United States Patent Office 2,855,351 Patented Oct. 7, 1958

2,855,351

PROCESS FOR ELECTROLYTICALLY PRODUCING OXIDE COATING ON ALUMINUM AND ALUMINUM ALLOYS

Robert Ernst, Los Angeles, Calif., assignor to Sanford Process Co., Inc., Los Angeles, Calif., a corporation of California

No Drawing. Application September 20, 1954
Serial No. 457,315

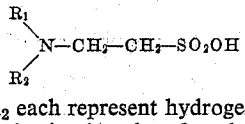
25 Claims. (Cl. 204—58)

This invention relates to the production of hard, wear and corrosion resistant aluminum oxide films on aluminum and aluminum alloys by electrolytic oxidation of the aluminum and the aluminum alloys.

As is well known in this art the anodic oxidation of aluminum to create oxide films in acid electrolytes, such as chromic acid, sulphuric acid, or oxalic acid, now generally employed, is limited to the production of thin films of oxide. Such films may not practicably be in excess of about .001" in thickness. The denseness of these films is also of moderate nature, being porous, especially when approaching in thickness the dimension of .001". An additional limitation lies in the fact that the processes of the prior art are limited to certain only of the aluminum alloys. Thus it has been reported that alloys containing high percentages of copper and/or silicon will not produce dense coatings of uniform thickness by such prior art processes. Further, in such prior art process, contamination of the bath by copper and iron ions materially affects the utility of the bath, and when such ions appear the current density must be substantially increased and soon reaches an impracticable value such as to result in corrosion, i. e. burning of the part being oxidized, and the bath must be discarded.

The process of my invention is capable of making thicker, denser and harder oxide coatings on aluminum and aluminum alloys than prior art processes known to me, and also produces thick, dense, hard oxide coatings on aluminum alloys which prior art processes are incapable of coating and is substantially insensitive to the presence of copper and iron ions in the bath. The current density at comparable voltage is not affected in the process of this invention by the presence of copper or iron ions in the electrolyte bath. Improved bonding of the oxide coating to the metal is also obtained, and the coating is deposited more rapidly than heretofore in prior art processes.

I have discovered that by employing as an additive to the electrolyte bath certain ampholytic substances, that is, substances having a positive and negative charge in the same molecule, I can produce the unique results of my invention. The ampholytic substances found suitable according to the invention are compounds which derive their positive charge from an amino or substituted amino group, and their negative charge from the $—SO_2OH$ group. I have found that effective substances of the above class are, for example, taurines (2-aminoethane sulfonic acid compounds) of the general formula



where R_1 and R_2 each represent hydrogen, or an alkyl or cycloalkyl group having less than 8 carbon atoms. Thus, for example, R_1 and R_2 may both be hydrogen or both may be alkyl or both cycloalkyl, or R_1 can be hydrogen and R_2 alkyl or cycloalkyl, or R_1 can be alkyl and R_2 cycloalkyl. Also, R_1 and R_2 includes the alkyl or cycloalkyl group which is further substituted, for example, by an aromatic radical. Illustrative examples of compounds which may be used are N-methyl, N-ethyl, N,N-dimethyl and N,N-diethyl taurine; N-isobutyl, N-isoamyl, N-benzyl, N-cyclohexyl, N,N-diisoamyl and N,N-dicyclohexyl taurine. The preferred compound is N-methyl taurine.

I prefer to employ those compounds within the general formula which are derived from amines having an ionization constant greater than 10^{-6} for my purposes. Examples of such amines and their ionization constants are noted below:

Methyl amine	5×10^{-4}
Isobutyl amine	3.1×10^{-4}
Isoamyl amine	5.0×10^{-4}
Benzyl amine	2.4×10^{-4}
Diisoamyl amine	9.6×10^{-4}
Cyclohexyl amine	10^{-4}

Further, I can use compounds wherein the negatively charged group of ion $—SO_2OH$ can be attached to a propyl group instead of to the ethyl group noted in the general formula above, these compounds being substantial equivalents for my purpose.

Generally, a minor amount of these compounds, either alone or in combination, is utilized. Thus, concentrations of the said additives of as little as .02 mol per liter of electrolyte solution can be used in my process, the amount preferably employed being in the approximate range of .02 to .10 mol per liter or electrolyte solution. Larger amounts can be used, if desired, but without any marked advantage. The compounds employed according to the invention are soluble in the electrolytic solution within the above range of concentration. The amount of my additive employed in a particular case depends, for example, on the type and amount of alloy being oxidized, its surface area, the thickness of oxide coating desired, etc.

My compounds may be employed either as the free sulfonic acid compound or in the form of a salt of the acid which is soluble in the electrolyte, such as the sodium or potassium salt. Thus, for example, I can use either

$CH_3—NH—CH_2CH_2—SO_2OH$ or
$CH_3—NH—CH_2CH_2SO_2ONa$

I have found that by employing my additive in the electrolyte bath I can operate at higher voltages than is used by the prior art and consequently I may increase the thickness of the oxide coat and increase the rate of growth of the coating.

I have also found that by reducing the temperature of the electrolyte solution containing my additive, I obtain better results than by operating with such solution at normal temperature. Hence, I prefer to carry out practice of my invention at reduced temperature although it is to be understood that such reduced temperature operation is not essential to my invention.

Further, I have discovered that my results are also facilitated by using a surface active compound in the electrolyte bath which is active in acid solutions, although the use of such a compound is likewise not essential.

In preparing the electrolyte I may employ any of the acids usually employed in making up the electrolyte for electrolytic oxidation of aluminum such as sulphuric acid, chromic acid, or oxalic acid or mixtures thereof. The latter acids are considered equivalents for the anodic oxidation of aluminum and its alloys, and are termed electro anodizing acids. Other acids in addition to sulphuric, oxalic and chromic acids have been suggested by the prior art for the anodic oxidation of aluminum, and those skilled in the art will understand the nature and type of such acids contemplated herein.

Thus I may use up to say about 70% H_2SO_4 in the

electrolyte, but I prefer to use dilute H_2SO_4 in an amount corresponding to a range of from about 1 part to 20 parts by volume of concentrated 100% sulphuric acid dissolved in 100 parts by volume of water. For example, I may employ an amount of H_2SO_4 in the electrolyte corresponding to from about 5 to 7% by volume of 66 Baumé sulphuric acid per 100 parts by volume of water. I then add to the bath my 2-aminoethane sulfonic acid additive in a proportion specified above.

To this aqueous electrolyte I may, but not necessarily, add an acid resistant wetting agent, usually in an amount of from 0.02% and higher, e. g. up to 1% or more, by weight of the aqueous electrolytic solution. The upper limit of the wetting agent is determined, as a practical matter, by the formation of a high froth or suds which is preferably avoided.

I may use various types of acid resistant wetting agents, especially in the form of ethers produced by reaction of ethylene oxide on alkyl phenols or alcohols. These ethers should contain a sufficiently long chain of ethylene glycol units to render the ethers soluble in acid solution. The above type wetting agents are preferred since they are resistant to hydrolysis in acid solution. A preferred wetting agent is the ether of nonyl phenol and polyethylene glycol.

The part to be coated is connected to the anode of an electrolytic cell by a wire and immersed in the electrolyte bath. Preferably, direct current is then applied until the desired thickness of coating is reached. If desired, however, an alternating current component may be added to the direct current.

The following are examples of operation according to the invention:

Example 1

A tough hard coating of oxide of aluminum having a thickness in excess of .001 inch can be produced on the high copper alloy of aluminum designated 24S and containing about 4.5% copper by applying a 44 to 48 ampere per square foot current density to a part formed from such alloy and submerged as the anode in an electrolyte composed of 12% by volume of 100% sulphuric acid in water solution to which is added about 0.02 to 0.05 mol/liter of N-methyl taurine, the temperature of the electrolyte being maintained between about 40° F. and about 50° F.

Example 2

The results of Example 1 may be substantially obtained by replacing the N-methyl taurine with taurine.

While the foregoing procedure produces satisfactory results according to the invention when employing my additive in an electrolyte maintained at a temperature as high as about 70° F., improved results are obtained by operating at low temperature less than about 55° F. The unique results of my process are improved as the temperature is lowered. I have used successfully temperatures ranging from about 34° F. to 55° F., but the preferred temperature is in the range of 34° F. to 40° F., for example, 34° F. to 36° F.

Various procedures may be employed in carrying out the electrolytic oxidation process employing my additive in the electrolyte. Thus, for example, I may carry out the process at a substantially constant current density, or I may operate at substantially constant or varying voltages. I have found that best results are realized by operating in accordance with the technique disclosed and claimed in U. S. application, Serial No. 438,349, filed June 21, 1954, by John B. Franklin.

The current is preferably applied to the electrolytic cell first at low voltage and then at rapidly increasing voltage until the desired thickness of coating is reached. Coating thickness is dependent on time and voltage. As the coating becomes thicker, its electrical resistance requires higher voltages for penetration. The higher voltages cause local heating and the heated aqueous acid, e. g. H_2SO_4, solution has greater dissolving power. By incorporating my additive in the electrolyte I can use a substantially lower concentration of H_2SO_4 than is employed in the prior art. The rapid increase of voltage at the end of the coating period produces the proper thickness quickly with little softening or solution of the aluminum oxide coating; hence harder and thicker coatings are obtained by my process than is obtainable by the prior art.

In preferred operation of my process in accordance with the technique of the above mentioned Franklin application, the voltage is gradually increased from a starting voltage determined by the resistance of the electrical circuit, to the starting voltage of the process which is in the range of from about 1 volt below the critical voltage to that determined by the resistance of the cell which may be at or below 40% of the critical voltage at which the coating starts to form. The initial or starting voltage depends on the nature of the aluminum surface or of the alloy when alloys are processed. The voltage is gradually increased, keeping the temperature low as stated above. A voltage is reached where anodic oxidation becomes observable in an amount to give a coating which is measurable by a micrometer, i. e., at least 0.0001" thick (the critical voltage). I note the current value when this occurs. At each increment of voltage or voltage step above the critical voltage the current rises as the voltage is increased. The voltage remains substantially constant for a period at each voltage step. During such period the current is at first constant for a period and then drops. This is believed caused by the growth of the oxide coating which increases the electrode resistance. When the current starts to decrease, I raise the voltage and therefore the current value, adjusting the voltage at each step to obtain approximation of the current value attained when preceptible measurable oxide coating first started to form. The voltage may be increased to give a higher current value provided care is taken to avoid a current so high as to cause a conversion, known in this art as "burning" of the part. Such a burning occurs usually in localized portions of the anode and unless voltage is adjusted to drop the current value disintegration of the aluminum anode may occur. The voltage is increased in steps adjusting the voltage increment each time to approximate the above noted current value, using the same precautions, and the current variation described above is repeated at each of these higher increments of voltage. The oxide coating increases in thickness until a point is reached where further increase in voltage acts to decrease the thickness of the coating.

If at any voltage level the amperage obtained is such as to produce burning, this burning can not be prevented by a mere reduction in voltage to a lower current value previously found safe and effective, since subsequent incremental voltage increases will not result in such safe current values but will again produce burning. In such a situation I have found that if I reduce the voltage to that at which the safe current value is obtained and add additional of my additive, I may then by incremental voltage increase attain the voltage at which burning previously occurred but now obtain a safe current value at which oxide is formed and grows. I have observed that parts previously burned as described above are recoated with a good oxide coating.

I have observed that if a light oxide coat is desired, it can be obtained about as easily while maintaining the electrolyte at 40–50° F. as at 34° F. However, if a heavy oxide coating, for example, say of .004" thickness, is desired, I prefer to maintain the temperature below about 40° F., for example, at about 34° F. If the parts to be coated have restricted areas where good circulation is not obtained, it is generally preferred to operate close to about 34° F. even where a light oxide coating is sought.

In my process I have found that aluminum and each

of its alloys has a critical voltage at which oxide deposition occures in measurable thickness. The magnitude of this critical voltage is dependent not only on the nature of the metal used, that is, aluminum or its alloys, but on the electrolyte and other factors influencing the internal and external resistance of the cell. Below this critical voltage measurable growth, that is, as available by micrometer measurement, is not observed. For each cell and each anode there is a critical voltage at which the deposit is made. This critical voltage is readily observable by visual inspection of the anode to determine the voltage at which deposit starts to form as described herein.

I have found that it is desirable to start the coating formation by adjusting the voltages from below the critical voltage up to critical voltage where coating formation is initiated. I have found that the coating will form at a lower voltage, that is, about 5 to 10% below the critical, but that in such case the time for forming the measurable coat is greatly prolonged, for example, up to 1 to 2 hours. Hence, I prefer to start my operation by producing the initial cost, that is, the first measurable coat, at a voltage value substantially equal to the critical value and not less than about 90% of the critical value.

In practical operation if the process is not initiated at the critical voltage within the limits described but at a higher voltage, for example, above 5–10% of the critical voltage, burning of the aluminum or aluminum alloy part results; that is, an actual destruction (pitting and dissolution) of the part being coated results which, if continued, could cause the part to substantially dissolve. Consequently, the practical voltage for initiation of oxide coat formation preferably should not be more than or less than about 10% of the critical voltage. I prefer to initiate the operation at at least one volt below the critical voltage of the aluminum and its alloys. But for some objects, particularly of small cross sectional area such as thin aluminum wire or thin aluminum sheets, I desire to initiate the process at at least about 5 to 10 volts below the critical voltage for aluminum.

It is noted that when a pure aluminum wire or an alloy wire of aluminum is used to connect the part to be coated with the cell bus bars, and the wire has a critical voltage less than that of the part to be coated, it is necessary to initiate the process at the critical voltage of the wire; in other words, the wire must first be anodized. If a connector wire is used which is of the same composition as the part to be anodized, or of any other composition having the same or a higher critical voltage than said part, operations can commence at a voltage closely approaching or at the critical voltage of the part to be oxidized. The operation can be also initiated at about the critical voltage of the part to be coated by using an anode connecting wire which is not attacked by the electrolyte, for example, a wire such as titanium wire or noble metal wire, or aluminum wire or other metal which is attacked by the electrolyte, plated with a noble metal such as silver or any other material to protect it against the electrolyte.

After initiating the oxidation below the critical voltage, operation is continued at any given voltage at each successive voltage step or increment of voltage above the critical for say 2 or 3 minute intervals. After each time interval the voltage is increased by an addition of an increment of voltage. Such increments of voltage may be, when close to the critical voltage, about 1 to 3 volts, but such increments may be of greater value as the oxide formation grows.

As a good operating technique the amperage during each voltage step should be permitted to drop materially, while maintaining the voltage substantially constant, to, for example, about 30% to 50% of the current value initially attained at each such voltage step after the incremental increase in voltage.

At each voltage increment after oxide formation has started the amperage should rise and start to fall after but a small interval of time within about the first 30 seconds after the voltage increment has been applied. If this phenomenon does not occur, the usual consequence is that the amperage will steadily increase, usually rapidly, and burning results. This is indicative that the voltage increment was too great, unless some mechanical or electrical failure is the cause of this rise. Thus, the voltage increment should in each case be less than that which permits such excessive current flow. For example, the voltage increment may be limited so as to establish a current value not more than about 125 to 175% of the amperage obtained when the previous voltage increment was applied, or not greater than 125–175% of the maximum amperage obtained at the critical voltage. Preferably, the voltage increment should be less than that which gives an amperage producing the burning phenomenon previously described.

Up to the critical voltage the magnitude of the voltage increments are not critical, nor is the amperage control critical as affecting the part to be coated with the oxide. As the critical voltage is approached the voltage should be changed about one or two volts at a time. Thus, the oxide coating is initiated at, for example, the critical voltage and the current value is observed during the initiation of oxide formation at such critical voltage. As oxide formation occurs the current drops. When it has dropped the degree specified above, the voltage is increased to reestablish approximately the value of the current observed at the initiation of oxide formation. I have observed as practical guide that if the current value is dropped to approximately 30% to 50% of the initial value, that a voltage increment of about 1 or 2 volts is sufficient during the early stages of oxide formation to reestablish approximately the aforementioned current value which will give good oxide coating without burning. Subsequent voltage changes are adjusted to reestablish at the initiation of each voltage step increase the amperage found safe, i. e., in order to obtain deposition without destruction of the oxide coat. The latter amperage corresponds approximately to the amperage at the critical voltage. During the latter stages of oxide formation, voltage increments of say 3 to 5 volts are usually required to approximately reestablish such current value.

The voltage may be increased according to the invention to and above 100 volts, and as high as about 130 volts, to wit, to the voltage at which the coating no longer increases thickness. During the operation, current density is generally maintained at less than 20 amps./sq. ft., generally dropping below 10 amps./sq. ft., and thus avoiding burning of the part being coated. Up to about 100 volts the growth of oxide on a particular aluminum alloy is uniform and reproducible. Above 100 volts I have found that the condition of the alloy, i. e., its porosity, grain size and density, affect the growth materially so that in many cases, similar alloys will react non-uniformly at these high voltages. Thus, while most aluminum alloys will produce a coating say of .006" thickness at 100 volts in my process, the coatings of some will increase to .010" at 130 volts, while other exactly similar alloys differently treated or handled differently in fabrication will not so improve in growth by an increase in voltage from 100 to 130 volts.

I have found that while I can produce an aluminum oxide coating up to .010 inch thickness by operating up to voltages between 100 and 130 according to my invention, coatings of a thickness greater than about .004 inch are not as dense and hard as the coatings obtained employing the invention principles and having a thickness of about .004" or less. Generally, operation at a voltage in excess of about 60 volts is required to obtain a coating of about .004" in thickness. These coatings are as uniform and as dense as a .001" coating of the same alloy produced by stopping the process at such point,

In contrast to this, alloys containing more than about 3% copper could not be coated even with a light oxide coat by conventional prior art processes.

I can build oxide coatings on various aluminum alloys employing an electrolyte containing my additive according to the invention process, an example of one such alloy being designated 24S containing about 91% aluminum and about 4.5% copper.

The following are given as additional examples illustrative but not as limitations of my invention:

Example 3

A 4" x 4" x ¼" thick test panel of 24ST aluminum alloy containing 4.5% copper was cleaned, and was then connected by means of a 3SO aluminum wire ⅛". in diameter to the anode of an electrolyte bath contained in a stainless steel tank which formed the cathode. The electrolyte was prepared by adding about 6 gallons of 66° Baumé H_2SO_4 to 60 gallons of water. To this solution was added about 4100 grams of a 50% solution of the sodium salt of N-methyl taurine corresponding to about .05 mol of this compound per liter of solution. Temperature of the solution during the electrolytic oxidation process was maintained at about 34° F.

In the table below is given approximate values of the time during which each applied voltage was maintained constant, the voltage to which the bath was raised in steps, the amperage during each voltage step, and the coat thickness obtained at each step:

Time (Minutes)	Volts	Amps.	Coating Thickness (Inches)
00	Start		
After 01 increase to	25	2	
After 03 increase to	26	3	
After 05 increase to	27	2	
After 07 increase to	28	3	
After 09 increase to	29	5-3	
After 11 increase to	30	5-4	
After 13 increase to	31	6-3	.0002
After 16 increase to	32	6-4	
After 19 increase to	33	6-4	
After 22 increase to	34	7-4	
After 25 increase to	35	7-4	.0005
After 28 increase to	37	8-5	
After 31 increase to	39	8-4	.0021
After 34 increase to	42	7-4	
After 37 increase to	45	7-4	.0015
After 40 increase to	48	7-5	
After 42 increase to	52	6-4	.002
After 46 increase to	56	6-4	
After 49 increase to	60	6-4	.003
After 52 increase to	64	7-4	
After 55 increase to	68	7-4	.0036

Example 4

The procedure of Example 3 was duplicated except that temperature was made to vary between 34° F. and 55° F. Results similar to those of Example 3 were obtained.

Experience has shown that at electrolyte temperatures below about 34° F. oxide coatings are formed according to the invention, but at a much slower rate than at the temperatures noted above. An increase in the amount of additive used appears to increase to some degree the rate of oxide coat formation at these lower temperatures.

Example 5

The following test shows the results obtained in conventional electrolytes not containing the additive of the invention.

The aluminum alloy coated was 24ST having 4.5% copper. The test pieces were 6" long, 4" wide, and .081" thick.

Aluminum wire was wrapped around the center of each panel and used as the anode current carrier from the copper bus bar to the panel immersed in the electrolyte.

Temperature of the electrolyte was about 34° F.

Agitation was obtained by air under pressure bubbling through the electrolyte.

Current was supplied by a D. C. motor generator set.

The tank carrying the electrolyte was made of stainless steel and served as the cathode. The electrolyte was composed of 93% water by volume and 7% by volume of 66° Baumé water white H_2SO_4.

The table below gives approximate values of the time during which each applied voltage was maintained constant, the voltage to which the bath was raised in steps, and the amperage during each voltage step.

Time (Minutes)	Volts	Amps.
00	Start	
After 03 raise to	25	15
After 06 raise to	27	16-10
After 09 raise to	29	17-12
After 12 raise to	30	16-16 (Panel had glazed appearance)
After 15 raise to	31	20-20
After 18 raise to	32	23

(Panel removed because amperage increased too rapidly. Panel burned in one corner. Balance of panel had clear glazed appearance. Measured physical oxide growth of .0001".)

A comparison of Examples 3 and 5 clearly shows the advantages of the use of my additive in the electrolytic bath when used in my process. It is seen that when my additive is not incorporated in the aqueous sulfuric acid solution, the amperage increases so rapidly even at low voltages of 32 volts that the panels burn, whereas in Example 3, involving the use of my additive in the sulfuric acid solution according to the invention, amperage remains relatively low even up to 68 volts, at which voltage a thick oxide coating of .0036" is obtained.

Surfaces processed by my method on threads, splines, or irregularities are uniform in thickness on crests and valleys, and the parts will coat uniformly regardless of their position in the tank.

The hardened oxide coating of the invention penetrates the parent metal and also builds up on the metal. Hence, bonding of the oxide to the parent metal is obtained by my process, and coatings with uniformly good bonding at all thicknesses including maximum can be produced.

According to my process as described above, employing my additive, thicker oxide coatings on aluminum and its alloys are obtained and I am able to apply any desired coating thickness more quickly. This is advantageous, as the coating of aluminum oxide grows on and penetrates into the surface. I thus obtain over double the coating thickness of the prior art because of several factors: First, I am able to use high voltages according to preferred procedure without "burning out" spots of aluminum oxide. A given thickness of coating is obtained more quickly and preferably at lower temperatures and with a lower concentration of H_2SO_4. All of these three factors decrease the attack on the aluminum oxide coating. The improvements obtained by the use of higher voltage, lower temperature and lower H_2SO_4 concentration in turn are made possible by using the additive in the electrolyte according to the invention.

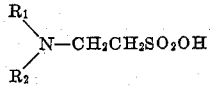
By using the relatively pure sulfonic acid compounds noted above as additive the chemical technique is simplified and the electrolyte bath containing such additive can be reproduced at any time, and the improved results obtained therewith according to the invention are also reproducible.

While I have described a particular embodiment of my invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention as set forth in the appended claims.

I claim:

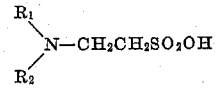
1. A process of coating aluminum and aluminum alloy articles with a coating of oxide of aluminum,

which comprises passing an electric current through an electrolytic cell with said article forming the anode, said cell containing an electrolyte comprising an aqueous solution of an electro anodizing acid as the major acid component and a compound of the group consisting of those of the general formula



and the soluble salts thereof, where R_1 and R_2 are each members of the group consisting of hydrogen, alkyl and cycloalkyl, each of R_1 and R_2 having less than 8 carbon atoms.

2. A process of coating aluminum and aluminum alloy articles with a coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell with said article forming the anode, said cell containing an electrolyte comprising an aqueous solution of an electro anodizing acid as the major acid component and a minor amount of a compound of the group consisting of those of the general formula



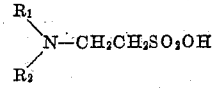
and the soluble salts thereof, where R_1 and R_2 are each members of the group consisting of hydrogen, alkyl and cycloalkyl, R_1 and R_2 each having less than 8 carbon atoms.

3. A process of coating aluminum and aluminum alloy articles with a coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell with said article forming the anode, said cell containing an electrolyte comprising an aqueous solution of sulfuric acid as the major acid component and a minor amount of a compound of the group consisting of those of the general formula

$$R_1—NH—CH_2CH_2SO_2OH$$

and the soluble salts thereof, where R_1 is an alkyl group having less than 8 carbon atoms.

4. A process for coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte with said article forming the anode, said electrolyte comprising a water solution of an electro anodizing acid as the major acid component and a minor amount of a compound of the group consisting of those of the general formula



and the soluble salts thereof, where R_1 and R_2 are each members of the group consisting of hydrogen, alkyl and cycloalkyl, R_1 and R_2 each having less than 8 carbon atoms, and increasing the voltage of said current by a plurality of voltage steps in a voltage range above the voltage at which measurable oxide coating commences to form on said article, the voltage at each such step being maintained substantially constant.

5. A process for coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature not less than about 34° F. with said article forming the anode, said electrolyte comprising a water solution of sulfuric acid as the major acid component and a minor amount of a compound of the group consisting of those of the general formula

$$R_1—NH—CH_2CH_2SO_2OH$$

and the soluble salts thereof, where R_1 is an alkyl group having less than 8 carbon atoms, and increasing the voltage of said current by a plurality of voltage steps in a voltage range above the voltage at which measurable oxide coating commences to form on said article, the voltage at each such step being maintained substantially constant and the voltage at one step being increased to the next step when the current at said one step decreases.

6. A process of coating aluminum and aluminum alloy articles with a coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell with said article forming the anode, said cell containing an electrolyte comprising an aqueous solution of an electro anodizing acid as the major acid component and N-methyl taurine.

7. A process of coating aluminum and aluminum alloy articles with a coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell with said article forming the anode, said cell containing an electrolyte comprising an aqueous solution of sulfuric acid as the major acid component and a minor amount of N-methyl taurine.

8. A process of coating aluminum and aluminum alloy articles with a hard tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell with said article forming the anode, the voltage of said current being above the voltage at which measurable oxide coating commences to form on said article, said cell containing an electrolyte at temperature not less than about 34° F. comprising an aqueous solution of sulfuric acid as the major acid component and a minor amount of the compound N-methyl taurine.

9. A process for coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte with said article forming the anode, said electrolyte comprising a water solution of an electro anodizing acid as the major acid component and a minor amount of N-methyl taurine, and increasing the voltage of said current by a plurality of voltage steps in a voltage range above the voltage at which measurable oxide coating commences to form on said article, the voltage at each such step being maintained substantially constant.

10. A process for coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature not less than about 34° F. with said article forming the anode, said electrolyte comprising a water solution of an electro anodizing acid as the major acid component and a minor amount of N-methyl taurine, and increasing the voltage of said current by a plurality of voltage steps in a voltage range above the voltage at which measurable oxide coating commences to form on said article, the voltage at each such step being maintained substantially constant and the voltage at one step being increased to the next step when the current at said one step decreases.

11. A process for coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature between about 34° F. and about 55° F. with said article forming the anode, said electrolyte comprising a water solution of an electro anodizing acid as the major acid component, a small amount of an acid resistant wetting agent, and a minor amount of N-methyl taurine, and increasing the voltage of said current by a plurality of voltage steps in a voltage range above the voltage at which measurable oxide coating commences to form on said article, the voltage at each such step being maintained substantially constant, and the voltage at one step being increased to the next step when the current at said one step decreases substantially.

12. A process for coating aluminum and aluminum alloy articles with a hard, dense and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature between about 34° F. and about 40° F. with said article forming the anode, said electrolyte comprising an aqueous solution of sulfuric acid as the major acid component and a minor amount of N-methyl taurine, and increasing the voltage of said current by a plurality of voltage steps in a voltage range above the voltage at which measurable oxide coating commences to form on said article, the voltage at each such step being maintained substantially constant for a period, and the voltage at one step being increased to the next step when the current at said one step decreases.

13. A process for coating aluminum and aluminum alloy articles with a hard, dense and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature of about 34° F. with said article forming the anode, said electrolyte comprising an aqueous solution of sulfuric acid as the major acid component and at least .02 mol per liter of solution of N-methyl taurine, and a small amount of an acid resistant wetting agent, and increasing the voltage of said current by a plurality of voltage steps in a voltage range above the voltage at which measurable oxide coating commences to form on said article, the voltage at each such step being maintained substantially constant for a period, and the voltage at one step being increased to the next step when the current at said one step decreases substantially.

14. A process for coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature less than about 55° F. with said article forming the anode, said electrolyte comprising an aqueous solution of sulfuric acid as the major acid component and a minor about of N-methyl taurine, and periodically increasing the voltage of said current from a voltage below the voltage at which measurable oxide coating commences to form on said article to an upper voltage above the last mentioned voltage by a plurality of voltage steps, said upper voltage being at least 60 volts, the voltage at each such step above the voltage at which measurable oxide coating commences to form being maintained substantially constant, and the voltage at one such step being increased to the next step when the current at the former step decreases, whereby incremental increases in coating thickness are obtained.

15. A process for coating aluminum and aluminum alloy articles with a hard, dense and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature between about 34° F. and about 40° F. with said article forming the anode, said electrolyte comprising an aqueous solution of sulfuric acid as the major acid component, a minor amount of N-methyl taurine and a small amount of an acid resistant wetting agent, increasing the voltage of said current by a plurality of voltage steps in a voltage range above the voltage at which measurable oxide coating commences to form on said article, the voltage at each such step being maintained substantially constant, and depositing a portion of oxide coating on said anode during each such step, the voltage at one step being increased to the next step when the current at said one step decreases substantially.

16. A process for coating aluminum and aluminum alloy articles with a hard, dense, and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature between about 34° F. and about 40° F. with said article forming the anode, said electrolyte comprising an aqueous solution of sulfuric acid as the major acid component, a small amount of an acid resistant wetting agent, and a minor amount of N-methyl taurine, and increasing the voltage of said current from a voltage below the voltage at which measurable oxide coating commences to form on said article to an upper voltage above the last mentioned voltage by a plurality of voltage steps, said upper voltage being at least 60 volts, the voltage at each such step above the voltage at which measurable oxide coating commences to form being maintained substantially constant and the voltage at one such step being increased to the next step when the current at said one step decreases.

17. A process for coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature not less than about 34° F. with said article forming the anode, said electrolyte comprising an aqueous solution of sulfuric acid as the major acid component and a minor amout of N-methyl taurine, and periodically increasing the voltage of said current by a plurality of increments in a voltage range below the voltage at which measurable oxide coating commences to form on said article up to said last mentioned voltage, and increasing the voltage of said current by a plurality of voltage steps in a voltage range above said voltage at which measurable oxide coating commences to form, the voltage at each such step above the last mentioned voltage being maintained constant for a period, and the voltage at one such step being increased to the next step when the current at said one step decreases substantially.

18. A process of coating aluminum and aluminum alloy articles with a coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell with said article forming the anode, said cell containing an electrolyte comprising an aqueous solution of an electro anodizing acid as the major acid component and N-methyl taurine, maintaining the voltage of said current at the voltage at which measurable oxide coating commences to form on said article, decreasing the current at said last named voltage, and raising the voltage to a value above the said last mentioned voltage to approximately reestablish the current value obtained when said voltage at which measurable oxide coating commences to form was initially applied and before the current at said voltage decreased.

19. A process for coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte with said article forming the anode, said electrolyte comprising a water solution of an electro anodizing acid as the major acid component and a minor amout of N-methyl taurine, initiating current flow at at least the voltage at which measurable oxide coating commences to form on said article, maintaing the voltage at said last mentioned voltage to produce an oxide coating on said anode, decreasing the current at said last named voltage, and raising the voltage to a value above the said voltage at which measurable oxide coating commences to form but insufficient to produce a current value of a magnitude to cause burning of said article.

20. A process for coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature not less than about 34° F. with said article forming the anode, said electrolyte comprising a water solution of an electro anodizing acid as the major acid component and a minor amount of N-methyl taurine, initiating current flow below the voltage at which measurable oxide coating commences to form on such article, raising the voltage to the last mentioned voltage, main-

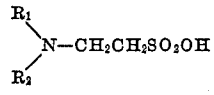
taining the voltage substantially constant at said voltage at which measurable oxide coating commences to form to produce an oxide coating on said anode, decreasing the current at said last named voltage, and raising the voltage to a value above the said voltage at which measurable oxide coating commences to form but insufficient to produce a current value of a magnitude causing burning of said article.

21. A process for coating aluminum and aluminum alloy articles with a hard and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolyte cell containing an electrolyte maintained at a temperature between about 34° F. and about 55° F. with said article forming the anode, said electrolyte comprising a water solution of an electro anodizing acid as the major acid component and a minor amount of N-methyl taurine, initiating current flow at at least the voltage at which measurable oxide coating commences to form on said article, maintaining the voltage of said current at said last mentioned voltage to produce a measurable oxide coating on said anode, decreasing the current at said last named voltage, raising the voltage by a plurality of voltage increments to values above said voltage at which measurable oxide coating commences to form to approximately reestablish at each said increment the current value attained when said last mentioned voltage was initially applied and before the current at such voltage decreased, and maintaining the higher voltage after the addition of each increment of voltage and oxidizing said metal article at a decreasing current value while maintaining said higher voltage after each increment of voltage has been applied.

22. A process for coating aluminum and aluminum alloy articles with a hard, dense and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature between about 34° F. and about 55° F. with said article forming the anode, said electrolyte comprising an aqueous solution of sulfuric acid as the major acid component and a minor amount of N-methyl taurine, initiating current flow at a voltage below the voltage at which measurable oxide coating commences to form on said article, raising the voltage to said last mentioned voltage, maintaining the voltage substantially constant at said last mentioned voltage until the current decreases, to produce an oxide coating on said anode, raising the voltage by a plurality of voltage steps to approximately reestablish at each said step the current value obtained when said voltage at which measurable oxide coating commences to form was initially applied and before the current at such voltage decreased, each of said voltage steps varying by a few volts from the voltage at the adjacent steps, and maintaining the higher voltage after the addition of each increment of voltage and oxidizing said metal article at a decreasing current value while maintaining said higher voltage after each increment of voltage has been applied.

23. A process for coating aluminum and aluminum alloy articles with a hard, dense and tough coating of oxide of aluminum, which comprises passing an electric current through an electrolytic cell containing an electrolyte maintained at a temperature between about 34° F. and about 40° F. with said article forming the anode, said electrolyte comprising an aqueous solution of sulfuric acid as the major acid component, a small amount of an acid resistant wetting agent, and from about .02 to .10 mol per liter of said solution of N-methyl taurine, initiating current flow at a voltage below the voltage at which measurable oxide coating commences to form on said article, raising the voltage by a plurality of increments to said last mentioned voltage, maintaining the voltage substantially constant at said last mentioned voltage until the current decreases, forming a measurable oxide coating on said anode, raising the voltage by a plurality of voltage steps each of which is insufficient to produce a current value of a magnitude causing burning of said article, each of said voltage steps varying by a few volts from the voltage at the adjacent steps, maintaining the voltage at each such step substantially constant until the current decreases, and forming additional oxide coating during each such voltage step.

24. An electrolyte for the anodic oxidation of aluminum and its alloys, which comprises an aqueous solution of an electro anodizing acid as the major acid component and from about .02 to about .10 mol per liter of said solution, of a compound of the group consisting of those of the general formula



and the soluble salts thereof, where R_1 and R_2 are each members of the group consisting of hydrogen, alkyl and cycloalkyl, each of R_1 and R_2 having less than 8 carbon atoms.

25. An electrolyte for the anodic oxidation of aluminum and its alloys, which comprises an aqueous solution of sulfuric acid as the major acid component and from about .02 to about .10 mol of N-methyl taurine per liter of said solution.

References Cited in the file of this patent

UNITED STATES PATENTS

672,913	Pollak	Apr. 30, 1901
2,019,994	Rhodes	Nov. 5, 1935
2,233,785	Korpiun	Mar. 4, 1941
2,550,388	Simon et al.	Apr. 24, 1951
2,692,851	Burrows	Oct. 26, 1954
2,692,852	Burrows	Oct. 26, 1954

OTHER REFERENCES

Edwards et al.: Transactions of the Electrochemical Society, 1941, vol. 79, pp. 135–142.

Lilienfeld et al.: Transactions of the Electrochemical Society, 1935, vol. 68, pp. 533–547.