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2,963,409

FLEXIBLE ANODIC COATING

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This invention relates to a novel method for the production of flexible anodic coatings on an aluminum surface. More particularly, the invention concerns a method of anodizing aluminum strip or wire in an anodizing bath containing a metal halide and an organic dicarboxylic acid.

The manufacture of aluminum products suitable for use in the electrical industry, especially for such applications as motor and transformer windings, requires that such products possess anodic insulating coatings with not only good dielectric properties, but with a high degree of flexibility. Anodically coated aluminum which retains its dielectric properties even under severe bending has not as yet been successfully produced by existing methods.

Methods of imparting enhanced flexibility to anodic coatings on aluminum have been described in the prior art. Thus, U.S. Patent 2,685,563 discloses adding halide salts of alkali or alkaline earth metal to a sulfuric acid anodizing bath for this purpose. Solutions of organic acids such as oxalic have been suggested as anodizing baths per se, while oxalic acid and other dibasic acids have been added to anodizing baths to improve the results of the anodizing process. Still other procedures have involved supplementing conventional anodizing treatments with hot oxalic acid dips to increase the porosity of the coating. In these prior art methods, experience has shown that the resultant coatings do not possess sufficient porosity and resistance to voltage breakdown to meet modern electrical standards.

In accordance with the present invention, we have found surprisingly and unexpectedly that the formation of a porous and flexible anodic coating on an aluminum surface is made possible by carrying out the anodization in a bath which contains both a metal halide and an organic dicarboxylic acid.

Coatings produced with the use of both of these additions are extremely adherent, and the strip or wire may be bent, for example to radii of between 4 and 5 times its thickness without significantly adversely affecting the dielectric properties of the coating. By comparison, the standard anodic procedures yield coatings which lose their entire dielectric properties after the product is bent through a radius of 15 times its thickness or less.

Anodic coating in accordance with our novel process may be carried out using either direct or alternating current sources. The use of direct current has been found preferable, however, since it is possible to obtain a high quality product more consistently than when using alternating current.

The anodizing baths which may be employed in ac-

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cordance with this invention are of the conventional type prepared from aqueous solutions of sulfuric, sulfamic, and chromic acid. A preferred type of bath is that employing sulfuric in a concentration between about 5% and 70% by weight.

In accordance with this invention, there is added to the anodizing electrolyte a quantity of metal halide ranging from about 0.1% to 10% by weight. When employing D.C. current, the amount of metal halide will preferably be about 0.5%, while with A.C. current, about 1.5% is found more effective. There is also added to the anodizing electrolyte a quantity of an organic dicarboxylic acid, ranging from about 0.2% by weight up to a percentage represented by the limit of solubility of the acid in the anodizing electrolyte. While aliphatic and aromatic dicarboxylic acids may be used, such as, for example, oxalic or maleic acids, it has been found preferable to employ for this purpose aliphatic dicarboxylic acid of between 2 and 5 carbon atoms. Examples of such acids include oxalic, malonic, succinic, and glutaric acids.

Among the metal halides which may be used in accordance with this invention, there are included halides which are soluble in the anodizing solution and which will disassociate to form halide ions therein. Advantageously there may be employed the chlorides, bromides, or iodides of the alkali metals or the alkaline earth metals, such as, for example, sodium chloride, potassium chloride, calcium chloride, sodium bromide, potassium iodide, calcium iodide, lithium chloride, and the like.

A typical anodizing electrolyte prepared in accordance with this invention would be a 17% sulfuric acid solution to which has been added about 0.5% sodium chloride and 2% oxalic acid.

The mechanism by which the combination of the metal halide and the organic dicarboxylic acid brings about the unexpectedly improved results in accordance with this invention is not clearly understood. Applicants do not wish to be bound by any particular theory, but a possible explanation for the improved coatings obtained with this combination, as compared with those with the metal halide, such as sodium chloride, alone, would be that where the anodization is conducted with the addition of sodium chloride alone, nascent chlorine (in active form) is liberated on the anode. This nascent chlorine, by reason of its relative high concentration interferes with the formation of an anodic coating of an adequate degree of flexibility. The further presence of the added dicarboxylic acid serves to react the acid with excess chlorine, and thus to bring about a limitation of chlorine concentration to the level most desirable for flexible anodic coating formation. At the same time the dicarboxylic acid, while itself possessing flexibility-imparting properties, is partially oxidized by the chlorine. The net result is a balance between chlorine and dicarboxylic acid functions and a coaction which produces a more flexible coating than is possible with either additive alone.

In making comparisons of anodic coating quality, the improvement in flexibility may be determined in terms of the so-called breakdown voltage test, as made upon wire or strip. The numerical indication of this test corresponds to the applied voltage at which dielectric breakdown occurs.

Thus, zero voltage would signify absence of insulating

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or dielectric value, such as on bare metal or at a break in the coating. Either D.C. or A.C. current may be used in this test.

The following tables set forth comparative test data showing the greatly improved results obtained with the anodization of 0.06" diameter EC grade aluminum wire (a high purity alloy known as electric conductor wire), when anodized in (a) sulfuric acid alone, (b) sulfuric acid and sodium chloride, (c) sulfuric acid, sodium chloride and oxalic acid, and (d) oxalic acid bath per se.

TABLE 1
A.C. anodizing (salt only added)

Electrolyte	Temperature, ° F.	Current Density (amps. per sq. ft.)	Anodizing Time	Breakdown of Wire Bent on ¼ inch Mandrel
30% H ₂ SO ₄	72	12	15 mins....	Immediate breakdown; 0 voltage.
1.5% NaCl, 16% H ₂ SO ₄	72	100	30 secs.....	Do.
1.5% NaCl, 16% H ₂ SO ₄	72	200	30 secs.....	Do.
1.5% NaCl, 16% H ₂ SO ₄	72	1,000	30 secs.....	300 Volts.
1.5% NaCl, 16% H ₂ SO ₄	72	1,200	30 secs.....	Do.
1.5% NaCl, 16% H ₂ SO ₄	72	1,400	30 secs.....	Do.

TABLE 2
D.C. anodizing (salt only added)

Electrolyte	Temperature, ° F.	Current Density (amps. per sq. ft.)	Anodizing Time	Breakdown of Wire Bent on ¼ inch Mandrel
16% H ₂ SO ₄ , .5% NaCl.....	72	12	15 mins....	Immediate breakdown. 0 voltage.
16% H ₂ SO ₄ , .5% NaCl.....	72	100	30 secs.....	Do.
16% H ₂ SO ₄ , .5% NaCl.....	72	200	30 secs.....	Immediate breakdown. 0 voltage.
16% H ₂ SO ₄ , .5% NaCl.....	72	300	30 secs.....	Erratic breakdown voltage with a crumbling oxide film (beginning at 50 volts).
16% H ₂ SO ₄ , .5% NaCl.....	72	400	30 secs.....	Do.
16% H ₂ SO ₄ , .5% NaCl.....	72	500	30 secs.....	Do.

TABLE 3
A.C. anodizing with salt and oxalic acid in H₂SO₄

Electrolyte	Temperature, ° F.	Current Density (amps. per sq. ft.)	Anodizing Time	Breakdown of Wire Bent on ¼ inch Mandrel
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	12	15 mins....	Immediate breakdown. 0 volts.
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	100	30 secs.....	Do.
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	200	30 secs.....	200 volts.
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	300	30 secs.....	300 volts.
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	400	30 secs.....	Do.
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	500	30 secs.....	Do.

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TABLE 4

D.C. anodizing with salt and oxalic acid in H₂SO₄

Electrolyte	Temperature, ° F.	Current Density (amps. per sq. ft.)	Anodizing Time	Breakdown of Wire Bent on ¼ inch Mandrel
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	12	15 mins....	Immediate breakdown 0 volts.
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	100	30 secs.....	Do.
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	200	30 secs.....	300 volts.
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	300	30 secs.....	Do.
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	400	30 secs.....	Do.
30% H ₂ SO ₄ , 1.5% Oxalic, .5% NaCl.....	72	500	30 secs.....	Do.

The breakdown voltages were observed on a sample of the wire bent on a ¼" mandrel.

It will be seen from Tables 1 and 2 that the use of a sulfuric acid anodizing electrolyte without additives results in a stiff coating with no resistance to bending. The addition of sodium chloride alone to the anodizing electrolyte produces no improvement at lower current densities, and at higher current densities the film is of poor quality, with breakdown voltages as low as 50 volts, where D.C. current is used. While better results are obtained when A.C. current is applied (Table 1), it becomes necessary to apply extremely high current densities of 1000 to 1400 amperes per sq. ft. to attain a breakdown voltage figure of 300 volts.

However, when oxalic acid is added to the sulfuric acid-salt bath, an immediate improvement is apparent in the case of D.C. current (Table 3) applications, while in the case of the use of A.C. current (Table 4) the current densities may be drastically reduced to the range of 200 to 500 amperes per sq. ft.

TABLE 5
Oxalic Acid Bath

Concentration of Bath, percent	Current Density (amps./sq. ft.)	Anodizing Time, sec.	Breakdown, Bend around ¼" mandrel, volts
2.....	200	30	0
2.....	400	30	0
2.....	500	30	0

Where oxalic acid alone was used as the anodizing electrolyte, as shown in Table 5, material bent around a ¼" mandrel showed zero breakdown voltage.

Tables 1 to 4 inclusive provide typical examples of the ranges of concentration of sulfuric acid in the anodizing electrolytes to be used in our process. The concentration is preferably maintained between about 10% and 30%. While various concentrations of metal halide, such as sodium chloride, and of dicarboxylic acid, such as oxalic acid, may be added to the bath, as indicated previously, the limited solubility of oxalic acid, for example, in the presence of sulfuric acid, results in confining the concentration for practical purposes to the point of complete solubility at the temperature employed.

It has been found that generally, higher current densities are needed to obtain adequately flexible coatings when A.C. current is used than is the case with D.C. current. In the case of D.C. current, current densities

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above 200 amperes per sq. ft. are preferred to produce flexible coatings, ranging up to about 500 amperes per sq. ft. In the case of A.C. current, current densities may range from about 400 or 500 up to 1000 or 1200 amperes per sq. ft.

The temperature of the electrolyte is not critical, and in general, a temperature range of about 65° to 95° F. will produce good results. Anodizing time is generally of the order of 30 seconds. The most important variables are therefore the concentration of the additives and the current density used.

Anodic coatings made by the process of this invention are very flexible and can be bent over a radius of 4 to 5 times the thickness of the strip or wire without appreciable loss in dielectric properties. This quality is confirmed by microscopic examination of the coatings, whereby it is possible to distinguish flexible coatings from the inflexible coatings after the same has been bent. While flexible coatings exhibit many cracks randomly on the surface, the inflexible coatings exhibit few but wide cracks running parallel to each other.

The prior art methods using sulfuric acid alone or oxalic acid alone furnish films with no flexibility. The addition of sodium chloride alone or of oxalic acid alone to a sulfuric acid bath will provide films with some flexibility, but with inadequate dielectric properties, in that when bent to a radius no greater than 10 to 15 times the thickness of the strip or wire, they exhibit complete voltage breakdown due to crack formation. In contrast thereto, the coatings of this invention made with, for example, sulfuric acid electrolyte to which both sodium chloride and oxalic acid have been added, may be bent to radii 4 to 5 times the thickness of the sample, with full retention of dielectric strength of the article.

The practice of our invention may be illustrated by the following examples, but it is to be understood that the invention is not limited thereto.

EXAMPLE 1

0.06" EC aluminum alloy wire was anodized for 30 seconds at 80° F. in an anodizing bath having the following composition:

	Percent
Sulfuric acid -----	30
Sodium chloride -----	1
Oxalic acid -----	2.5

with D.C. current at a current density of 400 amperes per sq. ft. A light grey coating was obtained which exhibited breakdown voltages of 300 to 350 volts when bent over rollers of 0.25", 0.5", and 1" diameter, respectively.

EXAMPLE 2

The same type of wire was anodized for 30 seconds at 72° F. in an anodizing bath having the composition:

	Percent
Sulfuric acid -----	30
Oxalic acid -----	1.5
Sodium chloride -----	0.5

with D.C. current at a current density of 400 amperes per sq. ft. The resulting anodic coating exhibited a breakdown voltage of 300 volts when bent to a radius of 0.25".

EXAMPLE 3

The same type of wire was anodized for 30 seconds at 85° F. in an anodizing bath of the following composition:

	Percent
Sulfuric acid -----	16
Sodium chloride -----	1.5
Oxalic acid -----	2.5

with A.C. current at a current density of 1400 amperes per sq. ft. A dark grey coating was obtained, which

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showed breakdown voltages of 300 volts when bent around rollers of 0.25", 0.5", and 1.0" diameter, respectively.

EXAMPLE 4

The same wire and bath and temperature were applied as in Example 2, but using A.C. at a current density of 400 amperes per sq. ft. A breakdown voltage of 300 volts was shown by the sample when bent to a radius of 0.25".

While we have illustrated and described present preferred embodiments of the invention, it will be recognized that the invention may be otherwise variously embodied and practiced within the scope of the following claims.

I claim:

1. The method of forming an anodic coating of high flexibility and dielectric strength upon an aluminum surface which comprises immersing the aluminum as anode in an aqueous acid anodizing electrolyte consisting essentially of a mineral acid and from about 0.1% to about 10% by weight of an alkali metal halide and from about 0.2% by weight to a percentage represented by the limit of its solubility therein of an aliphatic dicarboxylic acid of from 2 to 5 carbon atoms, and passing a current through said electrolyte at a current density above about 200 amperes per square foot.

2. The method of forming an anodic coating of high flexibility and dielectric strength upon an aluminum surface which comprises immersing the aluminum as anode in an aqueous sulfuric acid anodizing electrolyte consisting essentially of said acid and from about 0.1% to about 10% by weight of sodium chloride and about 0.2% by weight to a percentage represented by the limit of its solubility therein of oxalic acid, and passing a current through said electrolyte at a current density above about 200 amperes per square foot.

3. The method of forming an anodic coating of high flexibility and dielectric strength upon an aluminum surface which comprises immersing the aluminum as anode in an aqueous sulfuric acid anodizing electrolyte consisting essentially of said acid and from about 0.1% to about 10% by weight of sodium chloride and about 0.2% by weight to a percentage represented by the limit of its solubility therein of malonic acid, and passing a current through said electrolyte at a current density above about 200 amperes per square foot.

4. The method of forming an anodic coating of high flexibility and dielectric strength upon an aluminum surface which comprises immersing the aluminum as anode in an aqueous sulfuric acid anodizing electrolyte consisting essentially of said acid and from about 0.1% to about 10% by weight of sodium chloride and about 0.2% by weight to a percentage represented by the limit of its solubility therein of succinic acid, and passing a current through said electrolyte at a current density above about 200 amperes per square foot.

5. The method of forming an anodic coating of high flexibility and dielectric strength upon an aluminum surface which comprises immersing the aluminum as anode in an aqueous acid anodizing electrolyte consisting essentially of a mineral acid and from about 0.1% to about 10% by weight of a metal halide selected from the group consisting of alkali metal and alkaline earth metal halides, and from about 0.2% by weight to a percentage represented by the limit of its solubility therein of an aliphatic dicarboxylic acid of from 2 to 5 carbon atoms, and passing a direct current through said electrolyte at a current density above about 200 amperes per square foot.

6. The method of forming an anodic coating of high flexibility and dielectric strength upon an aluminum surface which comprises immersing the aluminum as anode in an aqueous acid anodizing electrolyte consisting essentially of a mineral acid and from about 0.1% to about 10% by weight of a metal halide selected from the group consisting of alkali metal and alkaline earth metal halides,

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and from about 0.2% by weight to a percentage represented by the limit of its solubility therein of an aliphatic dicarboxylic acid of from 2 to 5 carbon atoms, and passing an alternating current through said electrolyte at a current density above about 200 amperes per square foot.

7. An anodizing electrolyte consisting essentially of an aqueous solution of about 5% to about 70% sulfuric acid and from about 0.1% to about 10% by weight of an alkali metal halide and about 0.2% by weight to a percentage represented by the limit of its solubility therein of an aliphatic dicarboxylic acid of from 2 to 5 carbon atoms.

8. An anodizing bath consisting essentially of an aqueous solution of about 10% to about 30% sulfuric acid and about 0.5% to about 1.5% by weight of sodium chloride and about 0.2% to about 2.5% by weight of oxalic acid.

9. The method of forming an anodic coating of high flexibility and dielectric strength upon an aluminum surface which comprises immersing the aluminum as anode in an aqueous acid anodizing electrolyte consisting essentially of a mineral acid and from about 0.1% to about 10% by weight of a metal halide selected from the group consisting of alkali metal and alkaline earth metal halides and from about 0.2% by weight to a percentage represented by the limit of its solubility therein of an aliphatic dicarboxylic acid of from 2 to 5 carbon atoms, and passing a current through said electrolyte at a current density above about 200 amperes per square foot.

10. Aluminum strip or wire carrying upon its surface an anodic coating of high flexibility and dielectric

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strength, produced by the method which comprises immersing the aluminum as anode in an aqueous sulfuric acid anodizing electrolyte consisting essentially of said acid and from about 0.1% to about 10% by weight of sodium chloride and about 0.2% by weight to a percentage represented by the limit of its solubility therein of oxalic acid, and passing a current through said electrolyte at a current density above about 200 amperes per square foot.

11. Aluminum strip or wire carrying upon its surface an anodic coating of high flexibility and dielectric strength, produced by the method which comprises immersing the aluminum as anode in an aqueous acid anodizing electrolyte consisting essentially of a mineral acid and from about 0.1% to about 10% by weight of a metal halide selected from the group consisting of alkali metal and alkaline earth metal halides, and from about 0.2% by weight to a percentage represented by the limit of its solubility therein of an aliphatic dicarboxylic acid of from 2 to 5 carbon atoms, and passing a current through said electrolyte at a current density above about 200 amperes per square foot.

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