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3,649,489 PROCESS FOR ELECTROLYTICALLY STRIPPING COATINGS AND BATH THEREFOR Horst Dillenberg, 26 Kaiser-Wilhelm-Allee, 56 Wuppertal-Elberfeld, Germany No Drawing. Filed May 18, 1970, Ser. No. 38,568 Claims priority, application Germany, May 22, 1969, P 19 26 228.3 Int. Cl. B01k 1/00

U.S. Cl. 204-146

ABSTRACT OF THE DISCLOSURE

Process and aqueous bath for rapid stripping of thick nickel and/or chromium coatings from non-ferrous base metals, the coated non-ferrous base being connected as an anode under a voltage of about 8-15 volts at a current density of about 10-25 amperes per square decimeter and at a temperature of between 20 and 80° C., the aqueous 20 stripping containing from 50-95% of sulfuric acid or water-soluble alkyl or aryl sulfonic acid and 50-100 grams per liter of polycarboxylic acid compound selected from citric acid, lactic acid, oxalic acid, and water-soluble salts of said acids, e.g. the sodium, potassium, ammonium, and 25 acids are benzene sulfonic acid, toluene sulfonic acid

The invention relates to an aqueous electrolytic stripping bath for the electrolytic stripping of metal coatings composed of nickel and/or chromium from a metal substrate of non-ferrous metal and to a method of stripping nickel and chromium from non-ferrous substrates using said bath. The bath is intended especially for rapid stripping of thick coatings of nickel and/or chromium which are provided, for example, in the manufacture of dishes, cups, and other so-called hollow ware, which are given a thin silver or precious metal plating over the thick nickel or chromium plate.

The novel process and bath used herein are characterized by the rapid stripping of thick nickel and/or chromium coatings from non-ferrous base metals in an aqueous stripping medium containing from 50-95%, preferably 60-85%, of sulfuric acid or water-soluble alkyl or aryl sulfonic acid and from 50-100 grams per liter of polycarboxylic acid compound selected from the group consisting of citric acid, and water-soluble salts of these acids, such as sodium, potassium, ammonium and amine salts, with the coated non-ferrous base being connected as an 50 anode under a voltage of about 8-15 volts, at a current density of about 10 to about 25 amperes per square decimeter, and at a temperature of about 20 to 80° C., preferably 30° C.

There is a need to remove chemically defective or mechanically damaged nickel or chromium coatings from hollow ware and similar articles in order to permit the articles to be re-coated and thereafter plated with precious metals, and there is a further need to carry out the stripping process quickly without damaging the non-ferrous metal

The chemical separation processes used in the prior art have been too slow to gain present commercial acceptance and the present commercial practice is to employ electrolytic stripping to shorten the time in preparing the article for replating. One such commercial method used employs a sulfuric acid bath having a density of 1.57, equivalent to 65% sulfuric acid, for the removal of nickel or chromium coatings from copper base metal, and the etching of the base or damage to the base is inhibited, in 70 this commercial method, by adding small amounts of glycerin, especially when nickel is removed. This sulfuric

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acid electrolytic stripping method is very slow when thick coatings are to be removed.

In another known electrolytic process for stripping chromium coatings from nickel which covers iron, as described in British Pat. No. 336,532, the chromium is separated from the nickel layer by using an aqueous bath containing a polycarboxylic acid, such as oxalic, tartaric or citric acid. This bath has only limited utility because it strips chromium only and nickel cannot be removed 5 Claims 10 electrolytically using these organic acids.

The present invention is based on the discovery that a bath combining sulfuric acid and polycarboxylic acid for the electrolytic separation of coatings made of nickel and/ or chromium from base bodies of non-ferrous metals, especially copper and copper alloys, will achieve a very rapid stripping of the coatings and does not attack the non-ferrous base bodies. According to the present invention, this effect is achieved by means of a bath which consists of 50-95%, preferably 60-85%, sulfuric acid or water-soluble alkyl or aryl sulfonic acid and of one or more of the polycarboxylic acids or their salts.

Illustrative examples of water-soluble alkyl sulfonic acids are methane sulfonic acid and ethane sulfonic acid.

(ortho, meta and para isomers), nitrobenzene sulfonic acid (ortho, meta and para isomers), and xylene sulfonic

Preferably, the bath consists of 60-85% sulfuric or sulfonic acid and of 50-100 grams of citric, lactic, or oxalic acid, or their salts, per liter of sulfuric or sulfonic acid, whereby sodium oxalate, potassium oxalate, ammonium oxalate, sodium lactate, potassium lactate, ammonium lactate, sodium citrate, potassium citrate and/or ammonium citrate can be used as salts.

Furthermore, the invention relates to the process for quick electrolytic stripping of metal coatings from base bodies with the use of the previously described bath, and the process is characterized in accordance with the invention by the fact that one operates at a bath temperature of 20-80° C., preferably 30° C., at a voltage between 8 and 15 volts and a current density of 10-25 amperes per square decimeter, and that no corrosion of the underlying non-ferrous base results from such rapid stripping. The base body from which the coating is stripped is connected as the anode, as is well-known.

Practical tests have shown that all of the above-mentioned coating metals can be separated very rapidly with the bath according to the invention, without attack of the base body made of non-ferrous metal. The stripped metals are deposited as oxides and they must be removed at certain intervals in time from the container for the bath.

Three particularly preferred baths are given by way of illustration in the following examples:

EXAMPLE I

Composition of the bath

70% sulfuric acid-1 liter 60 Sodium citrate—75 grams

Conditions for the process

Voltage—12 volts Current density-15 amperes/dm.2 Bath temperature—30° C.

Result

With the above bath, nickel coatings of a thickness of 100 microns were completely separated from a base body made of copper within twenty minutes without the base body having been attacked.

Composition of the bath

75% sulfuric acid-1 liter Citric acid-80 grams

Conditions for the process

Voltage—12 volts Current density—20 amperes/dm.2 Bath temperature—50° C.

With the bath of this example, approximately 8 microns thickness of a layer of metal coating were removed per minute from a base body made of copper.

EXAMPLE III

Composition of the bath

75% nitrobenzenesulfonic acid-1 liter Lactic acid-50 cm.3

Conditions for the process

Voltage-12 volts Current density-20 amperes/dm.2 Bath temperature—40° C.

Results

Approximately 6 microns thickness per minute were stripped from a base body made of brass.

From the foregoing examples, it can be seen that coatings of 10 to 200 microns in thickness can be removed in a short time span of from 1 to 25 minutes, a result which cannot be achieved with the prior art electrolytic stripping baths and processes. Despite the rapidity of stripping, no corrosion or chemical attack of the underlying non-fer- 35 rous base is observed.

To increase the solubility of the organic sulfonic acids, water-soluble salts may be used; these being the sodium, potassium, ammonium, and amine salts.

1. An aqueous electrolytic stripping bath for the rapid removal of coatings composed of nickel and/or chromium from substrates of non-ferrous metals, comprising from 60-85% of a water-soluble sulfur-containing acid selected from the group consisting of sulfuric acid, alkyl sulfonic 45 JOHN H. MACK, Primary Examiner acid and aryl sulfonic acid as the stripping component and, as the accelerator for said stripping component, from 50-80 grams per liter of a polycarboxylic acid compound

selected from the group consisting of citric acid, lactic acid, tartaric acid, oxalic acid, and water-soluble salts of these acids, said bath adapted to rapidly strip thick coatings at a current density of 10-25 amperes per square decimeter at a temperature of 20-80° C.

2. A stripping bath as claimed in claim 1, wherein said water-soluble salts of said polycarboxylic acid compounds contain a cation selected from the group consisting of so-

dium, potassium, ammonium and amine.

3. A process for electrolytically stripping coatings of nickel and/or chromium from substances on non-ferrous metals comprising inserting a non-ferrous article coated with nickel or chromium into a stripping bath and passing an electric current at 8-15 volts from said article serving as anode to a cathode at a current density of between 10 to 25 amperes per square decimenter and at a temperature of 20-80° C., said stripping bath consisting essentially of from 50-95% of a water-soluble sulfurcontaining acid selected from the group consisting of sulfuric acid, alkyl sulfonic acid and aryl sulfonic acid as the stripping component and, as the accelerator for said stripping component, from 50-100 grams per liter of a polycarboxylic acid compound selected from the group consisting of citric acid, lactic acid, tartaric acid, oxalic 25 acid, and water-soluble salts of these acids.

4. A process as claimed in claim 3, wherein said temperature is from 30-50° C., said acid is sulfuric acid in a concentration of between 60 and 75%, and said poly-

carboxylic acid compound is citric acid.

5. A process as claimed in claim 3, wherein said temperature is 30-50° C. said acid is nitrobenzene sulfonic acid in a strength of 75%, and said polycarboxylic acid compound is lactic acid.

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