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(54) **"Anodizing process, with low environmental impact, for a workpiece of aluminium or aluminium alloys"**

(57) The process for anodizing a workpiece of aluminium or aluminium alloys provides for the use of the workpiece as the anode of an electrolytic cell in the presence of an aqueous acid solution which contains from 10 to 200 g sulphuric acid and from 5 to 200 g L(+)-tartaric acid.

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**Description**

**[0001]** The present invention relates to an anodizing process for a workpiece (such as, for example, a part or a component of a system) of aluminium or aluminium alloys, this definition being intended to comprise pure or almost pure aluminium, as well as combinations thereof in all percentages with other elements.

**[0002]** In greater detail, this process makes use of the above-mentioned workpiece as the anode of an electrolytic cell in the presence of an aqueous acid solution in order to form on the surface of the workpiece a coating of aluminium oxide.

**[0003]** This coating results in better properties concerning the resistance to corrosion and the adhesion of paints, bonding agents and other organic coatings suitable for improving the appearance or the resistance to corrosion of the finished workpiece.

**[0004]** Conventionally, this acid solution substantially comprises sulphuric acid at high concentrations or chromic acid, the latter being the compound mainly used in the field of aeronautics.

**[0005]** The problem addressed by the present invention is to provide an anodizing process having a lesser toxicological impact on the environment in comparison with the known types, avoiding the use of chromic acid whilst nevertheless obtaining anodized workpieces having properties which are at least equivalent to those of workpieces obtained by conventional means.

**[0006]** This problem is solved according to the invention by an anodizing process of the type indicated in the introduction to the present description and characterized in that the aqueous acid solution contains from 10 to 200 g sulphuric acid and from 5 to 200 g L(+)-tartaric acid per litre of solution.

**[0007]** The process according to the invention has the advantage of eliminating, or in any case greatly reducing, the production of industrial waste, in particular waste containing compounds of chromium, without causing the formation of other waste materials having particular toxic or dangerous properties.

**[0008]** The process according to the invention further has the advantage of having a cycle time which is approximately 40% short of that of the analogous process which makes use of chromic acid, producing anodized workpieces having properties at least equivalent if not superior. Consequently, the process according to the invention allows a considerable reduction in running costs to be obtained in that it results in lower costs for the treatment of the waste and involves a substantially lower rate of consumption for the different chemicals used for replenishing the baths, which have an operational life greater than those used in known processes.

**[0009]** The aqueous acid solution of the process according to the invention preferably contains from 20 to 80 g sulphuric acid and from 30 to 120 g L(+)-tartaric acid per litre of solution.

**[0010]** Again preferably, the aqueous solution is maintained, during the anodizing treatment, at a temperature of between ambient temperature and 120°C and, more preferably, between 25 and 35°C.

**[0011]** The electrolytic cell, in which the process according to the invention is carried out, is preferably subjected to a voltage of between 1 and 120 V and, more preferably, of between 10 and 30 V.

**[0012]** The process according to the invention advantageously has a duration of between 5 and 120 minutes and, preferably, of between 5 and 30 minutes.

**[0013]** The anodizing process is generally preceded by a cleaning and/or deoxidizing treatment of the workpiece to be anodized and can be followed by a sealing treatment and, optionally, rinsing for the anodized workpiece. In principle, these treatments are of conventional type and completely compatible with the present invention and can be selected at will from treatments known to this end by the person skilled in the art.

**[0014]** The workpiece advantageously has, upon completion of the anodizing treatment, an oxidized surface coating having a thickness of between a few micrometres and several tens of micrometres.

**[0015]** There now follow, merely by way of non-limiting, illustrative example, examples of the anodizing process according to the invention, as well as a comparative example performed by conventional techniques.

**EXAMPLE 1****Anodizing a 2000-series aluminium alloy with sulphuric-tartaric acid**

**[0016]** A workpiece (of a 2000-series aluminium alloy having dimensions of 150x100x1 mm) was first subjected in a conventional manner to cleaning and deoxidizing treatments, such as degreasing by immersion for approximately 10 minutes, rinsing by immersion in drinking water for approximately 3 minutes, pickling/deoxidation by immersion for approximately 10 minutes and rinsing by immersion in drinking water, preferably followed by further rinsing by immersion in deionized water for a total of approximately 3 minutes.

**[0017]** The workpiece was then used as the anode of an electrochemical cell, in which the cathode was constituted by corrosion-resistant steel of the type AISI 321 and having a surface area equal to or greater than that to be oxidized and in the presence of an aqueous acid solution containing 45 g sulphuric acid and 80 g L(+)-tartaric acid per litre of

solution and was maintained at a temperature of between 30 and 35°C. The workpiece was kept completely immersed in the acid solution.

[0018] The electrical voltage was increased from an initial value of 0 V to a value of 18 V at a rate in the order of 3.6 V/min. The final voltage value was maintained for 25 minutes, producing on the workpiece, upon completion of the anodizing treatment, an oxidized coating having a thickness of approximately 5 µm.

[0019] The anodized workpiece was then subjected to treatments which are conventional per se, such as rinsing with drinking water, preferably followed by further rinsing with deionized water for an overall immersion time of approximately 3 minutes and sealing by immersion for approximately 45 minutes. The workpiece was then dried with air, in particular at a low temperature, if good properties of adhesiveness were required for the oxide.

[0020] The properties of this oxide are indicated in Table I.

## EXAMPLE 2

### Anodizing a 7000-series aluminium alloy with sulphuric-tartaric acid

[0021] A workpiece (of a 7000-series aluminium alloy having dimensions of 150x100x1 mm) was first subjected in a conventional manner to cleaning and deoxidizing treatments, similar to those described with reference to Example 1.

[0022] The workpiece was then used as the anode of an electrochemical cell, in which the cathode was constituted by corrosion-resistant steel of the type AISI 321 and having a surface area equal to or greater than that to be oxidized and in the presence of an aqueous acid solution containing 45 g sulphuric acid and 80 g L(+)-tartaric acid per litre of solution and was maintained at a temperature of between 30 and 35°C. The workpiece was kept completely immersed in the acid solution.

[0023] The electrical voltage was increased from an initial value of 0 V to a value of 15 V at a rate in the order of 3 V/min. The final voltage value was maintained for 25 minutes, producing on the workpiece, upon completion of the anodizing treatment, an oxidized coating having a thickness of approximately 5 µm.

[0024] The anodized workpiece was then subjected to rinsing and sealing treatments, which are conventional per se, similar to those described with reference to Example 1.

[0025] The properties of the oxide coating obtained are indicated in Table I.

## EXAMPLE 3

### Anodizing plated or pure aluminium with sulphuric-tartaric acid

[0026] A workpiece (of a plated aluminium alloy or pure aluminium having dimensions of 150x100x1 mm) was first subjected, in a conventional manner, to cleaning and deoxidizing treatments, similar to those described with reference to Example 1.

[0027] The workpiece was then used as the anode of an electrochemical cell, in which the cathode was constituted by corrosion-resistant steel of the type AISI 321 and having a surface area equal to or greater than that to be oxidized and in the presence of an aqueous acid solution containing 45 g sulphuric acid and 80 g L(+)-tartaric acid per litre of solution and was maintained at a temperature of between 30 and 35°C. The workpiece was kept completely immersed in the acid solution.

[0028] The electrical voltage was increased from an initial value of 0 V to a value of 15 V at a rate in the order of 3 V/min. The final voltage value was maintained for 25 minutes, producing on the workpiece, upon completion of the anodizing treatment, an oxidized coating having a thickness of approximately 5 µm.

[0029] The anodized workpiece was then subjected to rinsing and sealing treatments, which are conventional per se, similar to those described with reference to Example 1.

[0030] The properties of the oxide coating obtained are indicated in Table I.

## EXAMPLE 4 (for comparative purposes)

### Anodizing with chromic acid

[0031] A workpiece (of a plated aluminium alloy or a pure aluminium having dimensions of 150x100x1 mm) was first subjected in a conventional manner to cleaning and deoxidizing treatments, similar to those described with reference to Example 1.

[0032] The workpiece was then used as the anode of an electrochemical cell, in which the cathode was constituted by corrosion-resistant steel of the type AISI 321 and having a surface area equal to or greater than that to be oxidized and in the presence of an aqueous acid solution containing 65 g chromic acid and was maintained at a temperature

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of between 35 and 40°C. The workpiece was kept completely immersed in the acid solution.

**[0033]** The electrical voltage was increased from an initial value of 0 V to a value of 40 V at a rate in the order of 5 V/min. The final voltage value was maintained for 45 minutes, producing on the workpiece, upon completion of the anodizing treatment, an oxidized coating having a thickness of approximately 3 µm.

5 **[0034]** The anodized workpiece was then subjected to rinsing and sealing treatments, which are conventional per se, similar to those described with reference to Example 1.

**[0035]** The properties of the oxide coating obtained are indicated in Table I.

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TABLE I

Property	Test method	Prior art Chromic acid (Example 4)	Prior art Sulphuric acid	INVENTION (Examples 1, 2, 3)
Weight of oxide	ASTM B 137	> 32 mg/dm <sup>2</sup>	> 32 mg/dm <sup>2</sup>	> 40 mg/dm <sup>2</sup>
Corrosion resistance	Tests in saline mist according to ISO 7253	No corrosion points after exposure for 500 hours	No corrosion points after exposure for 500 hours	No corrosion points after exposure for 750 hours
Paint adhesion	Impact test according to ASTM D 2794	No detachment of paint or only slight cracking of paint	NOT APPLICABLE	No detachment of paint
	Adhesion without conditioning according to ISO 2409	100% adhesion	90% adhesion	100% adhesion
	Adhesion after conditioning in water for 14 days according to ISO 2409	100% adhesion	80% adhesion	100% adhesion
Influence of oxide on fatigue life of base metal	Fatigue tests on cylindrical test pieces at frequency of 10-140 Hz, ratio R:0.1	Reduction in fatigue cycles not greater than 25%	Unsatisfactory	Reduction in fatigue cycles not greater than 15%

**[0036]** A comparison of the results of the tests carried out on the workpieces of the Examples according to the invention and the Example for comparative purposes establishes that the process according to the invention produces oxides having properties which are superior to those of the oxides obtained with conventional processes. Furthermore, the process according to the invention offers environmental advantages associated with the different types of product used, and has a duration which is substantially shorter.

**[0037]** Of course, without altering the principle of the invention, the details of implementation and the embodiments can vary extensively in relation to the description, which is given purely by way of example, without in any way departing from the scope thereof. In particular, the aqueous acid solution could contain, in addition to sulphuric acid and tartaric acid, any other components or combinations of components which are compatible with those substances.

## Claims

1. Process for anodizing a workpiece of aluminium or aluminium alloys, which provides for the use of the workpiece as the anode of an electrolytic cell in the presence of an aqueous acid solution, the process being **characterized in that** the aqueous acid solution contains from 10 to 200 g sulphuric acid and from 5 to 200 g L(+)-tartaric acid.
2. Process according to claim 1, **characterized in that** the aqueous acid solution contains from 20 to 80 g sulphuric acid and from 30 to 120 g L(+)-tartaric acid per litre of solution.
3. Process according to either of the preceding claims, **characterized in that** the solution is maintained, during the anodizing treatment, at a temperature of between ambient temperature and 120°C, and preferably between 25 and 35°C.
4. Process according to any one of the preceding claims, **characterized in that** the electrolytic cell is subjected to a voltage of between 1 and 120 V, and preferably of between 10 and 30 V.
5. Process according to any one of the preceding claims, **characterized in that** it has a duration of between 5 and 120 minutes, and preferably of between 5 and 30 minutes.
6. Process according to any one of the preceding claims, **characterized in that** it is preceded by a cleaning, deoxidizing and rinsing treatment for the workpiece to be anodized.
7. Process according to any one of the preceding claims, **characterized in that** it is followed by a rinsing and sealing treatment for the anodized workpiece.