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(54) Process for sealing anodised aluminium.

(57) Processes for sealing anodised aluminium carried out in a bath having a pH of at least 7 and in the presence of a smut,inhibiting additive have been discovered to give rapid, efficient sealing without the formation of bloom. Examples of smut-inhibiting additives are phosphonates, benzene hexacarboxylic acid, and the reaction products of an aldehyde or dimethylol urea with sulphonated aromatic compounds. The reduction in time required for sealing reduces energy consumption in the anodising operation.

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This invention relates to novel processes for the treatment of anodised aluminium surfaces by immersing them in aqueous liquors, and to novel compositions for addition to said liquors, and to novel liquors in which the aluminium is immersed.

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 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 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.

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 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 micron of thickness of the anodised layer are required to obtain adequate sealing. 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 1265424, 1302288, 1368336, 1398589,1419597, 1574161 and British Patent Application 2104921.

We have now discovered that the sealing of anodised coatings can be carried out rapidly, efficiently and without any significant smut formation by immersing the anodised surface in an aqueous medium containing at least one selected smut inhibiting additive and having a pH of at least 7.0. Accordingly, from one aspect our invention provides a method for treating the surface of anodised aluminium which comprises immersing said surface in an aqueous medium having a pH of at least 7.0 and an effective quantity of at least one smut-inhibiting additive.

The additives which are useful in the processes 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 processes. They are distinguished from the known "anti-smutting additives" in that not all of the known additives are effective in the novel alkaline sealing processes 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 processes of this invention.

The sealing processes of the present invention are advantageous in that they are carried out under such conditions that a sealed coating of acceptable quality which is free from smut is obtained in a shorter time than is attainable using comparable known sealing processes. Since the sealing bath must be maintained at an elevated temperature the energy requirement of the process is considerably reduced without the need to chemically or mechanically remove the smut. The present invention provides sealing processes wherein satisfactory sealing is achieved in less than 1.5 minutes per micron of thickness of the anodised layer, preferably less than 1.25 and more preferably less than 1.00 minutes per micron at bath temperatures of 95^{O}C or above. The rate of sealing may be less than this if the processes are carried out at temperatures of less than 95^{O}C. Generally the temperature of the sealing bath will be at least 80^{O}C since the rate of sealing at lower temperatures than this is unacceptably slow. The sealing temperature is preferably between 95^{O}C and the boiling point of the bath. Pressurised systems in which the temperature may be above 100^{O}C, e.g. 110^{O}C or even 115^{O}C may be employed.

The processes of the present invention are carried out under such conditions that no smut is formed during 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 processes of the present invention are 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 as 30 mg/dm^2.

(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 microns 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 us x um
Adequate	30	2	500
Preferred	20	1	400
Most Preferred	10	0	300

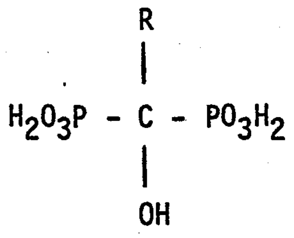
For the purpose of this disclosure the criterion used to evaluate the quality of the seal is an at least adequate performance in the weight loss in acid test.

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, peferably 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 processes 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 processes of the present invention can be selected from the group comprising dextrins (including commercial dextrins, especially those having a viscosity of 50 to 400cP in 50% by weight solution at 20^{o}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 0.75cP measured at 20^{o}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).

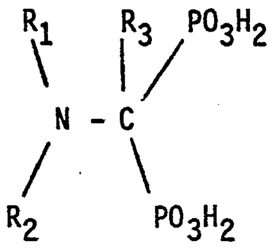
Other compounds which may be useful as smut-inhibiting additives include water-soluble phosphonic acids or one or more water-soluble salts of such acid each of which acid or salt forms one or more complexes with a divalent metal. A relatively large number of phosphonic acids are known which form complexes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



$$H_2O_3P - \overset{\displaystyle R}{\underset{\displaystyle OH}{C}} - PO_3H_2$$

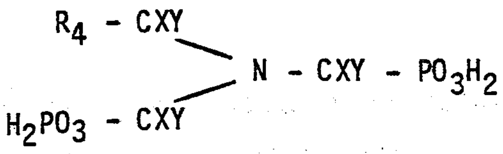
(1)

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



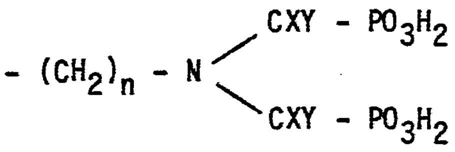
(11)

in which R_1 and R_2 each represent a hydrogen atom or alkyl residue with 1 to 4 carbon atoms, and R_3 represent a hydrogen atom or alkyl residue with 1 to 4 carbon atoms or a phenyl residue or those of the formula



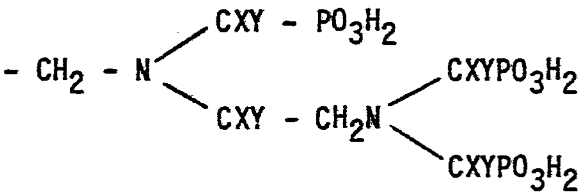
(111)

in which X and Y each represents a hydrogen atom or an alkyl residue with 1 to 4 carbon atoms, R_4 represents a PO_3H_2 group or an alkyl group having from 1 to 18 carbon atoms or a group of the formula



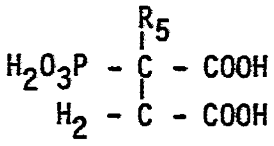
where n is zero or an integer having a value of from 1 to 5 and X and Y are as hereinbefore defined.

or



wherein X and Y are as hereinbefore defined

or



$$\begin{array}{rcl} & R_5 & \\ & | & \\ H_2O_3P - & C & - COOH \\ & | & \\ H_2 - & C & - COOH \end{array}$$

(1V)

wherein R_5 represents a hydrogen atom, a methyl group or a $- CH_2 - CH_2 - COOH$ 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, ethylenediaminotetramethylenephosphonic acid, diethylenetriaminopentamethylenephosphonic acid, n-propylimino bis (methylene phosphonic) acid and aminotri(2-propylene-2-phosphonic acid). Examples of phosphonic acids of the general formula 1V are phosphonosuccinic acid, 1-phosphono-1-methylsuccinic acid and 2-phosphonobutane-1,2,4 tricarboxylic acid.

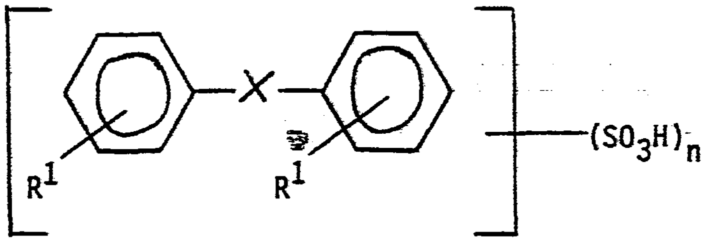
Especially valuable smut-inhibiting additives for use in the present invention are the phosphonic acids, especially ethylenediaminotetramethylenephosphonic acid, hexamethylenediaminetetra-(methylene phosphonic) acid, n-propyliminobis(methylene phosphonic) acid and benzene hexacarboxylic acid and salts 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 or 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.

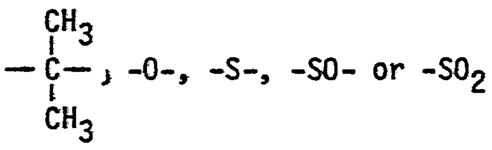
Preferably where the reaction product is formed with a mixture of formaldehyde and urea, the molar ratio of formaldehyde to urea is at leat 2:1.

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



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



$$-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-,\ -O-,\ -S-,\ -SO-\text{ or }-SO_2$$

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 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 be 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 ethylenediaminotetramethylenephosphonic acid will be in the range 1 to 500ppm 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 dimethylol-urea (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 ethylenediaminotetramethylene-phosphonic 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, di-ethanolamine 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 processes 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 1ppm to 10gms/litre. The preferred additive is carboxymethylcellulose, hereinafter referred to as CMC. The addition of from 5ppm to 100ppm of CMC will often 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 which, when added to water, form a sealing bath useful in the processes of the present invention are believed to be novel and form another aspect of our 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 processes 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 (175gms/litre at 18-20°C and 1.5A/dm^2) 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

(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

Bloom observed after 0.5 min/micron

(B) Demineralised Water + 2 mls/litre triethanolamine adjusted to pH 8.0 with acetic acid

pH of bath = 8.0 Bath Temperature = 98°C

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

Bloom formed after less than 0.5 min/micron

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

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

Example 2

(A) South Staffordshire Tap Water of total hardness expressed as $CaCO_3$ of 150 ppm.

pH of bath = 6.0 Bath Temperature = 98°C

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

Bloom present throughout

(B) To the bath used in (A) was added 2 mls/litre of triethanolamine and 40 ppm of ethylenediaminetetra(methylenephosphonic)acid.

pH of bath = 8.2 Bath Temperature = 98°C

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

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.micron	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

Demineralised water with ethylenediaminetetra(methylenephosphonic) acid. EDTMPA added as the smut-inhibitor. pH = 8.3 Sealing Time = 1 min/micron.

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.

Sufficient magnesium salt added to provide a molar ratio of EDTMPA : Mg^{2+} 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

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 60mg/litre illustrate the reduction of the quality of the seal produced by excessive quantitites of smut-inhibitor and how this effect can be overcome by raising the pH of the bath.

Example 5

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/micron.

A = Hexamethylenediaminetetra(methylene phosphonic) acid.
B = Diethylenetriaminepenta(methylene phosphonic) acid.
C = n-propyliminobis(methylenephosphonic) acid.

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.

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

Sealing Time Mins/microns	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

Claims

What we claim is

1. A process for sealing the surface of anodised aluminium which comprises immersing the anodised surface in an aqueous medium at a temperature of at least 80°C without the formation of any substantial quantity of smut which is characterised in that the pH of the aqueous medium is maintained at a value of at least 7.0 and the medium contains an effective quantity of a smut inhibiting additive (as hereinbefore described).

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 micron of the thickness of the anodised layer.

3. A process according to either if claims 1 or 2, characterised in that the sealing bath comprises one or more compounds selected from the group comprising dextrins, 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 suitable 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 ethylenediaminotetramethylenephosphonic acid, diethylenetriaminopentamethylene phosphonic acid, hexamethylene diamine tetra(methylenephosphonic) acid, n-propyliminobis(methylenephosphonic) acid, aminotri-(2-propylene-2-phosphonic acid, phosphonosuccinic acid, 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 claim 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 magnesim.

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 quantitiy 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.

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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 carboxymethylcellulose.

23. Anodised aluminium which has been sealed by a process according to any of claims 1 to 22.

24. A concentrate useful for addition to sealing baths which is characterised in that it comprises at least one smut-inhibiting additive as hereinbefore described and a water soluble base.