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AQUEOUS ELECTROLYTIC STRIPPING BATH

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ABSTRACT OF THE DISCLOSURE

An aqueous bath for the electrolytic stripping of coatings of silver, gold, chromium or nickel oxide from support bodies made of copper, copper alloy, tin alloy, stainless steel or high temperature alloys, the bath comprising as a main component over 80% sulfuric and/or sulfonic acid and as an additional component, an alcohol such as methanol or ethanol which does not enter into an olefin binding with sulfuric or sulfonic acid. Preferably the bath contains from about 800 up to about 940 cc. sulfuric and/or sulfonic acid and about 200 down to about 60 cc. alcohol per liter of bath and may contain as a further additional component, an aromatic hydrocarbon compound with at least one nitro group (—NO_2) bound directly to the benzene nucleus such as mononitrobenzene, trinitrobenzene, mononitrotoluene and/or nitrobenzoic acid.

The invention relates to novel aqueous baths for the electrolytic stripping of metal coatings, especially nickel oxide from support bodies of copper, copper alloy, tin alloy, stainless steel or high temperature alloys.

In practice, one often faces the task of having to strip coatings from support bodies, whereby, on the one hand one must effect a quick and completely efficient removal of the coatings while, on the other hand, the support body must not be subjected to any kind of corrosion or mechanical erosion.

A significant field of application lies in the production of gas turbine blades. These blades generally are made of so-called high temperature alloys, for example, a nickel base or chromium base alloy known under the trade name designations Inconel X, Refractaloy 26 or 70, Nimonic 80, 80A or 90, etc., and the workpieces are forged in several work steps until the final blade form is achieved. Prior to every workstep, the blades are "dead nickel" plated. During the forging process, a nickel oxide layer is formed. In order to start the next step, the nickel oxide layer and the old nickel layer must first be completely detached or stripped before the "dead nickel" plating required for the next forging step can be effected. The commercial stripping processes used heretofore are in most cases caustic processes and are quite expensive, hazardous and time consuming so that the stripping of the coatings that is to be carried out requires repeatedly that the baths be used and this is a main cost factor for the total cost in the large scale production of the blades for gas turbines. The reason for this is to be found especially in cost of the nickel oxide layer and in the cost of the electrolytic stripping of the nickel oxide layer for which no suitable commercial bath has been known up till now.

An object of the invention is to provide an aqueous electrolytic stripping bath for the electrolytic detachment of coatings of nickel oxide which will not chemically attack the support bodies which bear these coatings and which are made of copper, copper alloy, tin alloy, stainless steel or of high temperature alloys. This object according to the invention is achieved by means of an aqueous bath containing as a main component over 80% sulfuric and/or sulfonic acid and as an additive component, an alcohol such as methanol or ethanol which is water soluble will

not enter into an olefin formation with sulfuric and/or sulfonic acid, as practical tests have already shown. Outstanding results have been achieved with the bath of the present invention, but the limitation must be taken into account in the case of support bodies made of copper alloy, that the copper alloy must be free of phosphorus and that its nickel content be not too high, since, with an increasing nickel content, corrosion of the support body occurs and this corrosion must be avoided.

Methyl alcohol and/or ethyl alcohol and mixtures of these alcohols are well suited for the bath according to the invention. Since the coatings that have to be stripped are very thin a bath can be used, according to the invention, which contains from about 800 up to about 940 cc. concentrated sulfuric and/or sulfonic acid and from about 200 down to about 60 cc. alcohol per liter.

Preferably, however, the invention provides a bath which contains, as a further additive component, an aromatic hydrocarbon compound with at least one nitro group (—NO_2) bonded directly to the benzene nucleus. This acid bath containing the aromatic nitro compound can be used for thin as well as thicker coatings and even in the case of thicker coatings it provides relatively short stripping times. Examples of the additional aromatic nitro component, include mononitrobenzene, trinitrobenzene, mononitrotoluene and/or nitrobenzoic acid, these being useful as separate additives or as mixtures with each other in an amount of from 5–50 cc. or grams per liter. Preferably, a three component bath consists, per liter, of

	Cc.
Sulfuric and/or sulfonic acid	750–935
Alcohol	200–60
Aromatic nitro-hydrocarbon compound	50–5

During the stripping process, the support body is connected as an anode and operations are carried out at a temperature range of 20 to 60° C., in a voltage range of about 4 to 12 volts and in a current density range of about 5 to 25 amperes/dm.

In the following, preferred embodiments of the invention are given by way of example to illustrate advantages of the invention.

EXAMPLE I

Bath:
- 860 cc./liter of concentrated sulfuric acid
- 120 cc./liter ethyl alcohol
- 20 cc./liter mononitrobenzene

Temperature: 40° C.
Voltage: 8 v.

Example of application to demonstrate stripping efficiency

Case IIa:
- Support body: heating utensils made of stainless steel
- Coating: silver of 30 microns thickness
- Current density: 12 a./dm.
- Detaching time: 3 minutes

Case IIb:
- Support body: watch casing made of brass
- Coating: gold of 5 microns thickness
- Current density: 12 a./dm.
- Detaching time: 2 minutes

Case IIc:
- Support body: galvanic stand made of brass
- Coating: chromium of 5 millimeters thickness
- Current density: 40 a./dm.
- Detaching time: 5 hours

Case IId:

Support body: blade of a gas turbine made of nickel base alloy (high temperature alloy)
Coating: nickel oxide of 2 microns thickness (on the remaining nickel layer)
Current density: 12 a./dm.
Detaching time: 5 minutes.

In all cases of application, the coatings were completely detached while the support bodies showed no corrosion whatever. In regard to the case of application IId, it should be pointed out additionally that, after a forging process of the gas turbine blade, there will still remain, generally speaking, a more or less residual nickel layer after the nickel oxide layer is detached, which former will likewise have to be removed before the workpiece can be newly nickel plated for the next forgnig process. Different processes are known for the detachment of nickel coatings. For example, these nickel layers can be detached electrolytically using a bath which in an aqueous solution contains the following components:

(1) Ammonium nitrates and/or amines,
(2) Salts, especially ammonium salts or an organic acid,
(3) A chlorine compound and/or rhodanates.

In such a bath, the remaining nickel layer is removed from the workpiece within about one minute, when approximately the same remaining operating conditions for the process according to the preceding Example I are applied.

EXAMPLE II

Bath:	Cc./liter
Phenolsulfonic acid	900
Methyl alcohol	80
Nitrotoluene	20

Under otherwise the same operating conditions as in Example I, the same experiments were made with this bath. Almost the same detaching times according to Example I resulted.

In the foregoing examples there are illustrated stripping baths for the electrolytic stripping of coatings of silver, gold, chromium or nickel oxide from support bodies of copper, copper alloy, tin alloy, stainless steel or high temperature alloys wherein the main component provides over 80% sulfuric and/or sulfonic acid and as an additional component, an alcohol such as methanol or ethanol which does not enter into an olefin binding with sulfuric or sulfonic acid. The time for stripping or detaching is very rapid and can be controlled within one half minute up to fifteen minutes or longer depending upon the current density and thickness of the metal coating.

When the aromatic nitro hydrocarbon compound is added to the stripping baths in preferred proportions of 5 to 50 cc. of the aromatic nitro hydrocarbon compound per liter of the stripping bath, short stripping time is better controlled and the duration for stripping or detaching is diminished in comparison with the bath in which the nitro aromatic compound is omitted.

The temperature for stripping may be as high as about 80° C. but it is preferred to operate at temperatures between 20 and 60° C., for the reason that higher temperatures may create hazards to personnel and the higher temperatures are not necessary for efficient operation. The preferred voltage range is from about 4 volts to about 12 volts for most efficient operation but slightly higher or lower voltages can be employed under special circumstances where stripping time is not an important factor at the low voltage range and where the thickness which must be removed is very substantial at the high range. The preferred current density in the examples demonstrates the very effective results achieved in the range of 5 to 25 amperes per dm.

The critical strong acid ingredient may be concentrated (66 Beaume) sulfuric acid, or alkyl sulfonic acid such as methane sulfonic acid or ethane sulfonic acid such as phenol sulfonic acid or benzene sulfonic acid, but the cheaper mineral acid (sulfure acid) is preferred. The proportions of acid may vary from 75% to about 95% preferred proportions being from 85% to 93% by weight of the bath.

From the foregoing examples it is seen that coatings in thicknesses between .2 micron up to about 100 microns can be removed in a matter of minutes, e.g., from one half minute to 15 minutes depending upon the particular metal and that coatings in thickness of 1 to 10 millimeters can be removed very effectively in a matter of hours. Thus, the invention is very widely applicable for detaching the above enumerated metals without fear of corrosion to the base metal.

What is claimed is:

1. An aqueous electrolytic stripping bath for the removal of coatings composed of nickel oxide from support bodies of copper, copper alloy, tin alloy, stainless steel, high temperature nickel base alloy and high temperature chromium base alloy comprising:
from 750 to 935 cc. per liter of a sulfur containing acid selected from the group consisting of concentrated sulfuric acid, alkyl sulfonic acid and arylsulfonic acid as the stripping component;
an accelerating agent selected from the group consisting of mononitrobenzene, dinitrobenzene, trinitrobenzene, mononitrotoluene, and mono, di and trinitrobenzoic acids in an amount of about 5 cc. to 50 cc. per liter of said bath;
from about 60 to about 200 cc. per liter of an alcohol selected from the group consisting of methanol and ethanol; and
said bath adapted to strip the aforesaid coatings at a current density of 5 to 25 amperes per square decimeter at a temperature of 20° to 80° C.

2. A bath as claimed in claim 1 containing 860 cc. of 66 Beaume sulfuric acid per liter of bath and 120 cc. per liter of alcohol and 20 cc. of nitrobenzene.

3. A bath as claimed in claim 1 containing 900 cc. of phenol sulfonic acid, 80 cc. of methyl alcohol and 20 cc. of mononitrotoluene per liter.

4. A process for electrolytically stripping coatings of nickel oxide from support bodies of copper, copper alloy, tin alloy, stainless steel high temperature nickel base alloy and high temperature chromium base alloy, comprising inserting an article bearing said coating into a stripping bath at a temperature of about 40–80° C. and passing an electric current through said bath at a voltage of about 4–12 volts and current density of about 5 to 25 amperes per square decimeter, said stripping bath consisting essentially of 750 to 935 cc. per liter of a sulfur containing acid selected from the group consisting of concentrated sulfuric acid, alkyl sulfonic acid and arylsulfonic acid as the stripping component and from about 60 to about 200 cc. per liter of an alcohol selected from the group consisting of methanol and ethanol, and an accelerator consisting of a nitro aromatic compound in an amount of 5 to 50 cc. per liter of bath, said nitro aromatic compound selected from the group consisting of mononitrobenzene, dinitrobenzene, trinitrobenzene, mononitrotoluene and mono, di and trinitrobenzoic acids.

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