Erosion is slightly less at pH between 6.0 and 6.8 than at pH 5.0 to 6.0, and at pH below 5.0, erosion is substantial.
AQUEOUS ELECTROLYTIC STRIPPING BATH TO REMOVE METAL COATINGS FROM BASES OF STEEL

This invention relates to novel aqueous baths for the electrolytic stripping of metal coatings, namely nickel, chromium, zinc, tin, copper, cadmium and silver coatings, from bases of stainless steels such as chromium steel, nickel steel and chrome-nickel steel, and from bases of hardened or nitrided steels, and to electrolytic stripping methods employing the baths.

More particularly, the invention relates to novel aqueous baths which have almost universal stripping utility for electrolytic removal of metal coatings from stainless or nitriding or hardened steels, these aqueous baths containing ammonium or alkali nitrate in an amount of from 5 to 150 grams per liter, preferably from 20 to 100 grams per liter, the baths being buffered to a critical pH of between 5.0 and 6.8, preferably 6.0 and 6.8, with a water-soluble organic acid such as acetic acid, oxalic acid, citric acid and lactic acid, or with a water-soluble amine salt of these organic acids such as triethanolamine salt, ethylenediamine salt and the like, and an accelerator which speeds stripping while it is especially adapted to protect the base of steel from corrosive action during and after the stripping operation.

For stripping bases of stainless steel, the accelerator is preferably a water-soluble chlorine-containing compound, such as ammonium chloride, sodium chloride, potassium hypochlorite, etc., which is added to the bath in an amount of at least 0.5 grams per liter. Ammonium thiocyanate may be used as the accelerator in the same proportions.

For stripping bases of nitrided or hardened steel, the accelerator is preferably a water-soluble phenol which is added to the bath in an amount of from about 0.2 to about 30 cubic centimeters per liter. The phenol may be monovalent or polyvalent (1, 2 or 3 hydroxyl groups in the benzene ring) and alkyl homologues may be used.

Electrolytic stripping is essential when the metal coatings prove to be defective after the electroplating of stainless or hardened steel articles, such as gearwheels, combustion chambers, casings for gas turbines and tools. Stripping is necessary when the articles are damaged. The defective coatings must be completely stripped from the base before the articles can be replated.

The known chemical stripping processes were too slow to meet modern production schedules and have been displaced by fast electrolytic stripping methods. These known electrolytic methods have shortcomings, especially in respect to the corrosion of the base metal. In addition to the requirement for rapid and complete stripping of the coatings, there is the requirement that the base should not be attacked during the stripping step so that this base can be replated without a special machining or grinding step.

The known galvanic baths work on the basis of the stripping action of an aqueous solution of ammonium nitrate in highly acid medium, and these known baths have proved to be suitable to achieve short stripping times. However, these baths attack the base metal, especially when the baths are operated at a pH of below 5.0 down to about pH 3.0, this pH range being obtained by adjustment with nitric acid and amines. If the pH of the ammonium nitrate bath is raised so that the bath can be operated at just below the neutral point, e.g. with a pH range of about 6.0 to about 6.8, the base metal is not so much attacked but the time for complete stripping is increased to a point where uneconomical and uneconomical and where time schedules cannot be maintained. At a pH range of 2.0 to 3.0, the stripping time is considerably shorter, but the chemical attacks on the base metal increase. Therefore, it is essential to operate the known ammonium nitrate bath in a mean pH range of 4.0 to 5.0 to reach a tolerable compromise in which relatively long stripping times are accepted in order to restrict erosion of the base metal within acceptable limits.

It is the object of the invention to provide novel baths for electrolytic stripping of stainless steel and nitrided steel bases whereby shorter stripping times can be achieved while, at the same time, erosion of the base metal is avoided.

Starting with an aqueous solution of alkali or water-soluble nitrate, preferably ammonium nitrate, or of amines and nitric acid, the novel bath of the present invention is provided with two critical additional components. The first component is a buffering agent which brings the nitrate bath to an operational pH range of 5.0 to 6.8, preferably 6.0 to 6.8, the buffering agent being a salt of an organic acid, such as ammonium acetate, or the neutralization product of an amine (triethanolamine) and an organic acid (acetic acid). The second component is an accelerator. When the stripping is to be effected from bases of stainless steel, a water-soluble chloride compound and/or a water-soluble thioacynate compound constitute accelerators which are added to the bath in relatively small quantities. When the stripping is to be effected from bases of hardened or nitrided steel, an aromatic hydrocarbon compound with hydroxyl groups bonded directly on the benzene nucleus is added in relatively small quantities, whereby the base is bright, clean and free from corrosion after stripping.

As a result of the first-mentioned critical buffering agent, the bath is adjusted to just below the neutral point which is pH 7.0, to thereby provide assurance that there will be no appreciable erosion of the base metal. Examples of buffering agents include water-soluble salts of acetic acid, citric acid, lactic acid and oxalic acid, or the neutralization products of monovalent or polyvalent amines which are formed by the addition of the above-mentioned organic acids. Ethylene diamine or triethanolamine are illustrative of suitable amines.

The water-soluble salts are alkali metal, ammonium, primary, secondary or tertiary amine, quaternary ammonium or polyamine salts which are preferably of type to make them convenient to use. The primary amines such as monoethanolamine, butylamine, hexylamine, the secondary amines such as diethylamine and diethanolamine, and the tertiary amines such as dimethylaminine, triethyamine, tripropylamine are exemplary of aliphatic and aromatic amines which can be employed. Tetramethyl ammonium hydroxide is an example of a basic substance which can be added to make the organic acid salt for buffering purposes. When a water-soluble salt of an organic acid is used, it is preferred that the salt be of a substantially nonvolatilize amine which may be a primary, secondary or tertiary amine, for example, monoethanolamine, diethanolamine or triethanolamine.

The addition of buffering agent results in considerable extension of the stripping time, and this is counteracted by the second critical additive, the accelerating agent. Practical experience has shown that extremely short stripping times can be achieved by combining the first and second critical additives, while completely avoiding erosion of the base metal.

The second additive, the accelerator comprising a chlorine compound and/or thiocyanate or the phenolic compound, is less critical for stripping coatings of chromium, zinc, tin, copper, cadmium or silver than for stripping nickel coatings. If nickel is alloyed with chromium, zinc, tin, etc., the accelerating action is afforded by the additive is critical, particularly for dull-finished and semimatte nickel coatings. Since this second additive does not detract from the stripping of any of the other metal coatings, the invention provides a universal bath a pH just below neutrality.

However, a distinction must be made with regard to the bases to be treated, e.g. between those bases of stainless steel and those of hardened or nitrided steel, for the second additive. For bases of stainless steel, ammonium chloride and sodium hypochlorite exemplify water-soluble chlorine compounds, and ammonium thiocyanate exemplifies an equivalent accelerator. For bases of hardened or nitrided steel, monovalent or polyvalent phenols (phenol, dihydroxy benzene, trihydroxy benzene) and the homologues of phenol (cresol, thymol, xylene) may be used as accelerators which effectively strip irregular coatings and coatings on irregularly shaped articles.
To summarize, a bath for stripping nickel coatings from bases of stainless steel preferably contains, per liter of finished bath solution:
5 to 100 grams of ammonium nitrate, 50 to 400 grams of triethanolamine, 0.5 to 10 grams of ammonium chloride or ammonium thiocyanate and organic acids in an amount sufficient to adjust to a pH range of 5.0 to 6.8, preferably 6.0 to 6.8.

A bath for stripping nickel coatings, in particular, from bases of hardened or nitrided steel preferably contains, per liter of finished bath solution:
20 to 200 grams of ammonium nitrate, 50 to 400 grams of triethanolamine, 0.2 to 30 grams of phenol, and organic acids sufficient to adjust to a pH range of from 5.0 to 6.8, preferably 6.0 to 6.8.

The bath is used for electrolytic stripping with the anode connected as an anode and the stripping may be carried out at a temperature of 20–90° C, preferably 50–90° C, under a current density of 5 to 30 amperes per square centimeter and a voltage of about 10–20 volts.

When water-soluble inorganic hypochlorites are used, the potassium hypochlorite, sodium hypochlorite or ammonium hypochlorite can be used interchangeably.

The invention can be explained more fully by reference to the following specific examples which represent illustrative embodiments of the process with which practical operating success has been had.

EXAMPLE 1

For bases of stainless steel, the solution contains:

| Ammonium nitrate | 20 grams per liter |
| Triethanolamine | 200 cc. per liter |
| Ammonium chloride | 2 grams per liter |
| Acetic acid | sufficient for a pH of 6.5 |

The base is connected as an anode and the stripping process is carried out with a voltage of 15 volts, a current density of 20 amperes per square decimeter, and a temperature of 60° C. With such a bath, nickel coatings having a thickness of microns are completely stripped, within 1 minute, from the base of stainless steel without any erosion, corrosion or noticeable chemical attack of the base.

EXAMPLE 2

For bases of hardened or nitrided steels, a bath is used which is composed of:

| Ammonium nitrate | 100 grams per liter |
| Triethanolamine | 200 cc. per liter |
| Phenol | 5 cc. per liter |
| Acetic acid | sufficient for a pH of 6.5 |

The operating conditions are the same as in example 1. Nickel coatings with a thickness of 30 microns are likewise stripped completely from the base within 1 minute without erosion of the base metal.

The above-mentioned operating conditions merely represent optimum values and may be varied to a considerably extent while still achieving useful results. Thus, it is possible to operate within a voltage range of from 10 to 20 volts, within a temperature range of from 20° to 90° C, and within a range of current densities from 5 to 30 amperes per square decimeter.

The composition of the bath changes during use since the bath liquid is entrained by the articles dipped therein and removed to reduce the volume which makes it necessary to replenish the liquid. Also, as a result of the decomposition by the hydrogen which is released at the cathode, the ammonium nitrate decomposes. In addition, the components of the bath form complexes with the coating metals which are stripped, and this depletes the bath. Consequently, for prolonged operation, the bath must be monitored with regard to its strength, composition, and pH value, and must be replenished according to the consumption of the individual components.

Other modifications of the invention will fall within the scope of the following claims will be evident to those skilled in the art.

1. An aqueous electrolytic stripping bath to remove metal coatings from stainless steel comprising: ammonium nitrate and/or an amine nitrate salt as the sole stripping component in an amount of from 5 to 200 grams per liter; said bath being buffered with a water-soluble salt of an organic acid to a pH range of about 5.0 to about 6.8, preferably 6.0 to 6.8, and a water-soluble accelerator in an amount of from 0.5 to 10 grams per liter, said accelerator increasing the stripping rate of the ammonium nitrate under a current density of 5 to 30 amperes per square centimeter in a temperature range of 20–90° C, and being selected from the group consisting of water-soluble organic or inorganic compounds, ammonium thiocyanate and alkali metal thiocyanate.

2. An aqueous electrolytic stripping bath as claimed in claim 1, wherein said water-soluble salt of an organic acid is selected from the group consisting of alkali metal salts and ammonium salts.

3. An aqueous electrolytic stripping bath as claimed in claim 1, wherein said water-soluble salt of an organic acid is selected from the group consisting of those compounds which are formed by adding an organic acid selected from the group consisting of acetic acid, citric acid, lactic acid and oxalic acid to an amine.

4. An aqueous electrolytic stripping bath as claimed in claim 1, wherein the metal coating which is stripped is selected from the group consisting of nickel, chromium, zinc, tin, copper, cadmium and silver.

5. An aqueous electrolytic stripping bath as claimed in claim 1, wherein said bath contains 5 to 100 grams per liter of ammonium nitrate, 50 to 400 grams per liter of triethanolamine, 0.5 to 10 grams per liter of ammonium chloride, and wherein said organic acid is acetic acid.

6. An aqueous electrolytic stripping bath as claimed in claim 1, wherein said bath contains 5 to 100 grams per liter of ammonium nitrate, 50 to 400 grams per liter of triethanolamine, 0.5 to 10 grams per liter of ammonium thiocyanate, and wherein said organic acid is acetic acid.

7. An aqueous electrolytic stripping bath as claimed in claim 1, wherein said bath contains 20 grams of ammonium nitrate, 200 grams of triethanolamine, 2 grams of ammonium chloride, and wherein said organic acid is acetic acid.

8. An aqueous electrolytic stripping bath as claimed in claim 1, wherein said bath contains 20 grams of ammonium nitrate, 200 grams of triethanolamine, 2 grams of a hypochlorite selected from the group consisting of sodium hypochlorite, potassium hypochlorite and ammonium hypochlorite, and wherein said organic acid is acetic acid.

9. An aqueous electrolytic stripping bath to remove nickel coatings from hardened and nitrided steels comprising: ammonium nitrate or an amine nitrate salt as the sole stripping component in an amount of from 5 to 200 grams per liter; said bath being buffered with a water-soluble amine salt of an organic acid to a pH range of about 5.0 to about 6.8, preferably 6.0 to 6.8, and a water-soluble phenol as the accelerator for stripping in an amount of from about 0.2 to about 30 grams per liter, said phenol accelerator increasing the rate of removal of nickel by the ammonium nitrate under a current density of 5 to 30 amperes per square centimeter in a temperature range of 50° to 90° C.

10. An aqueous electrolytic stripping bath as claimed in claim 9, wherein said phenol is a monohydric phenol.

11. An aqueous electrolytic stripping bath as claimed in claim 9, wherein said phenol is dibromoacetic benzene.

12. An aqueous electrolytic stripping bath as claimed in claim 9, wherein said phenol is cresol.
13. An aqueous electrolytic stripping bath as claimed in claim 10, wherein said bath contains 20 to 200 grams of ammonium nitrate, 50 to 400 grams of triethanolamine, 0.2 to 30 cc. per liter of phenol, and wherein said organic acid is acetic acid.

14. An aqueous electrolytic stripping bath as claimed in claim 10, wherein said bath contains 100 grams of ammonium nitrate, 200 grams of triethanolamine and 5 grams of phenol, and wherein said organic acid is acetic acid.