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RECONSTITUTION OF ELECTRODES

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5 Claims

ABSTRACT OF THE DISCLOSURE

In a method of cleaning anodes comprising a conductive base coated with noble metals or chemical compounds thereof, the anodes are treated with a melt containing a basic material at a specific temperature and in the presence of an oxidant or oxygen.

This invention relates to a process for cleaning anodes for electrolysis such anodes consisting of a conductive base coated with noble metals or chemical compounds thereof, for example, oxides, possibly together with other conductors.

The cleaning of such anodes has always been a great problem in the past, because the normal methods of doing this often affected the conductive base, especially film forming metal such as, for example, titanium, rather than the noble metal coatings, because titanium and analogous conductors are generally less noble.

In other cases, chemical methods, for example, pickling, have given extremely poor effects, because even the smallest quantity of noble metal on the film forming metal, such as titanium, imparts a great chemical resistance to the titanium owing to anodic protection.

Yet the cleaning of these conductor coated anodes of base metals (base as opposed to noble metals) and other conductors, and particularly the class known as film forming metals, such as titanium, is very important because all of the noble metal residues must be removed in order that the base may be re-activated by pickling for recoating. As a matter of fact, such pickling is impossible so long as the smallest quantity of noble metal is present.

It is an urgent requirement, therefore, that prior to the reactivation all the noble metals or other conductors should be removed in order that an active base may be produced by pickling which may be recoated with a conductor.

I have now surprisingly found that practically any noble metal, alloys of noble metals and other conductors can be removed from these base metals, without causing any damage to the base, by immersing the partly coated base in a bath of a melt containing an alkaline substance in the presence of an oxidizing salt or oxygen at a temperature above 250° C.

As an oxidizing salt preferably an alkali metal salt is used, which brings about an oxidizing effect at 250–400° C.

Good results are obtained by means of a salt bath containing more than 50% by weight of an oxidizing salt, such as potassium nitrate or sodium nitrate, and less than 50% by weight of a base, such as sodium hydroxide or potassium hydroxide.

The salt melt itself can be produced by heating at a temperature of, for example, between 250 and 1000° C. An excellent salt melt for the purpose consists, for example, of 2 parts by weight of sodium nitrate and 1 part by weight of sodium hydroxide at a temperature ranging from 425 to 475° C. When titanium or another film forming metal coated with noble metals or other conductors, such as oxides and mixed oxides of noble metals and base

metals, is immersed in this salt melt for several minutes, all of the conductors present are removed, while no damage is done to the base metal.

The desired rough surface on the film forming metal, for example, titanium, produced for example the first time by pickling in hot aqueous oxalic acid or hydrochloric acid, is kept perfectly intact, so that mere pickling in a solution of a suitable substance, such as oxalic acid or tartaric acid, for $\frac{1}{40}$ or less of the period required for the first time of pickling, perfectly reactivates or reconstitutes this surface for receiving a next coating of the desired noble metals or other conductors. Tests have shown that the performance of, for example, a titanium anode thus recoated and used in the chlor-alkali electrolysis is superior to that of the original anode.

The salt melt can be prepared in any conventional, resistant vessels, but I preferably use stainless steel vessels. The source of heat may be electricity, gas, etc.

The noble metal dissolved in the salt melt can be recovered e.g. by connecting the stainless steel vessel as the anode, and using as the cathode a material resistant to the salt melt. By conducting a substantially direct current through the salt melt, the dissolved noble metal will then be deposited on the cathode in metallic form, from which it can later be removed. In actual practice a quantity of noble metal of up to 3% by weight can be incorporated in the salt melt.

Alternatively, the salt melt may be dissolved in water, and the dissolved metals recovered by chemical precipitation or electrolysis.

After cleaning of the anodes in the salt melt, it is recommendable to wash the anodes for a short length of time with a dilute acid, such as a solution of hydrochloric acid or sulphuric acid. Also, a dilute mixture of hydrochloric acid and nitric acid may be used, which does not dissolve the film-forming base metal, for example titanium, zirconium or tantalum. As a result the last residues of the coating will be completely removed.

The term film forming metals as used in this specification is to be understood to include: titanium, tantalum, niobium, zirconium, tungsten and bismuth.

By the term conductors (coating) used in this specification is to be understood those which will conduct electrical energy into aqueous electrolytes under anodic conditions.

EXAMPLE 1

2 parts by weight of potassium nitrate are admixed with 1 part by weight of potassium hydroxide. This mixture is heated to a temperature of 250–550° C. The resulting salt melt is eminently suitable for removing such noble metals as gold and silver, and metals of the platinum group, from film forming metals such as titanium and zirconium.

Preferred temperature: 340° C. for 70% Pt+30% Ir (mol percent).

Stripping time: 5 minutes.

Coating thickness: 20 g./m.² (about 1 micron).

EXAMPLE 2

A mixture of 2 parts by weight of potassium nitrate and 1 part by weight of sodium hydroxide is heated to a temperature of 300–600° C., with the mixture melting completely. This salt melt is excellently suitable for removing noble metals from film forming metals. This mixture is especially suitable for cleaning tantalum, zirconium and niobium, because this salt melt is somewhat less aggressive than is the mixture of Example 1.

Preferred temperature: 500° C. for Pt and/or Ir.

Stripping time: 5 minutes.

Coating thickness: 20 g./m.² (about 1 micron).

EXAMPLE 3

The salt melts according to Examples 1 and 2 are heated at a temperature of 400–800° C. They are excellently suited for removing the oxides of the noble metals, possibly admixed with the noble metals themselves and, if desired, in the presence of oxides from such film forming metals as titanium, tantalum, niobium, zirconium and aluminium. Values found for a coating of ruthenium oxide+titanium oxide:

Preferred temperature: 450° C.

Stripping time: 5 minutes.

Coating thickness: 10 g./m.² (about 2–2.5 microns).

The salt melts according to Examples 1 and 2 are also excellently suitable for removing mixed oxides consisting of oxides of metals or mixtures thereof, which oxides are electrically conductive under anodic conditions in an electrolyte, as well as oxides of film forming metals.

EXAMPLE 4

A mixture of 3 parts by weight of sodium hydroxide and 1 part by weight of potassium nitrate, heated at a temperature of 350–1100° C., is eminently suitable for cleaning film forming metals coated with metals of the platinum group, their oxides or mixtures thereof, together with the oxides of the non-noble metals.

Preferred temperature: 450° C.

Stripping time: 5 minutes.

With a coating thickness of 10 g./m.², the treatment is suitable for metals as well as oxides.

EXAMPLE 5

A salt melt consisting of 2 parts by weight of potassium nitrate, 1 part by weight of sodium hydroxide and 1 part by weight of sodium chloride, heated at a temperature of 300–1100° C., is also most excellent for cleaning film forming metal anodes coated with conductors. The quantity of sodium chloride can be increased without this having a disturbing effect, and the sodium chloride can be replaced with potassium chloride or potassium/sodium carbonate.

Temperature: 480° C.

Stripping time: 5 minutes.

Coating thickness: 20 g./m.² in the case of noble metal; 10 g./m.² in the case of the oxide of a noble metal.

It is also possible for the sodium/potassium hydroxide to be partly replaced with another base, e.g. lithium hydroxide. As a result, the activity of the salt melts will decrease considerably, which may be useful in some cases.

If the NaOH is replaced with lithium hydroxide, the temperature is also 480° C., but the stripping time is more than 5 minutes.

EXAMPLE 6

The salt melt consists of a mixture of 2 parts by weight of potassium nitrate and 1 part by weight of barium hydroxide. It is heated to a temperature ranging between 400° and 700° C., with the mixture melting completely.

Preferred temperature: about 500° C.

This mixture is suited for stripping metals as well as oxides applied to titanium, tantalum, zirconium, and niobium. The barium hydroxide may also be replaced with

lithium hydroxide, which is likewise very suitable for both metals and oxides.

EXAMPLE 7

The salt melt of Example 1, consisting of 2 parts by weight of potassium nitrate+1 part by weight of sodium hydroxide, may also be replaced with 2 parts by weight of sodium nitrate+1 part by weight of sodium hydroxide.

If sodium hydroxide alone is used at a temperature of 400° C., platinum-plated or ruthenium-plated titanium is stripped well, but this is coupled with a great loss of titanium or other base metals.

If 5% potassium nitrate or another oxidizing salt is added thereto, the losses will be at least 10 times as small.

The loss of weight decreases accordingly as larger quantities of potassium nitrate or sodium nitrate are added.

The bath starts working with 95% KNO₃ and 5% KOH or NaOH. If a melt consisting of NaOH and KOH is chosen, and if finely divided air or oxygen is blown through the bath, the loss of Ti will be approximately the same as in the case of 5% KNO₃. With zirconium and tantalum the situation is substantially the same.

I claim:

1. A method of cleaning anodes for electrolytic processes, said anodes comprising a conductive base coated with noble metals or chemical compounds thereof or mixture of these noble metals or compounds with other conductors, said method being characterized in that the anodes are treated with a melt containing a basic material at a temperature above 250° C. and in the presence of an oxidant or oxygen.

2. A method according to claim 1, wherein said oxidant is an alkali metal salt which has an oxidizing effect at a temperature of between 250° and 1100° C.

3. A method according to claim 1, wherein more than 50% by weight of an oxidizing salt, such as potassium nitrate or sodium nitrate, is used and less than 50% by weight of a basic material, such as sodium hydroxide or potassium hydroxide.

4. A method according to claim 1, wherein a salt bath is used comprising 2 parts by weight of sodium nitrate and 1 part by weight of sodium hydroxide at a temperature of from 425° C. to 475° C.

5. A method according to claim 1, wherein, after the cleaning of the anodes by means of the melt, the last residues of the coating are removed by means of a dilute solution of hydrochloric acid, sulfuric acid, or a mixture of hydrochloric acid and nitric acid.

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