

1

3,738,921

ANODIC OXIDATION OF ALUMINUM AND ALLOYS THEREOF TO FORM HARD ANODIZED COATINGS THEREON

Marguerite Elise Lestrade and Jean Herret, Tarbes, France, assignors to Etat Francais, Paris, France
No Drawing. Filed July 8, 1971, Ser. No. 160,921
Claims priority, application France, July 9, 1970, 7025414

Int. Cl. C23b 9/02

U.S. Cl. 204—58

3 Claims

ABSTRACT OF THE DISCLOSURE

Aluminum and alloys thereof are anodized with a hard coating by anodic oxidation at a temperature between 15 and 20° C. with a current density of 2.5 and 3.5 amperes/dm.² for a time between 1 and 2½ hours in an electrolyte having the following composition.

	G./liter
Al ₂ (SO ₄) ₃ ·18H ₂ O	200-400
(COOH) ₂ ·2H ₂ O	20-50
(CH ₂ OH—CHOH—CH ₂ OH)	7-20

BACKGROUND OF THE INVENTION**(a) Field of the invention**

The present invention relates to the oxidation of aluminum and its alloys, with the object of obtaining hard coatings on precision mechanical components, which require good resistance to friction, wear and corrosion.

(b) Description of the prior art

It is known that the metallic surface of such components can be transformed by electrolytic treatment into a homogeneous and compact layer of aluminum oxide, colored to a greater or lesser degree by the oxides of the addition metals of the alloy. This layer is very hard and can reach a thickness of 100 to 180 microns, depending on the alloy and the electrolysis parameters.

At the present time, in conventional hard anodic oxidation processes, a 10 to 20% sulphuric acid solution with various additives is used as an electrolyte. During the electrolysis, a well-known phenomenon occurs, which is the oxidation of the surface of the elements forming the anode, by the oxygen being formed by the decomposition of the water by the current: a more complex chemical phenomenon also occurs which is the attack of the aluminum oxide coating by the sulphuric acid.

In order for there to be a coating, it is necessary for the speed of oxidation to be higher than the speed of dissolution by the sulphuric acid. In the known processes for reducing the speed of dissolution, the electrolyte is cooled and it is necessary to maintain the electrolyte at a temperature from -5° to 0°. This necessitates large and costly installations. Furthermore, the coatings obtained under these conditions are fissured or cracked, and this discontinuous structure explains their fragility under shock. These disadvantages have considerably reduced the industrial development of hard anodization.

On the other hand, the alloys used for the mechanical parts contain addition elements which increase their mechanical characteristics. The constituents of alloys which give solid solutions are uniformly oxidized and have no harmful effect on the quality of the coatings, but the elements not in solution precipitate at the grain joints, and they are attacked by the sulphuric acid in the electrolyte and an inter-granular attack is produced.

SUMMARY OF THE INVENTION

The process according to the invention permits hard

2

anodic coatings to be obtained, whose thickness can reach and exceed 170 microns, while operating at ambient temperature, for example, in the region of 15° C.

In using the process according to the invention, not only is the formed aluminum oxide very slightly attacked, which permits working at ambient temperature, but the elements forming the alloy, even out of solid solution, are not attacked, because the electrolyte does not contain a strong acid.

The structure of the resulting coating is finer and more homogeneous than previously and the hardness is at least equal and the resistance to corrosion is improved.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The electrolyte according to the invention for anodic treatment of aluminum and its alloys is constituted as follows

	G./liter
Al ₂ (SO ₄) ₃ ·18H ₂ O	200 to 400
(COOH) ₂ ·2H ₂ O	20 to 50
CH ₂ OH—CHOH—CH ₂ OH	7 to 20

The invention is also directed to an anodic oxidation treatment with the above electrolyte, at a temperature which is between 15° and 20°, with a current of density between 2.5 and 3.5 amperes/dm.², for a period which is between one hour and 2½ hours.

The present invention is also directed to an anodic oxidation process for aluminum and its alloys, comprising the following additional operations:

Degreasing of the parts by immersion in a conventional liquid or gaseous organic solvent, cleaning with an alkali detergent aqueous bath of a pH lower than 12,

Treatment with 50% nitric acid at 40° Baumé, for 3 to 5 minutes, followed by cold rinsing,

Anodic oxidation with the above electrolyte at a temperature which is between 15 and 20°, using a current density which is between 2.5 and 3.5 amperes/dm.², for a period which is between 1 hour and 2½ hours, and

Cold rinsing.

The invention is also concerned with the products obtained by treatment with the above electrolyte.

By way of non-limiting example, the following table indicates the results obtained by application of the method of the invention to conventional aluminum alloys

Alloy	Vickers hardness values	Thickness in μ for an anodization time of 1½ hours at 15°	Breakdown voltage in volts	Resistance to salt spray, according to AFNOR standard PNX 41002
A 99-----	470-520	115-120	220-2500	More than 200 days.
AG 5-----	410-480	110-112	2,150-3,000	Do.
AZ5 gl-----	422-470	105-108	2,500-2,800	Do.
ASGM-----	396-450	102-105	2,300-2,500	Do.

It is possible to obtain coatings of greater thickness by extending the anodizing time. A treatment lasting 2 to 2½ hours gives anodic layers of 130 to 180 microns, depending on the alloys.

The coatings thus obtained have a very fine structure, without any crackling or powdering on the edges of the parts, and they can be obtained in the dimensions as required or corrected by grinding, permitting mechanical parts to be obtained which are of very high precision.

The application of the invention should permit a rapid industrial development of mechanical parts consisting of aluminum alloy, when it is desired simultaneously to obtain lightness, good surface hardness and high resistance to corrosion.

The hardness properties of the anodic coatings obtained by the method of the invention conform to the standards of US AMS 2 468 and in particular to the standard MPD 3 707 p 3-6, Knoop hardness corresponding to 427 HV.

The present invention offers the following advantages:

(1) Present installations for ordinary anodic oxidation can be adapted to enable obtaining hard coatings of 50 to 180 microns on aluminum alloys,

(2) A very stable electrolyte is formed from non-toxic and inexpensive commercial products, which can be more easily handled than the sulphuric acid usually employed,

(3) Coatings of high quality, which are very hard and not cracked, can be obtained in desired size or corrected by grinding.

What is claimed is:

1. A process for forming a hard, thick anodic coating on a surface of a pure or alloyed aluminum article, comprising anodizing the aluminum article in an aqueous bath consisting essentially of aluminum sulfate in the propor-

tion of 200 to 400 g./liter, 20 to 50 g./liter of oxalic acid, and 7 to 20 g./liter of glycerol.

2. A process as claimed in claim 1, wherein the anodizing is effected at a temperature between 15 and 20° C., with a current density between 2.5 and 3.5 amperes/dm.², over a period of from 1 to 2½ hours.

3. An electrolyte for forming hard anodizing coatings consisting essentially of an aqueous solution of 200 to 400 g./liter of aluminum sulfate, 20 to 50 g./liter of oxalic acid and 7 to 20 g./liter of glycerol.

References Cited

UNITED STATES PATENTS

2,682,503	6/1954	Hesch	204—33
3,494,840	2/1970	Deavick et al.	204—58
3,524,799	8/1970	Dale	204—58
3,616,308	10/1971	Cooke	204—58
3,616,297	10/1971	Cooke	204—58

20 F. C. EDMUNDSON, Primary Examiner