

**(12) PATENT**  
**(19) AUSTRALIAN PATENT OFFICE**

**(11) Application No. AU 199729598 B2**  
**(10) Patent No. 719630**

(54) Title  
**Short-term heat-sealing of anodized metal surfaces with surfactant-containing solutions**

(51)<sup>7</sup> International Patent Classification(s)  
**C25D 011/24**

(21) Application No: **199729598**

(22) Application Date: **1997.05.22**

(87) WIPO No: **WO97/46738**

(30) Priority Data

(31) Number	(32) Date	(33) Country
<b>19621818</b>	<b>1996.05.31</b>	<b>DE</b>

(43) Publication Date : **1998.01.05**

(43) Publication Journal Date : **1998.02.26**

(44) Accepted Journal Date : **2000.05.11**

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(56) Related Art  
**EP 122129**  
**EP 347663**



<p>(51) Internationale Patentklassifikation<sup>6</sup> :  <b>C25D 11/24</b></p>	<p><b>A1</b></p>	<p>(11) Internationale Veröffentlichungsnummer: <b>WO 97/46738</b>          (43) Internationales Veröffentlichungsdatum: 11. Dezember 1997 (11.12.97)</p>
<p>(21) Internationales Aktenzeichen: PCT/EP97/02620          (22) Internationales Anmeldedatum: 22. Mai 1997 (22.05.97)          (30) Prioritätsdaten:          196 21 818.7 31. Mai 1996 (31.05.96) DE          (71) Anmelder (für alle Bestimmungsstaaten ausser US): HENKEL          KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE];          Henkelstrasse 67, D-40589 Düsseldorf (DE).          (72) Erfinder; und          (75) Erfinder/Anmelder (nur für US): KÖRNER, Torsten [DE/DE];          Ludwigstrasse 22, D-40229 Düsseldorf (DE). KRESSE,          Josef [DE/DE]; Bachstrasse 25, D-41505 Rommerskirchen          (DE).</p>		<p>(81) Bestimmungsstaaten: AU, BG, BR, BY, CA, CN, CZ, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LT, LV, MD, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, UA, US, UZ, VN, europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).          Veröffentlicht  <i>Mit internationalem Recherchenbericht.          Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i></p>
<p>(54) Title: SHORT-TERM HEAT-SEALING OF ANODIZED METAL SURFACES WITH SURFACTANT-CONTAINING SOLUTIONS          (54) Bezeichnung: KURZZEIT-HEISSVERDICHTUNG ANODISierter METALLOBERFLÄCHEN MIT TENSIDHALTIGEN LÖSUNGEN          (57) Abstract          Described is a method of sealing anodized metal surfaces, the method being characterized in that the anodized metal is brought in contact, for a length of time between 0.5 and 2 minutes per micrometre of anodized-layer thickness, with an aqueous solution having a temperature between 75 °C and the boiling point and a pH in the range 5.5 to 8.5 and containing: a) a total of 0.0004 to 0.05 g/l of one or more cationic, anionic or non-ionic surfactants; and b) a total of 0.0005 to 0.5 g/l of one or more organic acids selected from the group comprising the cyclic polycarboxylic acids with 3 to 6 carboxyl groups and the phosphonic acids. The preferred surfactants are non-ionic surfactants and the preferred acids are polyphosphinocarboxylic acids. Optionally present are alkali-metal and/or alkaline-earth metal cations, preferably Li and/or Mg ions, in amounts of 0.0001 to 5 g/l.          (57) Zusammenfassung          Verfahren zum Verdichten anodisierter Metalloberflächen, dadurch gekennzeichnet, daß man das anodisierte Metall für eine Zeitdauer zwischen 0,5 und 2 Minuten pro Mikrometer Anodisierschichtdicke mit einer wäßrigen Lösung in Berührung bringt, die eine Temperatur zwischen 75 °C und dem Siedepunkt und einen pH-Wert im Bereich von 5,5 bis 8,5 aufweist und die a) insgesamt 0,0004 bis 0,05 g/l eines oder mehrerer kationischer, anionischer oder nichtionischer Tenside und b) insgesamt 0,0005 bis 0,5 g/l einer oder mehrerer organischer Säuren ausgewählt aus cyclischen Polycarbonsäuren mit 3 bis 6 Carboxylgruppen und/oder Phosphonsäuren enthält. Als Tenside sind nichtionische Tenside, als Säuren sind Polyphosphinocarbonsäuren bevorzugt. Fakultativ sind Alkali- und/oder Erdalkalimetallkationen, vorzugsweise Li- und/oder Mg-Ionen, in Mengen von 0,0001 bis 5 g/l anwesend.</p>		

Short-term Heat-sealing of Anodized Metal Surfaces  
with Surfactant-containing Solutions

This invention relates to the production of corrosion-inhibiting and/or decorative coatings on metals by anodic oxidation. It relates to an improved process for postsealing porous, electrochemically-produced anodised coatings in order further to improve the properties thereof.

Electrochemical anodic oxidation of metals in suitable electrolytes is a widely used process for the formation of corrosion-inhibiting and/or decorative finishes on metals suitable for this purpose. These processes are briefly described in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th edition, volume 9 (1987), pp. 175-176. According to this reference, titanium, magnesium and aluminium and alloys thereof are anodisable, the anodisation of aluminium and alloys thereof being of the greatest industrial significance. The electrolytically produced anodised coatings protect the aluminium surfaces from the action of weathering and other corrosive media. Anodised coatings are also applied in order to create a harder surface, thus increasing the wear resistance of aluminium. Particular decorative effects may be achieved by means of the intrinsic colour of the anodised coatings or by absorptive or electrolytic colouring. Aluminium is anodised in an acidic electrolyte, sulfuric acid being most commonly used. Other suitable electrolytes are phosphoric acid, oxalic acid and chromic acid. The properties of the anodised coatings may be varied widely by selection of the electrolyte, the temperature thereof and by the current density and duration of anodisation. Anodisation is conventionally performed using direct current or using direct current having a superimposed alternating current.

Freshly anodised coatings may subsequently be coloured by immersion in solutions of a suitable dye or by an alternating current treatment in an electrolyte containing a metal salt, preferably containing tin. As an alternative to subsequent colouring, coloured anodised coatings may be obtained by so-called colour anodisation processes, in which anodisation is performed in solutions of organic acids, such as in particular sulfophthalic acid or sulfanilic acid, each optionally mixed with sulfuric acid.

These anodically-produced protective coatings, the structure of which has been scientifically investigated (R. Kniep, P. Lamparter and S. Steeb: "Structure of Anodic Oxide Coatings on Aluminium", *Angew. Chem. Adv. Mater.* 101 (7), pp. 975-977 (1989)), are frequently described as "oxide coatings". The above investigation has, however, demonstrated that these coatings are vitreous and contain tetrahedrally-coordinated aluminium. Octahedrally-coordinated aluminium, as in aluminium oxides, was not found. Herein, the more general term "anodised coatings" is used instead of the misleading term "oxide coatings".

However, these coatings do not yet fulfil all requirements with regard to corrosion protection, as they still have a porous structure. It is consequently necessary to post-seal the anodised coatings. This post-sealing is frequently performed using hot or boiling water, alternatively using steam, and is described as "sealing". This treatment seals the pores, so considerably increasing corrosion protection. There are numerous literature references relating to this post-sealing process. The following may be mentioned by way of example: S. Wernick, R. Pinner and P.G. Sheasby: "The Surface Treatment and Finishing of Aluminium and its Alloys" (volume 2, 5th edition, Chapter 11:



"Sealing Anodic Oxide Coatings"), ASM International (Metals Park, Ohio, USA) and Finishing Publications Ltd. (Teddington, Middlesex, England) 1987.

However, not only the pores are sealed during post-sealing of the anodised coating, but a velvety deposit of a greater or lesser thickness, the so-called "sealing deposit", is formed over the entire surface. This deposit, which consists of hydrated aluminium oxide, is visually unattractive, reduces adhesion when bonding such aluminium components and promotes subsequent soiling and corrosion. Since the subsequent manual removal of this sealing deposit by mechanical or chemical methods is costly, attempts have been made to prevent the formation of this sealing deposit by means of chemical additives in the sealing bath. According to DE C-26 50 989, additions of cyclic polycarboxylic acids having 4 to 6 carboxyl groups per molecule, in particular cyclohexane hexacarboxylic acid, are suitable for this purpose. According to DE-A-38 20 650, certain phosphonic acids, for example 1-phosphonopropane-1,2,3-tricarboxylic acid, may also be used. The use of other phosphonic acids is known from EP-A-122 129. DE-C-22 11 553 describes a process for post-sealing anodic oxide coatings on aluminium and aluminium alloys in aqueous solutions containing phosphonic acids or salts thereof and calcium ions, wherein the molar ratio of calcium ions:phosphonic acid is adjusted to at least 2:1. A higher ratio of calcium ions:phosphonic acids of about 5:1 to about 500:1 is preferably used. Phosphonic acids which may, for example, be considered are: 1-hydroxypropane-, 1-hydroxy-butane-, 1-hydroxy-pentane-, 1-hydroxy-hexane-1,1-diphosphonic acid together with 1-hydroxy-1-phenyl-methane-1,1-diphosphonic acid and preferably 1-hydroxy-ethane-1,1-diphosphonic acid, 1-amino-ethane-, 1-amino-1-phenyl-methane-, dimethylamino-ethane-, dimethylamino-butane-, diethylaminomethane-, propyl- and butyl-aminomethane-1,1-diphosphonic acid, aminotrimethylene-phosphonic acid, ethylene-diamine-tetramethylene-phosphonic acid, diethylene-triamine-pentamethylene-phosphonic acid, aminotri-(2-propylene-2-phosphonic acid), phosphonosuccinic acid, 1-phosphono-1-methylsuccinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid. On the basis of the practical examples of the said patent, this process is a conventional hot post-sealing process using post-sealing times of between 60 and 70 minutes at anodised coating thicknesses of between about 18 and about 22µm. Post-sealing time is thus approximately 3 minutes per µm of coating thickness.

When using water which contains no additives other than the stated sealing deposit inhibitors, elevated temperatures (at least 90°C) and relatively long treatment times of the order of about 1 hour for an anodised coating of about 20µm have hitherto been necessary. This corresponds to a post-sealing time of about 3 minutes per micrometer of anodised coating thickness. The post-sealing process is thus highly energy intensive and, due to its duration, may act as a bottleneck in the production process. Attempts have thus already been made to find additives for the post-sealing bath which promote the post-sealing process, so that it may proceed at lower temperatures (so-called cold post-sealing or cold sealing) and/or using shorter treatment times. The following have, for example, been proposed as additives which facilitate post-sealing at temperatures of below 90°C: nickel salts, in particular fluorides, which are sometimes used in practice (EP 171 799), nitrosyl-pentacyanoferrate, complex fluorides of titanium and zirconium together with chromates or chromic acid, optionally in conjunction with further additives. As an alternative to actual post-sealing, hydrophobisation of the



oxide coating by means of long-chain carboxylic acids or waxes has been recommended, as has treatment with acrylamides, which should apparently be polymerised in the pore voids. Further details in this connection may be found in the above-mentioned reference by S. Wernick *et al.*. With the exception of post-sealing using nickel compounds, it has not proved possible to implement these proposals in practice.

Processes for cold post-sealing using nickel fluoride have been implemented industrially. However, due to the toxic properties of nickel salts, this entails costly waste water treatment measures.

There is thus still a need for alternative post-sealing processes for anodised surfaces which make it possible to increase the rate of production by shortened post-sealing times and/or to reduce the energy consumption necessary for post-sealing, without using heavy metals, such as nickel, which are questionable on environmental and health grounds.

An accelerated, hot post-sealing process is known from US-A-5 411 607 in which the anodised metal components are immersed in an aqueous solution containing lithium. The lithium concentration is preferably from 0.01 to 50g/L, in particular from 0.01 to 5g/L. It is moreover suggested that the sealing solution should additionally contain a sealing deposit inhibitor. This is preferably present in a concentration of between 0.1 and 10g/L and is preferably an aromatic disulfonate. According to US-A-5 478 415, which has the same priority as the above-mentioned US-A-5 411 607, accelerated hot post-sealing may proceed using an aqueous solution which contains at least 0.01g/L of lithium ions and 0.1 to 10g/L of a sealing deposit inhibitor. Here too, the sealing deposit inhibitor is preferably an aromatic disulfonate.

German patent application 195 38 777.5 discloses an accelerated hot post-sealing process in which the anodised metal components are contacted with an anodising solution which contains a total of 0.1 to 5g/L of one or more alkali metal and/or alkaline earth metal ions and a total of 0.0005 to 0.2g/L of a sealing deposit inhibitor in the form of phosphonic acids or cyclic polycarboxylic acids.

The teachings of the latter three cited documents allow hot post-sealing times to be shortened substantially. It would, however, be desirable on economic and environmental grounds to have post-sealing processes available which consume distinctly smaller quantities of chemicals. An object of the present invention is to provide such a process.

The present invention provides a process for post-sealing anodised metal surfaces, characterised in that the anodised metal is contacted with an aqueous solution for a period of between 0.5 and 2 minutes per micrometer of anodised coating thickness, which solution is at a temperature of between 75°C and its boiling point and has a pH of from 5.5 to 8.5 and which contains:

- (a) a total of 0.0004 to 0.05g/L, preferably 0.005 to 0.02g/L, of one or more cationic, anionic or non-ionic surfactants; and
- (b) a total of 0.0005 to 0.5g/L of one or more organic acids selected from cyclic polycarboxylic acids having 3 to 6 carboxyl groups and/or phosphonic acids.

The treatment solutions may be contacted with the anodised metals by spraying the solutions onto the metal surfaces or preferably by immersing the anodised metals in the solutions. At conventional industrial anodised coating thicknesses of approximately 20µm, the treatment times



required are still only 20 to 40 minutes. The temperature of the treatment solution is preferably from 94 to 98°C, preferably about 96°C.

The pH of the aqueous solution is preferably from 5.5 to 7, in particular from 5.5 to 6.5. The pH may, if necessary, be adjusted using ammonia or acetic acid. The pH may be maintained within the required range using an ammonium acetate buffer.

Cationic surfactants (a) may be selected, for example, from quaternary ammonium salts in which at least one alkyl or aralkyl residue has at least 8 carbon atoms. One example of such a substance is C<sub>12-14</sub>-alkyl-dimethyl-benzylammonium chloride. Pyridinium salts, such as dodecyl-pyridinium chloride, may also be used as cationic surfactants. Examples of anionic surfactants (a) which may be used are alkyl or alkaryl sulfates and sulfonates. In this case, linear alkyl sulfates, such as lauryl sulfate, are preferred for environmental reasons. The anionic surfactants are used as alkali metal or ammonium salts, lithium salts being particularly preferred. Preferably, however, non-ionic surfactants are used as the surfactants (a). These may be selected, for example, from alkoxyates, such as ethoxyates and/or propoxyates of fatty alcohols or fatty amines. For the present purposes, fatty alcohols and fatty amines are compounds having an alkyl residue containing at least 8 carbon atoms. Such substances may be pure substances having a defined alkyl residue or consist of product mixtures, such as are obtained from natural fats and oils. These alkoxyates may also be end-terminated, *i.e.* etherified again on the terminal OH group. Examples of such non-ionic surfactants are octanol × 4 EO (EO = ethylene oxide) and octanol × 4.5 EO-butyl ether. Better post-sealing results tend to be obtained if fatty amine ethoxyates, instead of fatty alcohol ethoxyates, are used as the non-ionic surfactants. Non-ionic surfactants (a) are thus preferably selected from fatty amine ethoxyates having 10 to 18 carbon atoms in the alkyl residue and 3 to 15 ethylene oxide units per molecule. Specific examples are coconut oil fatty amine × 5 EO and coconut oil fatty amine × 12 EO.

In a specific embodiment, the organic acids (b) are selected from saturated, unsaturated or aromatic carbocyclic six-membered ring carboxylic acids having 3 to 6 carboxyl groups. Preferred examples of such acids are trimesic acid, trimellitic acid, pyromellitic acid, mellitic acid and the particularly preferred cyclohexane-hexacarboxylic acid. The total quantity of carboxylic acids is preferably from 0.001 to 0.05g/L.

The preferred cyclohexane-hexacarboxylic acid exists as various stereoisomers. As is known from DE-A-26 50 989, preferred cyclohexane-hexacarboxylic acids are those which have 5 carboxyl groups in cis position and 1 in trans position or 4 carboxyl groups in cis position and 2 in trans position.

In another specific embodiment, the organic acids (b) are selected from the phosphonic acids: 1-phosphonopropane-1,2,3-tricarboxylic acid, 1,1-diphosphono-propane-2,3-dicarboxylic acid, 1-hydroxy-propane-1,1-diphosphonic acid, 1-hydroxy-butane-1,1-diphosphonic acid, 1-hydroxy-1-phenyl-methane-1,1-diphosphonic acid, 1-hydroxy-ethane-1,1-diphosphonic acid, 1-amino-ethane-1,1-diphosphonic acid, 1-amino-1-phenyl-methane-1,1-diphosphonic acid, dimethylamino-ethane-1,1-diphosphonic acid, propylamino-ethane-1,1-diphosphonic acid, butylamino-ethane-1,1-diphosphonic acid, aminotri(methylene-phosphonic acid), ethylene-diaminotetra(methylene-phosphonic acid), diethylene-triaminopenta(methylene-phosphonic acid), hexamethylene-diaminotetra-(methylene-



phosphonic acid), *n*-propyliminobis(methylene-phosphonic acid), aminotri-(2-propylene-2-phosphonic acid), phosphonosuccinic acid, 1-phosphono-1-methyl-succinic acid and 1-phosphonobutane-1,2,4-tricarboxylic acid. Of this selection, 1-phosphonopropane-1,2,3-tricarboxylic acid, 1,1-diphosphonopropane-2,3-dicarboxylic acid and aminotri-(methylene-phosphonic acid) are particularly preferred. The phosphonic acids (b) are preferably used in a quantity of 0.003 to 0.05g/L. Polyphosphinocarboxylic acids which may be considered as copolymers of acrylic acid and hypophosphites are also suitable. One example of such a compound is "Belclene® 500" from FMC Corporation, Great Britain.

It may moreover, be advantageous for the effectiveness of post-sealing if the aqueous post-sealing solution additionally contains a total of 0.0001 to 5g/L of one or more alkali metal and/or alkaline earth metal ions. These alkali metal or alkaline earth metal ions may be present as counter-ions to the acids (b). Preferably, however, the aqueous solution contains a larger quantity of alkali metal and/or alkaline earth metal ions than is required for complete neutralisation of the acids (b). It is particularly preferred if these additional alkali metal and/or alkaline earth metal ions, which exceed the quantity required for complete neutralisation of the acids (b), are selected from lithium and magnesium. In order to reduce the use of chemicals to a minimum, the content of the aqueous solution of these alkali metal and/or alkaline earth metal ions is generally limited to a maximum of 0.005g/L. Higher contents, for example up to 5g/L, do not, however, impair post-sealing results. These alkali metal and/or alkaline earth metal ions, in particular lithium and magnesium, may be used in the form of the salts thereof which are soluble in water in the stated range of concentrations. Anionic surfactants (a) may, for example, be used as the counter-ions. Acetates, lactates, sulfates, oxalates and/or nitrates are, for example, also suitable. Acetates are particularly suitable.

Particularly good post-sealing results are achieved if, immediately after the accelerated hot post-sealing described above, the metal surfaces are immersed in completely deionised water for a period of between 30 and 120 seconds, the water being at a temperature of above 90°C, preferably of above 96°C.

The post-sealing bath suitable for the post-sealing process according to the present invention may, in principle, be produced *in situ* by dissolving the constituents in (preferably completely deionised) water in the appropriate concentration range. Preferably, however, an aqueous concentrate already containing all the necessary constituents of the post-sealing bath in the correct quantity ratio is used, from which the ready-to-use solution is obtained by dilution with water, for example by a factor of between about 100 and about 1000. In so-doing, it may be necessary to adjust the pH to the range according to the present invention using ammonia or acetic acid. Accordingly, the present invention also relates to an aqueous concentrate for the preparation of the aqueous solution for use in the present accelerated hot post-sealing process, the concentrate yielding the ready-to-use aqueous solution by dilution with water by a factor of between about 100 and about 1000.

It is possible by using the accelerated and energy-saving process according to the present invention to produce post-sealed anodised coatings which, with regard to the coating properties thereof, are not inferior to conventionally produced coatings. Industrially significant test parameters for coating quality are, in particular, acid corrosion loss in chromic acid, admittance and the dye droplet



test. These coating quality parameters are tested using the standard test methods indicated in the Examples.

The post-sealing process according to the present invention is preferably used for anodised aluminium or anodised aluminium alloys. It may, however, also be used on the anodised coatings of other anodisable metals, such as titanium and magnesium or alloys of these metals. It may be used both for uncoloured anodised coatings and for those coloured using conventional methods, such as self-colouring, adsorptive colouring using organic dyes, reactive colouring to form inorganic colouring pigments, electrochemical colouring using metal salts, in particular tin salts, or interference colouring. In the case of adsorptively coloured anodised coatings, the process according to the present invention has the additional advantage that, due to the reduced duration of post-sealing, it is possible to reduce the bleeding of dye which is possible in conventional hot post-sealing.

### Examples

Al 99.5 grade aluminium sheets were conventionally anodised (direct current/sulfuric acid, 1 hour, coating thickness 20µm) and optionally coloured electrochemically or using organic dip dyes. The sheets were then immersed for 30 minutes in the post-sealing solutions according to the present invention or comparison solutions according to the Table. To this end, 2g of concentrate were in each case made up to 1 litre using completely deionised water. The solutions were at a temperature of 96°C. After treatment according to the Table, the sheets were immersed for 1 minute in boiling completely deionised water and then dried. The quality of post-sealing was then verified by the conventional quality tests described below. The results of these tests are also shown in the Table. They demonstrate that, using the process according to the present invention, post-sealing results are obtained after only 30 minutes which experience has shown are obtained only after 1 hour using a conventional hot post-sealing bath. In contrast, the post-sealing results after a ½ hour treatment using comparison solutions reveal inadequate quality.

Admittance  $Y_{20}$  was determined to German standard DIN 50 949 using an Anotest Y D 8.1 meter supplied by Fischer. The measuring system consists of two electrodes, one of which is conductively connected to the base material of the specimen. The second electrode is immersed in an electrolyte cell, which may be placed upon the coating to be tested. This cell takes the form of a rubber ring having an internal diameter of 13 mm and a thickness of 5mm, the annular surface of which is self-adhesive. The measurement area is 1.33cm<sup>2</sup>. A potassium sulfate solution (35g/L) in completely deionised water is used as the electrolyte. The admittance value read from the meter is converted, in accordance with the instructions of DIN 50 949, to a measurement temperature of 25°C and a coating thickness of 20µm. The resultant values, which should preferably be between about 10 and about 20µS, are shown in the Table.

Residual reflection after colouring with dye pursuant to German standard DIN 50 946 is measured as a parameter which reveals open-pored and thus poorly post-sealed coatings. The measurement area was delimited using a self-adhesive measurement cell from the previously-described Anotest device. The test area is wetted using an acid solution (25mL/L sulfuric acid, 10g/L KF). After exactly 1 minute, the acid solution is washed off and the test area dried. The test area is





then wetted with dye solution (5g/L of Sanodal blue) which is left to act on the surface for 1 minute. After rinsing under running water, the measurement cell is removed. Any dye loosely adhering to the dyed test surface is removed by rubbing with a mild powdered cleaner. Once the surface has been dried, a relative reflection measurement is made by placing the measuring head of light reflection meter (Micro Colour supplied by the company Dr. Lange) once on an uncoloured area of the surface and secondly on the dyed measurement surface. Residual reflection in % is obtained by multiplying the quotient of the measured value for the coloured surface divided by the measured value of the uncoloured surface by 100. Residual reflection values of between 95 and 100% indicate good post-sealing quality, while values of less than 95% are considered unacceptable. The higher the residual reflection value, the higher is the post-sealing quality. The values found are shown in the Table.

Acid corrosion loss is also measured to ISO 3210. To this end, the test sheet is weighed to an accuracy of 0.1mg and then immersed for 15 minutes at 38°C in an acid solution containing 35mL of 85% phosphoric acid and 20g of chromium(VI) oxide per litre. On completion of the test period, the specimen is rinsed with deionised water and dried for 15 minutes at 60°C in a drying cabinet. The specimen is then re-weighed. The difference in weight between the first and second weighings is calculated and divided by the size of the surface in dm<sup>2</sup>. Weight loss is expressed as  $\Delta G$  in mg/dm<sup>2</sup> (1dm<sup>2</sup> = 100cm<sup>2</sup>) and should not exceed 30mg/dm<sup>2</sup>.

The following concentrates for comparison solutions and treatment solutions according to the present invention were prepared by dissolving the active ingredients in completely deionised water:

20 Comparison 1: 25g/L of polyphosphinocarboxylic acid solution (45 wt.% in water)

(Acrylic acid/sodium hypophosphite copolymer, "Belclene® 500", FMC Corporation, Great Britain)

Example 1: As Comparison 1, plus:

10g/L of coconut amine  $\times$  5 EO

25 Example 2: As Comparison 1, plus:

10g/L of coconut amine  $\times$  12 EO

Example 3: As Comparison 1, plus:

5g/L of coconut amine  $\times$  5 EO

Example 4: As Comparison 1, plus:

30 10g/L of coconut amine  $\times$  5 EO

2g/L of magnesium acetate

Example 5: As Comparison 1, plus:

10g/L of coconut amine  $\times$  5 EO

0.5g/L of magnesium acetate

35 Example 6: As Comparison 1, plus:

10g/L of coconut amine  $\times$  12 EO

2g/L of lithium acetate

Example 7: As Comparison 1, plus:

2g/L of coconut amine  $\times$  5 EO

40 Example 8: As Comparison 1, plus:



15g/L of coconut amine  $\times$  5 EO

Example 9: As Comparison 1, plus:

5g/L of octanol  $\times$  4 EO

Example 10: As Comparison 1, plus:

5g/L of Li lauryl sulfate

Example 11: As Comparison 1, plus:

5g/L of lauryl-dimethyl-benzylammonium chloride

For the tests, 2g of concentrate were made up to 1 litre with completely deionised water.

**Table:**

**Test results**

Solution from	Admittance $Y_{20}$ ( $\mu$ S)	Residual reflection (%)	Acid corrosion loss (g/100 cm <sup>2</sup> )
Comparison 1	27	98	24.1
Example 1	19	100	12
Example 2	20	99	15
Example 3	19	99	13
Example 4	16	100	9
Example 5	18	100	12
Example 6	18	100	10
Example 7	21	98	16
Example 8	18	100	12
Example 9	20	99	14
Example 10	22	98	24
Example 11	23	98	20



**The claims defining the invention are as follows:**

1. A process for postsealing anodised metal surfaces, characterised in that the anodised metal is brought into contact with an aqueous solution for a period of between 0.5 and 2 minutes per micrometre of anodised coating thickness, which solution is at a temperature of between 75°C and its boiling point and has a pH value in the range from 5.5 to 6.5 and which contains
  - a) a total of 0.0004 to 0.05g/L of one or more cationic, anionic or nonionic surfactants selected from quaternary ammonium salts, in which at least one alkyl or arylalkyl residue comprises at least 8 C atoms, pyridinium salts, alkyl or alkylaryl sulfates and sulfonates, and from alkoxylates of fatty alcohols or fatty amines having an alkyl residue with at least 8 C atoms, and
  - b) a total of 0.0005 to 0.5g/L of one or more organic acids selected from cyclic polycarboxylic acids having 3 to 6 carboxyl groups and/or phosphonic acids.
2. A process as claimed in claim 1, characterised in that the aqueous solution is at a temperature in the range from 94 to 98°C.
3. A process as claimed in claim 1 or claim 2, characterised in that the surfactants of group a) are nonionic surfactants.
4. A process as claimed in claim 3, characterised in that the nonionic surfactants are selected from fatty amine ethoxylates having 10 to 18 C atoms in the alkyl residue and 3 to 15 ethylene oxide units per molecule.
5. A process as claimed in any one of claims 1 to 4, characterised in that the group b) organic acids are selected from saturated, unsaturated or aromatic carbocyclic six-membered ring carboxylic acids having 3 to 6 carboxyl groups.
6. A process as claimed in claim 5, characterised in that the carboxylic acids are selected from trimesic acid, trimellitic acid, pyromellitic acid, mellitic acid and cyclohexanhexacarboxylic acid.
7. A process as claimed in claim 5 or claim 6, characterised in that the aqueous solution contains the carboxylic acids in a total quantity of 0.001 to 0.05g/L.
8. A process as claimed in any one of claims 1 to 4, characterised in that the group b) organic acids are selected from 1-phosphonopropane-1,2,3-tricarboxylic acid, 1,1-diphosphonopropane-2,3-dicarboxylic acid, 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-phenylmethane-1,1-diphosphonic acid, dimethylaminoethane-1,1-diphosphonic acid, propylaminoethane-1,1-diphosphonic acid, butylaminoethane-1,1-diphosphonic acid, aminotri(methylenephosphonic acid), ethylenediaminetetra(methylenephosphonic acid), diethylenetriaminopenta(methylenephosphonic acid), hexamethylenediaminetetra(methylene phosphonic acid), n-propyliminobis(methylenephosphonic acid), aminotri-(2-propylene-2-phosphonic acid), phosphonosuccinic acid, 1-phosphono-1-methylsuccinic acid, 1-phosphonobutane-1,2,4-tricarboxylic acid and polyphosphinocarboxylic acids.
9. A process as claimed in claim 8, characterised in that the group b) organic acid is selected from polyphosphinocarboxylic acids.



10. A process as claimed in claim 8 or claim 9, characterised in that the aqueous solution contains the group b) acids in a quantity of 0.003 to 0.05g/L.

11. A process as claimed in one or more of claims 1 to 10, characterised in that the aqueous solution additionally contains a total of 0.0001 to 5g/L of one or more alkali metal and/or alkaline earth metal ions.

12. A process as claimed in claim 11, characterised in that the aqueous solution contains a larger quantity of alkali metal and/or alkaline earth metal ions than is required for complete neutralisation of the acids of group b).

13. A process as claimed in claim 12, characterised in that the aqueous solution contains a total of up to 0.005g/L of alkali metal and/or alkaline earth metal ions.

14. A process as claimed in any one of claims 11 to 13, characterised in that the alkali metal and/or alkaline earth metal ions are selected from Li and Mg.

15. A process for postsealing anodised metal surfaces, characterised in that after treatment according to one or more of claims 1 to 14, the metal surfaces are immersed for a period of between 30 and 120 seconds in completely deionised water, which is at a temperature of above 90°C.

16. A process for postsealing anodised metal surfaces, substantially as hereinbefore described with reference to any one of the examples but excluding the comparative example.

17. An aqueous concentrate for preparing the aqueous solution when used in the process according to any one of claims 1 to 16, which concentrate yields the ready-to-use aqueous solution by dilution with water by a factor of between 100 and 1000.

18. Anodised metal surfaces postsealed by the process of any one of claims 1 to 16.

**Dated 9 March, 2000**

**Henkel Kommanditgesellschaft auf Aktien**

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