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⑤ **Process for sealing anodised aluminium.**

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DE-A-1 944 452
FR-A-2 175 808
FR-A-2 370 110
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**The file contains technical information
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Description

This invention relates to a novel process for the treatment of anodised aluminium surfaces by immersing them in aqueous liquors.

5 The resistance of the surface of aluminium and aluminium alloys to corrosion and abrasion is conventionally improved by subjecting them to anodic oxidation so as to form a substantially anhydrous layer of adherent aluminium oxide. Surfaces which have been subjected to this treatment are referred to as having been "anodised". The anodising treatment can be carried out in a variety of ways, for example, by the application of direct current in dilute aqueous solutions of sulphuric acid, or organic acids such as
10 oxalic acid or mixtures thereof with sulphuric acid. These coatings can be coloured by immersion in a solution of a suitable dye or by treatment with alternating current in an electrolyte containing metal salts. Alternatively, the anodising can be carried out in solutions of organic acids such as sulphophthalic acid or sulphosalicylic acid or mixtures thereof with sulphuric acid.

The oxidised layer formed by these anodising treatments has a porous structure and is insufficiently
15 durable to fully protect the metal surface. For this reason the anodised metal is usually subjected to a further treatment known as sealing. Sealing is usually carried out by immersing the metal in hot or boiling water, which process is believed to cause the hydration of the substantially anhydrous aluminium oxide in the anodised layer thus causing a swelling of that layer which serves to seal the pores in its structure. Whatever the mechanism, the durability of the anodised surfaces is considerably increased by sealing.

20 One attendant disadvantage of sealing processes is that the treatment affects not only the pores in the oxide layer but also the surface of that layer. Sealed surfaces tend to have a layer of loosely adherent material formed at their surface, which layer is visually unattractive and also detracts from the useful properties of the metal. This surface layer which is commonly termed "smut" is usually removed prior to sale by mechanical or chemical treatment. The use of an alkaline sealing bath is known to significantly
25 accelerate the sealing process, but the problem of smut formation worsens as the alkalinity increases and sealing is normally carried out in baths which are slightly acidic, e.g. the pH of a sealing bath is normally maintained within the range 5.5 to 6.5 and sealing times of from 2 to 4 minutes per micrometer of thickness of the anodised layer are required to obtain adequate sealing (see for example *The Technology of Anodising Aluminium* by A. W. Brace and P. G. Sheasby publishers Technicopy Ltd., 2nd edition, 1979, p
30 224—5. Recently in an attempt to overcome the problem of smut formation a variety of additives to the sealing bath which are claimed to inhibit the formation of smut have been described, which additives will hereinafter be referred to as "anti-smutting additives". Examples of anti-smutting additives are the compounds disclosed in British Patents 1265465, 1302288, 1368336, 1398589, 1419957, 1574161 and British Patent Application 2104921. British Patent 1574161 mentions that the sealing bath, in which the additives
35 described therein are used, may have a pH of 4—8.

We have now discovered that the sealing of anodised coatings can be carried out rapidly and efficiently and without any significant smut formation by immersing the anodised surface in an aqueous medium containing an effective quantity of at least one selected smut inhibiting additive and having a pH of at least
40 7.0. Accordingly, from one aspect our invention provides a process for the hydrothermal sealing of anodised aluminium which comprises immersing the anodised surface in an aqueous medium at a temperature of at least 80°C wherein satisfactory sealing is effected without the formation of any substantial quantity of smut whilst immersing the surface in the aqueous medium for a period of not more than 2 minutes per micrometer of the thickness of the anodised layer and maintaining the pH of the
45 aqueous medium at a value of at least 7.0 and ensuring that the medium contains an effective quantity of a smut inhibiting additive.

The additives which are useful in the process of this invention are "anti-smutting additives" in that they are selected so as to avoid the formation of smut during the novel alkaline sealing process. They are distinguished from the known "anti-smutting additives" in that not all of the known additives are effective
50 in the novel alkaline sealing process and in that the smut-inhibiting additives need not be effective as anti-smutting additives in the acidic sealing processes of the prior art. For reasons of clarity the term "smut-inhibiting additives" will be used hereafter in relation to those additives which are effective in the novel sealing process of this invention.

The sealing process of the present invention is advantageous in that it is carried out under such conditions that a sealed coating of acceptable quality which is free from smut is obtained in a shorter time
55 than is attainable using comparable known sealing processes. Since the sealing bath must be maintained at an elevated temperature the energy required of the process is considerably reduced without the need to chemically or mechanically remove the smut. The present invention provides a sealing process wherein satisfactory sealing is achieved in not more than 2 minutes per micrometer of thickness of the anodised layer advantageously less than 1.5 minutes, preferably less than 1.25 and more preferably less than 1.00
60 minutes per micrometer at bath temperatures of 95°C or above. The rate of sealing may be less than this if the process is carried out at temperatures of less than 95°C. Generally the temperature of the sealing bath will be at least 80°C since the rate of sealing at lower temperatures than this is unacceptably slow. The sealing temperature is preferably between 95°C and the boiling point of the bath. Pressurised systems in which the temperature may be above 100°C, e.g. 110°C or even 115°C may be employed.

65 The process of the present invention is carried out under such conditions that no smut is formed during

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the sealing step. A smut-free product is one upon which no smut is visually detectable. Products which are deemed "smut-free" may carry small particles of smut which are detectable by careful scrutiny, but which do not detract from the appearance of the sealed article as a whole.

The process of the present invention is carried out under such conditions so as to seal the product to the desired degree.

Anodised aluminium which is to be used in architecture and exposed to weathering will normally be sealed as efficiently as is practicable in order to maximise its corrosion resistance. The quality of sealing may be evaluated using one or more of three classes of standard tests; the weight loss in acid test, the dyespot test and the conductivity test. These tests can be carried out using the following techniques.

Methods for measuring these criteria are laid down in the relevant British Standards. The methods used in this disclosure are

(i) Weight loss in phosphoric/chromic acid — BS6161: Part 3:1981 (ISO3210—1974). The maximum permissible loss in mass for the coating under test is commonly accepted at 30 mg/dm².

(ii) Dye adsorption — BS6161: Part 5:1982 (ISO 2413—1981) — using Acid A and Dye B an intensity of stain of 2 or less (rated according to BS6161: Parts 5:1982) is satisfactory.

(iii) Electrical conductivity BS1615: 1972 Appendix G — to take account of the variations in the thickness of the anodic film the result is expressed as the product of the conductivity in microsiemens and the thickness of the coating in micrometers which to satisfy BS 1615 should be less than 500.

Satisfactory and preferred levels of performance in these tests are set out in the following table.

	Acid Test mg/dm ²	Dyespot Test Intensity	Conductivity μs × μm
Adequate	30	2	500
Preferred	20	1	400
Most Preferred	10	0	300

For the purpose of this disclosure the criterion used to evaluate the quality of the seal is an at least adequate performance in the weight loss in acid test.

The pH of the sealing bath is at least 7.0 and more preferably at least 7.5 or 8.0. Higher pH's promote the rapid sealing of the anodised coating but may have detrimental effects upon the quality of that coating and also may encourage the formation of smut. The maximum pH of the bath will vary with its composition and the temperature of operation, but will generally be below 10.0, preferably below 9.5 and most preferably below 9.0. Thus, preferably, the pH of the sealing bath will be maintained at a value in the range 7.0 to 9.0, e.g. 7.5 to 8.5.

The compounds which are effective smut-inhibiting agents in the sealing process of the present invention must be water soluble and must not adversely effect the quality of the seal. Compounds which inhibit crystal growth in alkaline aqueous media when present in threshold quantities, e.g. from 1 to 1000 ppm are potentially valuable as smut-inhibiting additives although not all known threshold treatment agents are useful as smut-inhibiting additives in the process of the present invention either because they do not inhibit smut formation or because they retard the sealing process.

Not all compounds are equally effective as smut-inhibitors. Under conditions which are known to favour the formation of smut, e.g. high alkalinity and high temperatures, some compounds will not adequately suppress the formation of smut even when present in large quantities. However, such compounds may function adequately under less onerous conditions or may be useful in combination with other smut-inhibiting additives which are more effective under particular conditions. Smut inhibiting additives which may be useful in the process of the present invention can be selected from the group comprising dextrans (including commercial dextrans, especially those having a viscosity of 50 to 400 cP in 50% by weight solution at 20°C as measured with a Brookfield rotary viscometer, e.g. as described in British Patent 1302288); acrylic acid, methacrylic acid and water soluble polymers derived therefrom, especially those polymers having a specific viscosity of up to 0.75 cP measured at 20°C in 2N caustic soda and at a concentration of 0.7%, e.g. those described in British Patent 1368336, and lignin sulphonates (including all those described in British Patent 1368336); acids such as cycloaliphatic or aromatic polycarboxylic acid having from 4 to 6 carboxylic acid groups per molecule such as benzene penta carboxylic acid, benzene tetracarboxylic acid, benzene hexacarboxylic acid, cyclohexane tetracarboxylic acid and cyclohexane hexacarboxylic acid (in any of their various isomeric forms) or a water soluble salt thereof, e.g. the alkali metal, alkaline earth metal ammonium and alkanolamine salts especially those described in British Patent 1574161, certain hydroxy carboxylic acids for example gallic acid and saccharic acid; the reaction products of one or more sulphonated aromatic compounds with an aldehyde and/or dimethylol urea or a mixture of formaldehyde and urea (including all those which are described or disclosed in British Patent Application 2104921).

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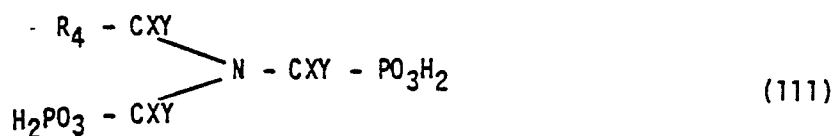
Other compounds which may be useful as smut-inhibiting additives include water-soluble phosphonic acids or one or more water-soluble salts of such acid each of which acid or salt forms one or more complexes with a divalent metal. A relatively large number of phosphonic acids are known which form complexes with divalent metals. It is preferred to use compounds which correspond to the following general formula:



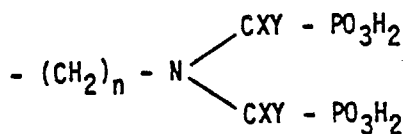
in which R represents a phenyl residue or alkyl residue with 1 to 5 carbon atoms, or those of the formula:



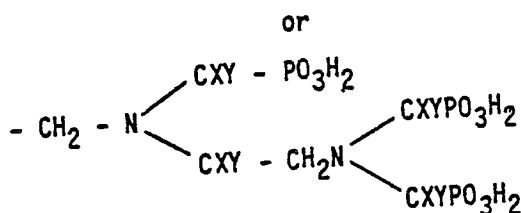
in which R₁ and R₂ each represent a hydrogen atom or alkyl residue with 1 to 4 carbon atoms, and R₃ represent a hydrogen atom or alkyl residue with 1 to 4 carbon atoms or a phenyl residue or those of the formula



in which X and Y each represents a hydrogen atom or an alkyl residue with 1 to 4 carbon atoms, R₄ represents a PO₃H₂ group or an alkyl group having from 1 to 18 carbon atoms or a group of the formula



where n is zero or an integer having a value of from 1 to 5 and X and Y are as hereinbefore defined.



wherein X and Y are as hereinbefore defined



wherein R_5 represents a hydrogen atom, a methyl group or a $-\text{CH}_2-\text{CH}_2-\text{COOH}$ group.

Examples of hydroxyalkanediphosphonic acids of Formula 1 which may be used are 1-hydroxypropane-, 1-hydroxybutane-, 1-hydroxypentane- and 1-hydroxyhexane-1,1-diphosphonic acid as well as 1-hydroxy-1-phenylmethane-1,1-diphosphonic acid and preferably 1-hydroxyethane-1,1-diphosphonic acid. Examples of phosphonic acids of the general formula 11 are 1-aminoethane-, 1-amino-1-phenylmethane-, dimethylaminoethane-, propyl- and butyl-aminoethane-1,1-diphosphonic acid. Examples of phosphonic acids of formula 111 are aminotrimethylene phosphonic acid, hexamethylenediaminetetra(methylene phosphonic) acid, ethylenediaminetetramethylenephosphonic acid, diethylenetriaminopentamethylenephosphonic acid, n-propylimino bis (methylene phosphonic) acid and aminotri(2-propylene-2-phosphonic acid). Examples of phosphonic acids of the general formula IV are phosphonosuccinic acid, 1-phosphono-1-methylsuccinic acid and 2-phosphonobutane-1,2,4 tricarboxylic acid.

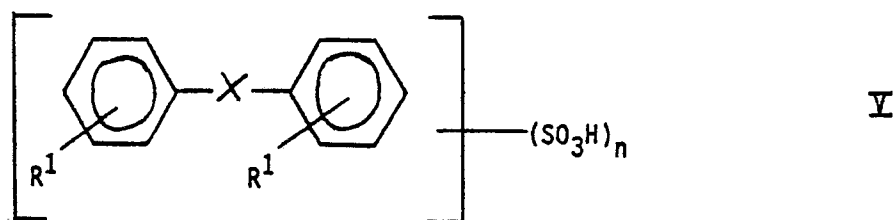
Especially valuable smut-inhibiting additives for use in the present invention are the phosphonic acids, especially ethylenediaminetetramethylenephosphonic acid, hexamethylenediaminetetra(methylene phosphonic) acid, n-propyliminobis(methylene phosphonic) acid and benzene hexacarboxylic acid and salts thereof and the reaction products of sulphonated aromatic compounds with an aldehyde and/or dimethylolurea or a mixture of formaldehyde and urea especially those products formed by the reaction of the sulphonation products of diphenyl, phenyltoluene, dimethyldiphenyl, diphenylether, diphenylsulphide, diphenylsulphoxide, dihydroxydiphenylsulphone, diphenylene oxide, diphenylene sulphide and bis phenol with an aldehyde and/or dimethylolurea or a mixture of formaldehyde and urea or where the sulphonated aromatic compound is a sulphonated derivative of phenol, cresol or naphthol the reaction products thereof with dimethylolurea or a mixture of formaldehyde and urea.

The preferred sulphonated aromatic compounds are sulphonated diphenyl, dimethyldiphenyl, diphenyl ether and additionally, when reacted with dimethylolurea (or a mixture of formaldehyde and urea), unsubstituted phenol and cresol.

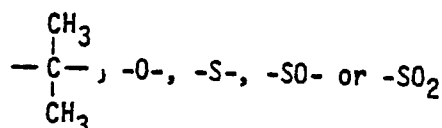
Preferred aldehydes used in the preparation of the reaction product are acetaldehyde and formaldehyde, more preferably formaldehyde.

Preferably where the reaction product is formed with a mixture of formaldehyde and urea, the molar ratio of formaldehyde to urea is at least 2:1.

Preferred reaction products are those formed by the reaction of formaldehyde with a compound containing no halogen or hydroxyl groups, or the reaction of sulphonated phenols with dimethylolurea. More preferred is the reaction product of formaldehyde with a compound of formula V



in which R represents a hydrogen atom an alkyl group having 1 to 4 carbon atoms, a hydroxyl group or a halogen atom X represents a direct bond or a group of the formula



and n has an average value in the range 1 to 4.

When the mixture to form the reaction product is sulphonated phenol, cresol or naphthol with dimethylolurea (or a mixture of formaldehyde and urea) further compounds such as phenols and naphthols may be included into the product by polymerisation with formaldehyde.

The sulphonated aromatic compounds are known and may be made according to known methods. For the sulphonation reaction of compounds of formula V one uses preferably 1—2 moles (more preferably 1.5

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moles) of sulphuric acid per mole of the aromatic compound to be sulphonated at a temperature of from 80 to 180°C in the presence of a sulphonating medium.

The reaction of a compound of formula V with formaldehyde or dimethylolurea is known and may be carried out in accordance with known methods.

The phosphonic acid smut-inhibiting additives must be used in combination with a divalent metal ion M^{2+} in a molar ratio of at least $2M^{2+}:1$ phosphonate group in order to be effective, i.e. the molar proportion of divalent metal ions must be at least sufficient as is theoretically required to form a complex with all of the phosphonate groups present. If the necessary quantity of divalent metal ions is not present in the sealing bath, e.g. in the form of calcium and magnesium salts dissolved in tap water, it is necessary to add a sufficient quantity of a soluble salt of a divalent metal to raise the molar ratio of metal ions to phosphonate groups to at least 2:1. Preferably the molar ratio of divalent metal ions to phosphonate group is at least 4:1.

In some instances certain divalent metal ions appear to deactivate the phosphonate. Where this effect is observed a sufficient quantity of phosphonate can be added which will form a complex with the deactivating metal ion. Thereafter the addition of a further quantity of phosphonate together with the appropriate quantity of a salt of an acceptable divalent metal will be effective in inhibiting smut formation. In general we prefer to use salts of calcium magnesium, nickel or cobalt as the divalent metal salt. Examples of ions which may deactivate the phosphonate and whose presence is thereby less preferred are ferric ions and cupric ions. In general ions which complex strongly with the phosphonate appear to deactivate it as a smut-inhibiting agent and their presence is correspondingly less preferred. The use of ethylenediamino tetramethylene phosphonic acid or its water soluble salts as a smut-inhibiting agent especially its magnesium salt is particularly preferred.

The quantity of anti-smutting agent which is present in the bath varies with the nature of that agent. The quantity which is sufficient to suppress smut formation in a particular sealing process and the minimum effective quantity will normally be determined empirically. When the formation of a sealed anodised surface of a satisfactory quality is accompanied by the formation of smut it is necessary to adjust one or more of the parameters which effect the efficiency of the bath, e.g. by increasing quantity of smut-inhibiting additive in the bath or to select a more effective smut-inhibiting additive.

By way of example, the quantity of some of the preferred anti-smutting agents e.g. benzene hexacarboxylic acid, 1-hydroxyethane-1-1 diphosphonic acid, and ethylenediaminetetramethylenephosphonic acid will be in the range 1 to 500 ppm of the bath, e.g. 2 to 300 and more preferably 5 to 200 ppm of the bath. The reaction product of sulphonated aromatic compounds with an aldehyde and/or dimethylolurea (or a mixture of formaldehyde and urea) will preferably be present in a quantity of from 0.01 to 5.0 gms/litre of the bath. The effective quantity will vary according to the anti-smutting agent which is selected and will normally be determined empirically under the conditions which are to be employed in the sealing process. For the preferred anti-smutting agents the quantity will be from 5 to 500 ppm in the case of benzene hexacarboxylic acid, from 5 to 100 ppm in the case of ethylenediaminetetramethylenephosphonic acid. The use of excessive quantities of anti-smutting additives may have a detrimental effect upon the quality of the anodised coating and is thereby preferably avoided. Where the pH of the bath is relatively high the maximum amount of a particular anti-smutting agent which may be tolerated without damage to the anodised coating will be increased.

In order to maintain the pH of the sealing bath above 7.0 and preferably within the preferred ranges set out above, it will usually be necessary to add a quantity of a water-soluble base to the sealing bath. The preferred bases for present use are Lewis bases. Examples of suitable bases are triethanolamine, sodium borate, sodium carbonate, sodium bicarbonate, mono-ethanolamine, diethanolamine and hexamine or mixtures thereof. The most preferred base for present use is triethanolamine. Commercial grades of triethanolamine which contain minor quantities of diethanolamine and monoethanolamine may be used if desired. The addition of a base which might inhibit the sealing process should preferably be avoided. Thus, bases which liberate phosphate silicate and fluoride ions on dissolution in water are preferably not employed.

The sealing process of the present invention may be carried out in demineralised water or in tap water. The use of demineralised water is advantageous in that the sealing process is more likely to proceed without complication. However, in a commercial operating process the bath will inevitably become contaminated by the carry-over of material from previous processing steps, e.g. the anodising bath and subsequent rinsing steps. Although a certain amount of this contamination may be tolerated the efficiency of the sealing process is decreased and eventually the bath must be discarded.

The use of tap water to make up the bath may be disadvantageous in that the minerals which are dissolved in it may affect the efficiency of the sealing process. The presence of dissolved minerals may also lead to the precipitation of solid material in the sealing bath which can form an unsightly crusted coating upon the anodised surface. This tendency is most common when the anti-smutting agent comprises a phosphonic acid or a phosphonate as hereinbefore described. Although the deposited solids can usually be removed by rinsing with water, it is preferred to operate the sealing bath under such conditions as will avoid the need for such a rinsing step. We have discovered that this tendency to the formation of solid material can be reduced by the addition of a surface active agent to the bath. The quantity of such a compound may vary through a wide range say 1 ppm to 10 gms/litre. The preferred additive is carboxymethylcellulose, hereinafter referred to as CMC. The addition of from 5 ppm to 100 ppm of CMC will often

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be sufficient to prevent the formation of solid material in the bath.

The sealing bath may also contain conventional additives e.g. additives which are known to inhibit the leaching of dye such as nickel acetate. The bath may also advantageously contain a wetting agent, the presence of which enhances the efficiency of the sealing process. Relatively small quantities of wetting agent, say wetting agent, say from 2.0 to 2000 ppm of the bath may be employed. Where heavy metal ions are present in the bath whether by addition, e.g. of tap water or by contamination from other parts of the anodising plant, which ions interfere with the efficiency of the sealing process, the efficient operation of the bath may be prolonged by the addition of an agent which is capable of complexing with the metal. An example of a suitable agent is citric acid. Such agents may be effective when present in quantities which are significantly less than would be required to complex the metal ions which are present in the bath. The baths may also advantageously contain a buffering agent to assist the control of the pH. Suitable buffering agents include salts of acetic acid and formic acid.

The various ingredients of the sealing bath may be added separately if so desired. It is preferred by way of convenience to formulate the various additives as a separate concentrate and then add that concentrate to the bath. Concentrates, when added to water, form a sealing bath useful in the process of the present invention.

Such concentrates comprise at least one anti-smutting agent, as hereinbefore defined, and at least one base, as hereinbefore defined. Optional ingredients include salts of organic acids such as acetic acid to regulate the pH thereof, other additives such as nickel acetate and any other compatible ingredients of the bath. Additives such as nickel acetate are preferably solubilised in the concentrate e.g. by the addition of triethanolamine to form a water soluble complex.

In a preferred embodiment of the process of the present invention the pH of the sealing bath is established by the addition of such a concentrate to water and maintained within the desired limits by the addition of further quantities of reagents as the sealing operation progresses.

The invention is illustrated by the following examples:—

In the Examples the sealing baths were assessed using the methods hereinbefore described and in addition by visually inspecting the sealed product the visible presence of any velvety bloom being regarded as unsatisfactory.

In these examples the pieces used were formed of Type 6063 aluminium alloy which had been alkaline etched (5% NaOH + additives) and anodised in sulphuric acid (175 gms/litre at 18—20°C and 1.5A/dm²) to provide an anodic film of 20 microns thickness.

Each test was carried out on uncoloured specimens for measurement of sealing quality and on replicate specimens which were black dyed prior to sealing (using standard anodising dye) to aid detection of surface films of bloom.

Example 1

Comparative

(A) Standard Demineralised Water Sealing
pH of bath = 6.0. Bath Temperature = 98°C

Sealing Time (mins. per microns)	Admittance	Dyespot	Acid wt. Loss	Finish
0.5	926	4	62	Heavy Bloom
1.0	520	1—2	34	Heavy Bloom
2.0	333	1	25	Heavy Bloom
4.0	278	1	18	Heavy Bloom

Smut observed after 0.5 min/micrometer.

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Comparative

(B) Demineralised Water + 2 mls/litre triethanolamine adjust to pH 8.0 with acetic acid
pH of bath = 8.0. Bath Temperature = 98°C

5	Sealing Time	Admittance	Dyespot	Acid wt. Loss	Finish
	0.5	900	1—2	35	Bloom
10	1.0	400	1	22	Bloom
	2.0	300	1	16	Bloom

Smut formed after less than 0.5 min/micrometer.

Example of Invention

(C) To the bath of (B) was added 20 ppm of the ammonium salt of ethylenediamine-tetra (methylenephosphonic) acid and 10 ppm of nickel in the form of nickel sulphate.

20	Sealing Time	Admittance	Dyespot	Acid wt. Loss	Finish
	0.5×	800	0—1	31	No Bloom
25	1.0	400	0	24	No Bloom
	2.0	280	0	17	No Bloom

× comparison.
No smut observed.

Example 2

Comparative

(A) South Staffordshire Tap Water of total hardness expressed as CaCO₃ of 150 ppm.
pH of bath = 6.0. Bath Temperature = 98°C

35	Sealing Time	Admittance	Dyespot	Acid wt. Loss	Finish
40	1.0	2000	4	68	Heavy Bloom
	2.0	900	2	41	Heavy Bloom

Smut present throughout

Examples of Invention

(B) To the bath used in (A) was added 2 mls/litre of triethanolamine and 40 ppm of ethylenediamine tetra (methylenephosphonic) acid.
pH of bath = 8.2. Bath Temperature = 98°C

50	Sealing Time	Admittance	Dyespot	Acid wt. Loss	Finish
	0.5×	2000	4	64	No Bloom
55	1.0	480	1—2	29	No Bloom
	2.0	300	1	22	No Bloom

× comparison
No smut observed

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Example 3

Demineralised water with mellitic acid (benzene hexacarboxylic acid) added in the quantities shown. The pH of the bath was raised by the addition of triethanolamine.

Conc. mg/litre	pH	Time Mins.micro- meter	Admittance	Dyespot	Acid wt. loss	Finish
100	5.8	1.0	800	2—3	48	No bloom
100	5.8	2.0	300	1—2	36	No bloom
100	8.5	1.0	500	1	30	No bloom

The first two results illustrate comparative procedures. The seal obtained in the time used is not of adequate quality. The third result is an Example according to the invention showing satisfactory sealing is obtained in a significantly shorter time.

Example 4

Comparative

Demineralised water with ethylene diamine tetrakis (methylene phosphonic) acid. EDTMPA added as a smut-inhibitor. pH = 8.3. Sealing Time = 1 min/micrometer.

Conc'n mg/litre	Admittance	Dyespot	Acid wt. loss	Finish
10	460	0—1	16	Heavy Bloom
40	460	0—1	26	Heavy Bloom
100	500	0—1	23	Heavy Bloom

These results show that the phosphonate is ineffective as a smut-inhibitor in the absence of divalent metal ions.

Example of Invention

Sufficient magnesium salt added to provide a molar ratio of EDTMPA: Mg²⁺ of 1:4.

Conc. mg/litre	pH	Admittance	Dyespot	Acid wt. Loss	Finish
20	8.6	489	0	18	No Bloom
40	8.5	422	0	24	No Bloom
60×	8.2	400	1	54	No Bloom
60	8.7	293	0	24	No Bloom

× comparative

These results show that the phosphonate is effective as a smut-inhibitor in the presence of divalent metal ions.

The results at a concentration of 60 mg/litre illustrate the reduction of the quality of the seal produced by excessive quantities of smut-inhibitor and how this effect can be overcome by raising the pH of the bath.

Example 5

(of Invention)

A set quantity of one of three phosphonates A, B and C was added to a sealing bath comprising demineralised water together with sufficient magnesium ion to give a molar ratio of phosphonate:Mg = 1:4. The sealing time was 1 min/micrometer.

A = Hexamethylenediaminetetrakis (methylene phosphonic) acid.

B = Diethylenetriaminepentakis (methylene phosphonic) acid.

C = n-propyliminobis(methylenephonic) acid.

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Compound	Conc. mg/litre	pH	Admittance	Dyespot	Acid wt. loss	Finish
A	20	8.5	400	0—1	23	No Bloom
B	20	8.5	400	0—1	29	No Bloom
C	20	8.5	440	0—1	30	No Bloom

All these additives are effective as smut inhibitors.

Example 6

A commercial product sold under the Trade Name ANODAL SH1* by the Sandoz Company was added to demineralised water in varying quantities to form sealing baths. The baths were tested at various pH's and various sealing times, as shown in the following tabular summary of results.

*ANADOL SH1 is an aqueous solution comprising a reaction product of a sulphonated aromatic compound with an aldehyde or dimethylolurea (or a mixture of formaldehyde and urea).

Sealing Time Mins/micrometers	Conc. mls/litre	pH	Acid wt. loss	Finish
1×	2	5.6	38	No Bloom
2×	2	5.6	19	No Bloom
1×	5	5.6	34	No Bloom
2×	5	5.6	28	No Bloom
1	2	8.3	28	No Bloom
1	5	8.3	23	No Bloom
1	10	8.3	29	No Bloom

× Comparative

Claims

1. A process for the hydrothermal sealing of the surface of anodised aluminium which comprises immersing the anodised surface in an aqueous medium at a temperature of at least 80°C wherein satisfactory sealing is effected without the formation of any substantial quantity of smut whilst immersing the surface in the aqueous medium for a period of not more than 2 minutes per micrometer of the thickness of the anodised layer and maintaining the pH of the aqueous medium at a value of at least 7.0 and ensuring that the medium contains an effective quantity of a smut inhibiting additive.

2. A process according to claim 1, characterised in that satisfactory sealing is effected in a time which is not more than 1.5 minutes per micrometer of the thickness of the anodised layer.

3. A process according to either of claims 1 and 2, characterised in that the sealing bath comprises one or more compounds selected from the group comprising dextrans, acrylic acid, methacrylic acid, water-soluble polymers derived from acrylic acid or methacrylic acid lignin sulphonates; cycloaliphatic or aromatic polycarboxylic acids and cyclohexane hexacarboxylic acids, water-soluble phosphonic acids which are capable of forming complexes with a divalent metal and the reaction product of one or more sulphonated aromatic compounds with an aldehyde and/or dimethylolurea or a mixture of formaldehyde and urea.

4. A process according to claim 3, characterised in that the sealing bath comprises a water soluble phosphonic acid together with a divalent metal ion.

5. A process according to claim 4, characterised in that the phosphonic acid is selected from the group comprising 1 hydroxypropane 1, 1 diphosphonic acid, 1-hydroxybutane 1, 1 diphosphonic acid, 1-hydroxy 1-phenylmethane-1, 1 diphosphonic acid, 1 hydroxyethane 1, 1 diphosphonic acid, 1 aminoethane 1, 1 diphosphonic acid, 1 amino-1-phenyl methane 1, 1 diphosphonic acid, dimethylaminoethane-1,1-diphosphonic acid, propylaminoethane 1,1 diphosphonic acid, butylamino ethane-1,1-diphosphonic acid, amino trimethylenephosphonic acid ethylenediaminetetramethylenephosphonic acid, diethylenetriamino-pentamethylene phosphonic acid, hexamethylene diamine tetra(methylenephosphonic) acid, n-propyl-aminobis(methylenephosphonic) acid, aminotri-(2-propylene-2-phosphonic acid, phosphonosuccinic acid,

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1-phosphono-1-methylsuccinic acid and 1-phosphono-butane-1,2,4-tricarboxylic acid.

6. A process according to claim 5, characterised in that the phosphonate is selected from the group comprising ethylenediamino tetramethylene phosphonic acid hexamethylene diamine tetra (methylenephosphonic) acid and n-propylimino bis-(methylenephosphonic) acid.

7. A process according to claim 3, characterised in that the bath comprises benzene hexacarboxylic acid.

8. A process according to 7, characterised in that the bath contains from 5 to 500 ppm of benzene hexacarboxylic acid.

9. A process according to either of claims 7 or 8, characterised in that the bath is maintained at a pH of from 7.0 to 10.0.

10. A process according to any of claims 1 to 6, characterised in that the bath comprises at least one divalent metal ion and a phosphonate in a molar ratio of at least 2:1.

11. A process according to claim 10, characterised in that the molar ratio of divalent metal ions to phosphonate ions is at least 4:1.

12. A process according to either of claims 10 or 11, characterised in that the divalent metal ion is selected from the group comprising calcium, magnesium, nickel or cobalt.

13. A process according to claim 12, characterised in that the divalent metal ion is magnesium.

14. A process according to any of claims 1 to 6 and 9 to 13, characterised in that the pH of the bath is from 7.0 to 10.0.

15. A process according to claim 14, characterised in that the pH of the bath is from 7.0 to 9.0.

16. A process according to any of claims 1 to 6 and 9 to 15, characterised in that the smut-inhibiting agent is present in a quantity of from 1 to 500 ppm.

17. A process according to claim 16, characterised in that the smut inhibiting agent is present in a quantity of from 5 to 100 ppm.

18. A process according to claim 3, characterised in that sealing bath comprises one or more of the products formed by the reaction of the sulphonation products of diphenyl, phenyltoluene, dimethyldiphenyl, diphenylether, diphenylsulphide, diphenylsulphoxide, dihydroxydiphenylsulphone, diphenylene oxide, diphenylenesulphide and bisphenol with an aldehyde and/or dimethylolurea or a mixture of formaldehyde and urea or where the sulphonated aromatic compound is a sulphonated derivative of phenol, cresol or naphthol the reaction products thereof with dimethylolurea.

19. A process according to claim 18, characterised in that the sealing bath contains from 0.01 to 5.0 gms/litre of the reaction product.

20. A process according to any of the preceding claims characterised in that the sealing bath comprises a surface active agent.

21. A process according to claim 20, characterised in that the surface active agent is carboxymethylcellulose.

22. A process according to claim 18, characterised in that the bath contains from 5 to 100 ppm of carboxymethyl cellulose.

Patentansprüche

1. Verfahren zur hydrothermalen Versiegelung der Oberfläche von anodisiertem Aluminium, bei welchem die anodisierte Oberfläche bei einer Temperatur von mindestens 80°C in ein wässriges Medium getaucht wird, in dem eine ausreichende Versiegelung ohne Bildung einer wesentlichen Menge an Belag hervorgerufen wird, wobei die Oberfläche in das wässrige Medium während eines Zeitraums von nicht mehr als 2 Minuten pro Mikrometer Dicke der anodisierten Schicht getaucht, der pH-Wert des wässrigen Mediums auf einem Wert von mindestens 7,0 gehalten und gewährleistet wird, daß das Medium eine wirksame Menge eines belagsverhindernden Additivs enthält.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß eine zufriedenstellende Versiegelung in einer Zeit durchgeführt wird, die nicht mehr als 1,5 Minuten pro Mikrometer Dicke der anodisierten Schicht beträgt.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Versiegelungsbad eine oder mehrere Verbindungen enthält, die ausgewählt sind aus der Gruppe umfassend Dextrine, Acrylsäure, Methacrylsäure, wasserlösliche Polymere von Acrylsäure oder Methacrylsäure, Ligninsulfonate; cycloaliphatische oder aromatische Polycarbonsäuren und Cyclohexanhexacarbonsäuren, wasserlösliche Phosphonsäuren, die zur Komplexbildung mit einem zweiwertigen Metall befähigt sind, und das Reaktionsprodukt von einer oder mehreren sulfonierten aromatischen Verbindungen mit einem Aldehyd und/oder Dimethylharnstoff oder einer Mischung aus Formaldehyd und Harnstoff.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß das Versiegelungsbad eine wasserlösliche Phosphonsäure gemeinsam mit einem zweiwertigen Metallion enthält.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß die Phosphonsäure ausgewählt ist aus der Gruppe umfassend 1-Hydroxypropan-1,1-diphosphonsäure, 1-Hydroxybutan-1,1-diphosphonsäure, 1-Hydroxy-1-phenylmethan-1,1-diphosphonsäure, 1-Hydroxyethan-1,1-diphosphonsäure, 1-Aminoethan-1,1-diphosphonsäure, 1-Amino-1-phenylmethan-1,1-diphosphonsäure, Dimethylaminoethan-1,1-diphosphonsäure, Propylaminoethan-1,1-diphosphonsäure, Butylaminoethan-1,1-diphosphonsäure, Aminotri-

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methylenphosphonsäure, Ethylendiaminotetramethylenphosphonsäure, Diethylentriaminopentamethylenphosphonsäure, Hexamethylendiamintetra(methylenphosphon)säure, n-Propyliminobis(methylenphosphon)säure, Aminotri-(2-propylen-2-phosphonsäure, Phosphonobernsteinsäure, 1-Phosphono-1-methylbernsteinsäure und 1-Phosphonobutan-1,2,4-tricarbonsäure.

5 6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß das Phosphonat ausgewählt ist aus der Gruppe umfassend Ethylendiaminotetramethylenphosphonsäure, Hexamethylendiaminotetra(methylenphosphon)säure und n-Propylimino-bis-(methylenphosphon)säure.

7. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß das Bad Benzolhexacarbonsäure enthält.

10 8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das Bad 5 bis 500 ppm Benzolhexacarbonsäure enthält.

9. Verfahren nach Anspruch 7 oder 8, dadurch gekennzeichnet, daß das Bad bei einem pH-Wert von 7,0 bis 10,0 gehalten wird.

15 10. Verfahren nach irgendeinem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Bad zumindest ein zweiwertiges Metallion und ein Phosphonat in einem Molverhältnis von zumindest 2:1 enthält.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das Molverhältnis der zweiwertigen Metallionen zu den Phosphonationen mindestens 4:1 beträgt.

12. Verfahren nach einem der Ansprüche 10 oder 11, dadurch gekennzeichnet, daß das zweiwertige Metallion ausgewählt wird aus der Gruppe umfassend Calcium, Magnesium, Nickel oder Cobalt.

20 13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß das zweiwertige Metallion Magnesium ist.

14. Verfahren nach irgendeinem der Ansprüche 1 bis 6 und 9 bis 13, dadurch gekennzeichnet, daß der pH-Wert des Bades zwischen 7,0 und 10,0 liegt.

25 15. Verfahren nach Anspruch 14, dadurch gekennzeichnet, daß der pH-Wert des Bades zwischen 7,0 und 9,0 liegt.

16. Verfahren nach irgendeinem der Ansprüche 1 bis 6 und 9 bis 15, dadurch gekennzeichnet, daß das belagsverhindernde Mittel in einer Menge von 1 bis 500 ppm vorliegt.

17. Verfahren nach Anspruch 16, dadurch gekennzeichnet, daß das belagsverhindernde Mittel in einer Menge von 5 bis 100 ppm vorliegt.

30 18. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß das Versiegelungsbad ein oder mehrere Produkte aus der Reaktion der Sulfonierungsprodukte von Diphenyl, Phenyltoluol, Dimethyldiphenyl, Diphenylether, Diphenylsulfid, Diphenylsulfoxid, Dihydroxydiphenylsulfon, Diphenylenoxid, Diphenylensulfid und Bisphenol mit einem Aldehyd und/oder Dimethylolharnstoff oder einer Mischung von Formaldehyd und Harnstoff oder, wenn die sulfonierte aromatische Verbindung ein sulfoniertes Derivat von Phenol, Kresol oder Naphthol ist, dessen Reaktionsprodukte mit Dimethylolharnstoff enthält.

35 19. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß das Versiegelungsbad 0,01 bis 5,0 g/l des Reaktionsproduktes enthält.

20. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Versiegelungsbad ein oberflächenaktives Mittel enthält.

40 21. Verfahren nach Anspruch 20, dadurch gekennzeichnet, daß das oberflächenaktive Mittel Carboxymethylcellulose ist.

22. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß das Bad 5 bis 100 ppm Carboxymethylcellulose enthält.

45 Revendications

1. Procédé pour le colmatage hydrothermique de la surface d'aluminium anodisé qui comprend l'immersion de la surface anodisée dans un milieu aqueux à une température d'au moins 80°C dans lequel un colmatage satisfaisant est effectué sans formation d'aucune quantité substantielle de saleté, au cours duquel on immerge la surface dans le milieu aqueux durant une période de pas plus de 2 minutes par micromètre de l'épaisseur de la couche anodisée, on maintient le pH du milieu aqueux à une valeur d'au moins 7,0 et on s'assure que le milieu contient une quantité efficace d'un additif inhibiteur de saleté.

50 2. Procédé selon la revendication 1, caractérisé en ce qu'un colmatage satisfaisant est effectué en une période de temps qui n'est pas supérieure à 1,5 minutes par micro mètre de l'épaisseur de la couche anodisée.

3. Procédé selon n'importe laquelle des revendications 1 et 2, caractérisé en ce que le bain de colmatage comprend un ou plusieurs composés choisis parmi le groupe consistant en dextrans, acide acrylique, acide méthacrylique, polymères solubles dans l'eau dérivés d'acide acrylique ou d'acide méthacrylique, des sulfonates de lignine; des acides polycarboxyliques aromatiques ou cycloaliphatiques et des acides cyclohexane hexacarbonyliques, des acides phosphoniques solubles dans l'eau qui sont capables de former des complexes avec un métal divalent et le produit de la réaction de un ou plusieurs composés aromatiques sulfonés avec un aldéhyde et/ou la diméthylolurée ou un mélange de formaldéhyde et d'urée.

65 4. Procédé selon la revendication 3, caractérisé en ce que le bain de colmatage comprend un acide phosphonique soluble dans l'eau en même temps qu'un ion de métal divalent.

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5. Procédé selon la revendication 4, caractérisé en ce que l'acide phosphonique est choisi parmi le groupe consistant en acide 1-hydroxypropane-1,1-diphosphonique, acide 1-hydroxybutane-1,1-diphosphonique, acide 1-hydroxy-1-phénylméthane-1,1 diphosphonique, acide 1-hydroxyéthane-1,1-diphosphonique, acide 1-aminoéthane-1,1-diphosphonique, acide 1-amino-1-phényl-méthane-1,1 diphosphonique, acide diméthylaminoéthane-1,1-diphosphonique, acide propylaminoéthane-1,1-diphosphonique, acide butylamino-éthane-1,1-diphosphonique, acide amino-triméthylène phosphonique, acide éthylènediaminotétraméthylène phosphonique, acide diéthylènetriaminopentaméthylène phosphonique, acide hexaméthylène-diaminotétraméthylène phosphonique, acide n-propyliminobis-(méthylène phosphonique), acide aminotri-(2-propylène-2-phosphonique), acide phosphosuccinique, acide 1-phosphono-1-méthylsuccinique et acide 1-phosphono-butane-1,2,4-tricarboxylique.

6. Procédé selon la revendication 5, caractérisé en ce que le phosphonate est choisi parmi le groupe consistant en acide éthylènediamino-tétraméthylène-phosphonique, acide hexaméthylène-diamine-tétraméthylène phosphonique) et acide n-propylimino-bis-(méthylène phosphonique).

7. Procédé selon la revendication 3, caractérisé en ce que le bain comprend de l'acide benzène-hexacarboxylique.

8. Procédé selon la revendication 7, caractérisé en ce que le bain contient de 5 à 500 ppm d'acide benzènehexacarboxylique.

9. Procédé selon n'importe laquelle des revendications 7 ou 8, caractérisé en ce que le bain est maintenu à un pH de 7,0 à 10,0.

10. Procédé selon n'importe laquelle des revendications 1 à 6, caractérisé en ce que le bain comprend au moins un ion de métal divalent et un phosphonate en un rapport molaire d'au moins 2:1.

11. Procédé selon la revendication 10, caractérisé en ce que le rapport molaire entre les ions de métal divalent et les ions phosphonates est d'au moins 4:1.

12. Procédé selon n'importe laquelle des revendications 10 ou 11, caractérisé en ce que l'ion de métal divalent est choisi parmi le groupe consistant en calcium, magnésium, nickel ou cobalt.

13. Procédé selon la revendication 12, caractérisé en ce que l'ion de métal divalent est magnésium.

14. Procédé selon n'importe laquelle des revendications 1 à 6 et 9 à 13, caractérisé en ce que le pH du bain est de 7,0 à 10,0.

15. Procédé selon la revendication 14, caractérisé en ce que le pH du bain est de 7,0 à 9,0.

16. Procédé selon n'importe laquelle des revendications 1 à 6 et 9 à 15, caractérisé en ce que l'agent inhibiteur de souillure est présent en une quantité de 1 à 500 ppm.

17. Procédé selon la revendication 16, caractérisé en ce que l'agent inhibiteur de souillure est présent en une quantité de 5 à 100 ppm.

18. Procédé selon la revendication 3, caractérisé en ce que le bain de colmatage comprend un ou plusieurs produits formés par la réaction des produits de sulfonation du diphenyle, phényltoluène, diméthylidiphényle, diphényléther, diphénylsulfure, diphénylsulfoxyde, dihydroxydiphénylsulfone, diphénylène oxyde, diphénylènesulfure et bisphénol avec un aldéhyde et/ou la diméthylolurée ou un mélange de formaldéhyde et d'urée ou, quand le composé sulfoné aromatique est un dérivé sulfoné du phénol, du cresol ou du naphthol, leurs produits de réaction avec la diméthylolurée.

19. Procédé selon la revendication 18, caractérisé en ce que le bain de colmatage contient de 0,01 à 5,0 g/litre du produit de réaction.

20. Procédé selon n'importe laquelle des revendications précédentes, caractérisé en ce que le bain de colmatage comprend un agent tensio-actif.

21. Procédé selon la revendication 20, caractérisé en ce que l'agent tensio-actif est la carboxyméthylcellulose.

22. Procédé selon la revendication 18, caractérisé en ce que le bain contient de 5 à 100 ppm de carboxyméthyl cellulose.