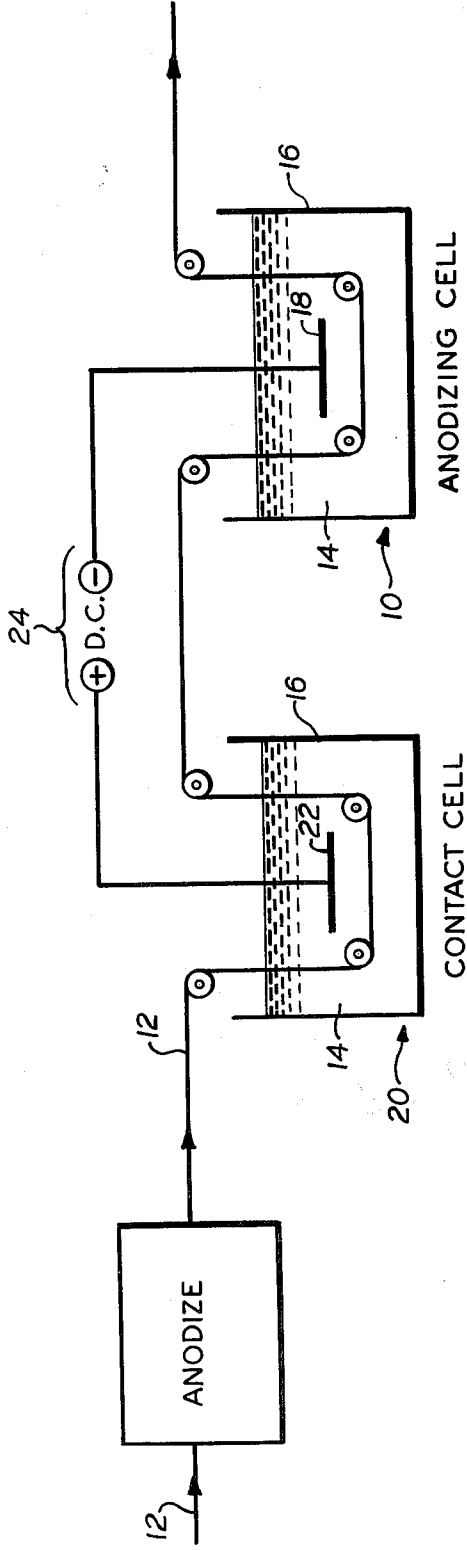
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ABSTRACT

Aluminum is continuously anodized using direct current in an anodizing cell which is preceded by a cathodic contact cell having an anode connected to a source of direct current. The aluminum already has an anodized oxide coating formed thereon before entering the contact cell and direct current is introduced into the already anodized aluminum in the contact cell for further anodizing the already anodized aluminum.

4 Claims, 1 Drawing Figure





PROCESS FOR CONTINUOUSLY ANODIZING ALUMINUM

RELATED APPLICATIONS

This application is a continuation-in-part of co-pending application Ser. No. 361,720 filed May 18, 1973, now U.S. Pat. No. 3,865,700.

BACKGROUND

This invention relates to a process for continuously anodizing aluminum. The term aluminum is used herein to include aluminum base alloys which, like pure aluminum, can be electrolytically anodized to form oxide coatings. More particularly, this invention relates to a technique for continuously anodizing coils or lengths of aluminum, such as aluminum sheets, strips, wire, rods, shapes and the like (hereinafter collectively referred to as aluminum web), by introducing anodizing direct current via a cathodic contact cell into an aluminum web passing therethrough which already has an oxide coating formed thereon.

The direct current is picked up in the cathodic cell by the already anodized web and is transferred therealong in the direction of movement of the web to an anodizing cell where a further oxide coating is formed.

Aluminum and aluminum base alloys in sheet, strip and wire form have been continuously anodized by a number of techniques for many years. Such anodized products are used for electrical and decorative purposes, in the manufacture of household appliances, automotive trim, building materials, farm equipment, furniture, sporting goods, cans, container closures, lithographic plates, transformers, and in many other market and product areas.

Two basic techniques are used to introduce current into a moving aluminum web. The first involves the use of a contact roll or bar and the second is an electrochemical technique utilizing a cathodic contact cell.

The contact roll or bar technique suffers from many deficiencies. For example, the aluminum web must be dry to avoid electrolysis which, if it occurs, dissolves the contact roller or bar anodically leaving pits in the surface thereof. Another problem is arcing between the two surfaces as they become separated which is brought about by the presence of edge burrs or slivers of aluminum on the web surface itself. Arcing causes pitting of the aluminum as well as pitting and oxidation of the contact member itself.

When using the cathodic contact cell technique, one of the limits on how much current can be introduced into the web is the fact that all of the current has to be introduced into a single cross-sectional area of the moving web. This causes a surge of current into the unanodized web which is unprotected by an oxide coating and tends to cause burning resulting in the formation of unsound oxide coatings. Up to now, the problem of arcing in the use of a solid contact member and the problem of burning due to a solid contact member, and the problem of burning due to a surge of current in the contact cell technique, have been accepted as inherent limitations in the continuous anodizing of aluminum it was thought that all of the current for the anodizing operation had to be picked up by the unanodized moving web in one pass. Behind this thinking is the fact that an anodic oxide coating formed in an anodizing operation is an electrical insulator and because of this further an-

odizing through the oxide coating was thought to not be possible.

The present invention now makes it possible to introduce anodizing current into more than one cross-section of a moving aluminum web.

SUMMARY

The present invention provides an improvement in a process for continuously electrolytically anodizing aluminum web. The direct anodizing current is introduced into the aluminum web in a cathodic contact cell, the web having an anodized oxide coating formed thereon before entering the contact cell.

Stated differently, the process of the invention for continuously electrolytically anodizing aluminum web first involves continuously anodizing an aluminum web using conventional techniques, preferably by a contact cell system, and then continuously passing the already anodized aluminum web into a cathodic contact cell having an anode connected to a source of direct current, thereby introducing anodizing direct current into the already anodized aluminum web in the contact cell for further anodizing the already anodized aluminum web. Preferably, the contact cell has a second anode connected to a second source of direct current and the unanodized aluminum web is continuously passed into a preceeding anodizing cell having a cathode connected to the second source of direct current. In this embodiment, anodizing direct current is introduced into two cross-sections of the web in the same contact cell for the preceeding initial anodizing treatment and the succeeding further anodizing treatment.

DESCRIPTION OF THE DRAWING

The present invention will be more fully understood from the following description taken in conjunction with the accompanying drawing which is a schematic flow diagram illustrating the features of the invention.

DESCRIPTION

The present invention makes it possible to introduce anodizing current into a moving aluminum web into more than one cross-section thereof where the web already has at least some protective oxide layer formed thereon. This can be accomplished by using a cathodic contact cell, in which the aluminum web is cathodic, between two anodizing cells in which the aluminum strip is anodic, or by utilizing a multiplicity of contact-anodizing cells in which the aluminum web is alternatively negative or positive. When utilizing the preferred embodiment of the cathodic contact cell between two anodizing cells, the current introduced into the contact cell will travel in both directions thus effectively doubling the current carrying capacity of the moving aluminum web.

Referring now to the drawing, the process and apparatus for continuously electrolytically anodizing aluminum web 12 includes conventional anodizing using a contact roll/anodizing cell, a contact cell followed by an anodizing cell, or the reverse, an anodizing cell followed by a contact cell as described in my U.S. Pat. No. 3,865,700 where the web is anodized by the action of direct current introduced in the preceeding contact cell. Next comes a contact cell indicated generally by reference numeral 20 followed by an anodizing cell indicated generally by reference numeral 10. Each cell includes a suitable tank member 16 for containing an electrolyte 14. The anodizing cell 10 has a cathode 18

therein connected to a source of direct current 24. The contact cell 20 has an anode 22 therein which is connected to the same source of direct current 24. The aluminum web 12 with an already formed anodized coating thereon continually passes through the contact cell 20 followed by the anodizing cell 10 with the aid of conventional guide rollers positioned as shown.

The anodizing direct current is introduced into the web 12 in the contact cell 20. The web 12 has an anodized oxide coating already formed thereon before entering the contact cell 20 and the direct current introduced into the web 12 in the contact cell 20 produces further anodizing in cell 10.

In a preferred embodiment a second anodizing preceeds contact cell 20. The second cell contains a cathode connected to a second source of direct current. The contact cell contains a second anode which is connected to the same second source of direct current. By utilizing a contact cell between two anodizing cells, the direct anodizing current introduced into the contact cell from the two separate sources of direct current travels in both directions thus effectively doubling the current carrying capacity of the moving aluminum web 12. Thus, anodizing current is introduced into the web in the center contact cell 20 from one current source which flows in a direction opposite to the direction of movement of the web into the preceding anodizing cell wherein an initial portion of the oxide coating is formed. The anodizing operation is continued in the second anodizing cell by anodizing current from a second source which is picked up by the already anodized strip 12 in the contact cell and is transmitted there along to the second anodizing cell. The web from the second anodizing cell with a given thickness of oxide coating formed thereon and if desired, further anodizing can be carried out in accordance with the invention in a succeeding contact cell/anodizing cell set up as shown in the drawing and so on.

With respect to the basic embodiment shown in the drawing, the invention can be carried out by passing aluminum web 12 through two or more successive pairs of contact cell 20 followed by anodizing cell 10.

As is well known in the art, the aluminum web 12 can be cleaned, de-greased or otherwise pretreated using conventional techniques before anodizing and after anodizing, it can be sealed, dyed or otherwise post-treated using known techniques. The web 12 is passed through

EXAMPLE 1

Aluminum samples were anodized in the sulfuric acid electrolyte at constant electrolyte concentration and temperatures. DC voltage breakdown values were determined and are summarized in Table 1 below:

TABLE 1

CURRENT (in amps)	Time ANODIC (sec.)	Time CATHODIC (sec.)	VOLTAGE BREAKDOWN (volts DC)
25	60	—	380
25	60	60	380
25	60	30	380
25	30	—	290
25	30	30	290
25	30	15	290
20	20	20	220

The results of this Example indicate that reversing the polarity, or passing current through an oxide coating, has no detrimental or adverse effect on the anodized oxide coating. This is indicated by the DC voltage breakdown values which are identical for samples which were subjected to cathodic time and for samples which were not so subjected to cathodic time.

EXAMPLE 2

Triple sets of aluminum samples were prepared and all were anodized for the same period of time and at the same current density. Set number 1 was anodized only. Set number 2 was anodized and allowed to sit in the electrolyte while the polarity was reversed (samples Cathodic). Set number 3 was anodized and allowed to sit in the anodizing electrolyte without applying any current. For all three sets the anodizing time, the time the polarity was reversed and the time the anodized samples were allowed to sit in the electrolyte was the same.

All of the samples were sealed in boiling water. The weight of the oxide coating formed were determined by first weighing the sample and then stripping off the oxide coating by soaking in a hot chromic-phosphoric acid solution and thereafter re-weighing the sample. The difference in weight divided by the total area of the sample gives the milligrams per square inch of oxide coating on the original sample. The results are summarized in Table 2.

TABLE 2

TIME (sec)	CURRENT DENSITY (a/ft ²)	ACTUAL CURRENT (amps)	VOLTAGE (volts)	"RE- VERSED" VOLTAGE (volts)	TEMP. (°C)	WEIGHT OF SET NO. 1 (mg/in ²)	WEIGHT OF SET NO. 2 (mg/in ²)	WEIGHT OF SET NO. 3 (mg/in ²)	%WEIGHT LOSS BETWEEN SET 1 and 2
150	40	15.5	16	2	30	5.57	5.45	5.21	2
150	40	15.5	13	2	40	5.09	4.62	4.67	9
150	40	15.5	10	2	50	4.56	2.94	3.09	33

the anodizing operation of the invention using conventional winding and feeding equipment.

The present invention will be more fully understood from the following examples which are not intended to limit or otherwise restrict the invention in any way. In the examples, 4 × 8 inch sheets were employed. In all of the examples both sides of the aluminum sheets were anodized and the electrolyte concentration was 230 grams per liter of aqueous sulfuric acid.

This example illustrates that there is very little difference in the weight of the oxide coating between samples where the polarity was reversed and samples where the anodized samples were allowed to soak in the anodizing electrolyte. This indicates that the loss in oxide weight is due primarily to solvent action of the electrolyte and is not attributable to the passage of current through the coating when the polarity is reversed and the samples are cathodic. In evaluating the data of Table 2 it should be pointed out that the solvent action of the anodizing electrolyte is increased as the tempera-

ture increases which accounts for the greater loss in oxide weight at the tests run at higher temperatures.

EXAMPLE 3

Aluminum samples were anodized following three steps:

1. The sample was anodized at 40°C. at a current density of 50 a/ft² for a specific length of time.

2. With the current density remaining at 50 a/ft², the polarity was reversed making the sample cathodic while varying in temperature and time.

3. The aluminum sample was again anodized at 40°C. at a current density of 50 a/ft² for a specific length of time.

Control samples were anodized at 40°C. at current density of 50 a/ft² for a period of time equalling the total time in steps 1 and 3. Step 2 was eliminated.

All samples in this Example were sealed in hot water and the oxide coating weights were determined as described in Example 2. The data are summarized in Tables 3 and 4 below:

TABLE 3

TIME STEP 1 (sec)	VOLTAGE STEP 1 (volts)	TIME STEP 2 (sec)	VOLTAGE STEP 2 (volts)	TEMP STEP 2 (°C)	TIME STEP 3 (sec)	VOLTAGE STEP 3 (volts)	TIME STEP 1 & 2 (sec)	SAMPLE COATING WEIGHT (mg/in ²)	CONTROL COATING WEIGHT (mg/in ²)	% WEIGHT LOSS OF SAMPLE
54	13.5	48	2	60	66	13	120	4.488	4.946	9.26
54	13.0	48	2	50	66	13	120	4.496	4.804	6.41
54	13.0	48	2	40	66	13	120	4.867	5.013	2.90
54	13.0	48	2	40	66	13	120	4.788	4.875	1.78
108	13.5	96	4	60	132	13	240	7.229	9.229	21.67
108	13.5	96	2	50	132	13	240	8.179	9.329	12.32
106	13.0	96	2	40	132	13	240	8.558	2.279	7.77

TABLE 4

TOTAL AMPERE— MIN	TEMP STEP 2 (°C)	WEIGHT OF SAMPLE (mg/in ²)	WEIGHT OF CONTROL (mg/in ²)	% WEIGHT LOSS OF SAMPLE vs. CONTROL
100	60	4.488	4.946	9.26
100	50	4.496	4.804	6.41
100	40	4.788	4.875	1.78
100	40	4.867	5.013	2.90
200	60	7.229	9.229	21.67
200	50	8.179	9.329	12.32
200	40	8.558	9.279	7.77
320	60	8.304	13.942	40.43
320	50	10.729	14.025	23.50
320	40	12.817	13.984	8.34

Note:

Ampere — min. = time anodized × current density.

C.D. = 50 a/ft²

Anodizing Temperature = 40°C.

It is known that anodic oxide requires a forming voltage of somewhere between 12 and 13 volts (cf. *Finishing Of Aluminum*, Wernick and Pinner). The foregoing Examples demonstrate that when the polarity is reversed and the anodized aluminum samples are made the negative or cathodic pole of the cell, the anodized samples exhibit an unusual phenomenon and at the same current density used to anodize, the voltage drops to between 1 and 2 volts. Only minor heat is generated by resistance and there is practically no weight loss as demonstrated herein. This unique property makes it possible to continue to introduce or feed current into the aluminum web at portions where the anodic oxide coating has already been formed. By using this technique, it now becomes possible to continuously DC anodize aluminum webs without the limitations imposed

by the contact roll method or the standard contact cell method where all of the current is introduced in one pass through a single cross-section of the web.

In an alternated embodiment the process of the invention for further anodizing an aluminum web already having an anodized oxide coating thereon includes passing the already anodized aluminum web through a cathodic contact cell under conditions of temperature, time and electrolyte concentration (as demonstrated by the foregoing examples) such that the weight loss does not exceed 50%. Preferably the weight loss is not greater than 10–15% by weight. In this manner the process of the invention increases the weight of the finished anodized coating on the aluminum web. Weight loss can be described as the reduction in overall weight per unit of area and is the result of the solvent effect of the electrolyte on the anodized coating itself. In carrying out the process of the invention weight loss due to solvent action is tolerated and is offset by the greater increase in the quantity, that is, thickness in weight of the finished anodized coating.

The initial anodizing can be carried out as mentioned previously in an anodizing cell preceded by a contact roll or a contact cell for purposes of introducing the anodizing current into the web. The present invention in effect starts in a contact cell with the web entering same having an already formed anodized coating thereon. The process of the invention can be duplicated as many times as desired using successive pairs of contact cells followed by an anodizing cell. It is important to note that the initial contact cell utilized in the process of the invention is not electrically connected to the initial anodizing step which applies an anodized oxide coating to the unanodized aluminum web.

It should also be noted that the preferred embodiment described above involving an anodizing cell followed by a second anodizing cell can be carried out

with an anodizing section and a contact section contained in the same tank so long as there is sufficient spacing between the respective electrodes for each section.

German Auslegeschrift 1,005,191 describes apparatus for forming etched anodes for electrolytic condensers. The anode foil is anodized or formed while it passes through a forming bath. In the first portion of the bath, up-forming cathodes are used whose distance from the foil diminishes in the direction of passage as the coating is increasingly built up, such that, at constant forming current density, the sum of the inverse voltage increasing with the coating density and the voltage drop which diminishes in the direction of passage, remains always constant in the forming electrolyte along the forming cathodes. A down-forming section follows the up-forming section and serves to densify the coating produced in the up-forming section. Shielding electrodes are also utilized to de-gas the anode foil without any potential drop in the electrolyte. The foil already has a positive charge when it enters the forming bath. After the up-forming section the foil is de-gased and the coating produced is densified. This publication is thus limited in its forming voltage. Stated differently, this publication is limited to the introduction of current through one cross-section of the foil before it enters the forming bath. Subsequent de-gasing and densifying sections do not introduce any further current into the foil. This is in contrast to the present invention which makes it possible to introduce anodizing current at a successive plurality of cross-sections in the web, each with an anodized coating already formed thereon, as described in greater detail herein.

In the alternate embodiment wherein conditions of temperature, time and electrolyte concentration are such that weight loss does not exceed 50%, when using aqueous sulfuric acid electrolyte, the concentration

can range from about 100 to 350 grams per leader. Temperatures can range from about 20°C to about 60°C and anodizing times can run from about 20 seconds to about 5 minutes. Similar conditions will be employed with other anodizing acids such as phosphoric acid, oxalic acid, chromic acid and the like. In each instance anodizing time and temperature will depend on the concentration and conductivity of the aqueous acid electrolyte.

What is claimed is:

1. In a process for continuously electrolytically anodizing aluminum, the improvement which comprises introducing anodizing direct current into said aluminum in a cathodic contact cell, said aluminum having an anodized oxide coating formed thereon before entering said cell.

2. Process for continuously electrolytically anodizing an already anodized aluminum web comprises continuously passing said web through a cathodic contact cell having therein an anode connected to a source of direct current, continuously passing said web from said contact cell into an anodizing cell having therein a cathode connected to said source of direct current thereby introducing anodizing direct current into said web in said contact cell and further anodizing said web.

3. Process for further anodizing an anodized aluminum web which comprises passing said anodized web through a cathodic contact cell and an anodizing cell under conditions of temperature, time and electrolyte concentration such that the weight loss of the anodized web leaving the anodizing cell does not exceed 50% thereby increasing the weight of the anodized coating on said web.

4. Process of claim 3 wherein the weight loss is from about 10 to about 15%.

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Disclaimer

3,920,525.—*Howard A. Fromson*, Weston, Conn. PROCESS FOR CONTINUOUSLY ANODIZING ALUMINUM. Patent dated Nov. 18, 1975.
Disclaimer filed Jan. 24, 1977, by the inventor.

Hereby enters this disclaimer to claim 1 of said patent.

[*Official Gazette March 8, 1977.*]

Dedication

3,920,525.—*Howard A. Fromson*, Weston, Conn. PROCESS FOR CONTINUOUSLY ANODIZING ALUMINUM. Patent dated Nov. 18, 1975. Dedication filed Oct. 29, 1979, by the inventor.

Hereby dedicates to the Public the entire remaining term of said patent.
[*Official Gazette January 22, 1980.*]