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3,542,658

ELECTROLYTIC BATH CONTAINING AMMONIUM NITRATE AND A PHENOL

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7 Claims

ABSTRACT OF THE DISCLOSURE

An aqueous electrolytic stripping bath to remove nickel coatings from ferrous metal articles comprising ammonium nitrate as the sole stripping component in an amount of from 50–400 grams per liter and a water-soluble phenol as the sole accelerator in an amount of from 1–20 grams per liter. In the absence of the phenol accelerator complete stripping of complex shapes having deep corners at a current density of 8 amperes per square decimeter takes many hours while in the presence of the critical amount of phenol, complete stripping is accomplished in as little as 10–20 minutes at a pH of 4–6. The phenol is consumed during the course of the stripping and the invention contemplates replenishing it in order to maintain the concentration between the level of 1–20 grams per liter. Illustratively, 800 grams of phenol may be needed during the stripping of one kilogram of semi-lustrous nickel or of mat nickel coating.

This invention relates to a novel electrolytic stripping bath for the removal of galvanic coatings or deposits, such as nickel coatings, from ferrous metal articles, the bath comprising, as its sole stripping component, a major proportion of an aqueous solution of ammonium nitrate (on a dry chemical basis) and a minor but critical proportion of a water-soluble phenol which serves as the sole accelerator for the stripping of the metal coating by the ammonium nitrate.

The invention also relates to a new method of stripping metal coatings, especially nickel coatings, from ferrous metal articles wherein a ferrous metal article having a nickel coating is immersed in the stripping bath containing as its essential stripping ingredient, an aqueous solution of from 50–400 grams of ammonium nitrate per liter of solution and from about 1–20 grams per liter of a water-soluble phenol serving as the accelerator for the stripping action of the ammonium nitrate solution, there being present a pH buffer consisting of the alkali metal salt of an organic acid, e.g. sodium acetate or sodium citrate, in an amount to maintain the pH at between 4 and 6 during the passage of direct current through the stripping bath.

The ferrous metal article having the nickel coating is placed in the stripping bath which is held in a corrosion resistant tank, and the ferrous metal article connected as the anode to the electrolytic stripping apparatus employing a stainless steel plate as the cathode. Rapid and complete stripping occurs at temperatures of from 20–100° C., preferably 40–60° C., at a current density of 8 amperes per square decimeter as the minimum density up to about 36 amperes per square decimeter as a desirable top limit of current density.

It is frequently necessary to strip galvanic coatings, especially nickel coatings, during the manufacture of automobile bumpers, camera housings, automobile rods and the like, in order to remove unwanted coatings from the supporting structure and the methods heretofore used have presented manufacturing disadvantages because the known

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methods generally use highly corrosive chemicals and concentrated acids, such as chromic and sulfuric acids, are slow and give less than complete stripping, and are expensive to carry out because of the high cost of skilled labor and of chemicals.

Stripping baths containing concentrated sulfuric acid at 52° to 56° Beaumé are slow in their action and, when accelerated with catalytic agents, result in attack by the acid on the base metal. Alkali metal nitrate baths, such as sodium or potassium nitrate, have been used to avoid the attack on the base metal, but these are unsatisfactory because they are no faster than the sulfuric acid bath. Also, potassium nitrate and sodium nitrate have the additional disadvantage of setting free hydroxide during the stripping process, this hydroxide forming a slush which renders the stripping bath unusable in a relatively short period of time.

In contrast to these disadvantages of sodium and potassium nitrate, a stripping bath based upon ammonium nitrate as the sole stripping agent has the advantage of avoiding the slush buildup, but is nevertheless extremely slow in its stripping action and also tends to corrode the ferrous base metal, especially alloy steels and ordinary steels with carbon content greater than 0.1%.

As pointed out in the examples of Bell et al., U.S. Pat. 2,549,411, the current densities of ammonium nitrate stripping solutions vary from 108 amperes per square foot, which is about 11.6 amperes per square decimeter, up to 475 amperes per square foot, which is 51.1 amperes per square decimeter, the higher current densities demanding higher voltages and producing more rapid stripping, and the lower current densities permitting undesirable etching of the ferrous base metal. Bell et al. found that sulfates did not detract from the efficiency of their stripping method if a nitrogen base were present, such as guanidine, diethanolamine, trimethyl amine, ethylene diamine, urea, aniline etc., in an amount of at least 50 grams per liter and at a pH of about 3 to 6.

The present invention distinguishes over the teaching of Bell et al., U.S. Pat. 2,549,411, in the employment of a water-soluble phenol selected from the group consisting of phenol, pyrocatechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol, oxyhydroquinone, nitrophenol, nitropyrocatechol and dinitrophenol, which serves as the sole accelerator of stripping at low current densities in the range of from 8 amperes per square decimeter to about 36 amperes per square decimeter.

It is possible to use higher current densities since, in theory, there is no upper limit to current density, but the practical advantages of complete stripping, lower costs and higher production rates are achieved at the lower current densities of from 8 to 36 amperes per square decimeter. This advantage of complete stripping is achieved in the absence of non-volatile, inorganic acid, such as chromic or sulfuric acid. The pH of the stripping bath is adjusted with nitric acid. Only after the pH of 4–6 is attained by nitric acid addition, is the water-soluble salt of weak organic acid, e.g. sodium acetate or sodium citrate, added to the bath to serve as buffer. However, this buffer is not critical since the utilization of the bath with nickel coated low-carbon steels is less efficient in the presence of acetate or citrate buffer. A low-carbon stripping bath need contain only ammonium nitrate and phenol, the preferred amounts being 200 grams of ammonium nitrate and 5 cubic centimeters of the phenol, the preferred phenol being phenol.

The density of pure phenol is 1.07 grams per milliliter. The water-soluble phenols other than phenol itself are each measured in grams, while phenol is most conveniently liquefied by heating to above 41° C. and is measured in cubic centimeters.

The preceding description referring to the critical proportions of the phenol in grams is based upon the equivalence of grams to cubic centimeters.

An object of the invention is to provide a stripping bath which is free from nonvolatile, inorganic acid such as sulfuric acid or chromic acid but which is adapted for rapid and complete electrolytic stripping of a nickel coating from ferrous articles of complex shapes, without attacking or etching the ferrous base.

Another object is to provide an aqueous solution of ammonium nitrate as the sole stripping component with a water-soluble phenol as the accelerator for the stripping action, which solution is acidified to a pH of 4-6 with nitric acid, the proportions of the phenol being maintained between 1 and 20 grams per liter by replenishing during usage and being particularly adapted for stripping low-carbon steels.

Other and further objects of the invention will be seen from the representative illustrative embodiments hereinbelow with which there has been achieved practical operating success.

EXAMPLE I

A solution is prepared containing 200 grams of ammonia nitrate, 2 cc. of phenol measured when melted to 45° C. and 100 grams of sodium acetate in 1 liter of water. A high carbon steel angle-iron (more than 0.1% carbon) which bears a semi-lustrous nickel coating in a thickness of .0008 inch is submerged in the solution constituting the bath in a corrosion-resistant tank formed of molded synthetic resin, such as polystyrene or polyethylene. The bath is maintained at 45° C. The angle-iron is made the anode and a stainless steel plate is used as the cathode. The pH of the bath is adjusted to four by adding nitric acid. A current density of 8 amperes per square decimeter is applied and the nickel coating is completely stripped from the angle-iron in about 10 minutes, leaving the angle-iron bright and in condition to be replated without repolishing.

EXAMPLE II

Instead of using a high-carbon ferrous base as in Example I, a low-carbon angle-iron (less than 0.1% carbon) coated with nickel having a thickness of .00125 inch is stripped in 20 minutes using a bath solution consisting of 200 grams of ammonium nitrate and 5 cc. of phenol per liter of water, the solution being adjusted to pH 4 with nitric acid and being free of buffer, such as sodium acetate or sodium citrate.

Example I illustrates a bath which is particularly useful for stripping ferrous metals with a carbon content greater than 0.1%. Example II illustrates a bath useful for stripping ferrous metals with a carbon content less than 0.1%. At pH values above 6.0, the stripping rate becomes so slow as to make the process impractical. Raising the current density up to about 36 amperes per square decimeter tends to cause loss of the stripping solution and requires higher voltages so as to increase operating costs, but stripping can be hastened. It is preferred to carry out the stripping operation at lower cost keeping in mind that phenol is consumed and required replenishment. Operating at higher current densities increases the temperature of the bath making the replenishment with phenol more difficult. If phenol is objectionable, the dihydric phenols such as resorcinol may be used, or the trihydric phenols such as pyrogallol may be used, these being less volatile and odorless than phenol. The advantages of low cost and simplicity of operation with phenol can outweigh the disadvantages of odor and volatility in installations provided with good ventilation.

If the phenol accelerator in Example I is eliminated, the semi-lustrous nickel coating is not completely removed, even after 24 hours. Therefore, the effect of the phenol is to accelerate stripping from a time period of about a day to about 10-20 minutes, as shown in Examples I and II. In the unbuffered and buffered baths, the present composition serves as a "universal" solution for

electrolytic stripping of nickel coatings from ferrous metal articles, whether of high or low carbon content.

The procedure to be used with any particular complex ferrous shape bearing thicker nickel coatings than those illustrated above will depend upon the greater thickness, it being kept in mind that for each kilogram of semilustrous nickel coating removed, it is necessary to add about 800 cc. of phenol. The phenol content of the bath is checked by known procedures and it is preferred to adjust the addition of the phenol to maintain a preferred minimum level of 2 cc. per liter for high-carbon ferrous base metals or of 5 cc. for low-carbon ferrous base metals.

Obviously, if the production requirements permit operation at lower temperatures, e.g. 40-60° C. Instead of 60-80° C., then the control of phenol replenishment is easier and the full benefits of the invention can be realized with simpler equipment. Any conventional electro-stripping apparatus may be used.

The stripping bath of the present invention is useful not only for removing nickel coatings from a ferrous base, but also may be used for stripping any non-ferrous coating, such as chromium, cobalt and the like.

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

I claim:

1. An aqueous electrolytic stripping bath to remove nickel coatings from ferrous metal articles comprising ammonium nitrate as the sole stripping component in an amount of from 50-400 grams per liter and a water-soluble phenol having from 1 to 3 hydroxyl groups and no other functional group than the nitro group as the sole accelerator in an amount of from 1-20 grams per liter, said bath being acidified with nitric acid to a pH of between 4 and 6 and being adapted to completely strip the nickel coating at a current density of at least 8 amperes per square decimeter and at a temperature of 20-100° C.

2. A bath as claimed in claim 1 wherein said water-soluble phenol is selected from the group consisting of phenol, pyrocatechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol, oxyhydroquinone, nitrophenol, nitropyrocatechol and dinitrophenol.

3. In the stripping of nickel from ferrous metals, the process which comprises inserting a ferrous metal article coated with nickel in a stripping bath and passing an electric current from said article, serving as anode, to a cathode, said stripping bath consisting essentially of an aqueous solution of ammonium nitrate, as the sole stripping component, in an amount of from 50-400 grams per liter and a water soluble phenol having from 1 to 3 hydroxyl groups and no other functional group than the nitro group, as the sole accelerator, in an amount of from 1-20 grams per liter, said bath being acidified with nitric acid to a pH of between 4 and 6 and being adapted to completely strip the nickel coating at a current density of at least 8 amperes per square decimeter and at a temperature of 20-100° C.

4. A process as claimed in claim 3 wherein said water-soluble phenol is phenol which is continuously added during the course of the stripping process to maintain the level of phenol in the solution at a value of at least about 2 cubic centimeters of phenol per liter of water making up the bath, there being consumed an amount of said phenol during stripping to require about 800 cubic centimeters of phenol for each kilogram of nickel which is stripped.

5. A process as claimed in claim 3 wherein said water-soluble phenol is phenol which is present in an amount of 2 cubic centimeters per liter of water in the bath and said stripping bath contains about 200 grams of ammonium nitrate and about 100 grams of sodium acetate.

6. A process as claimed in claim 3 wherein said water-soluble phenol is phenol which is present in an amount of about 5 cubic centimeters per liter of water in the bath and said stripping bath contains about 200 grams of ammonium nitrate which adapts the bath, free from acetate

or citrate, for the stripping of nickel from low-carbon steel containing less than 0.1% carbon.

7. A process as claimed in claim 3 wherein said water-soluble phenol is selected from the group consisting of phenol, pyrocatechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol, oxyhydroquinone, nitrophenol, nitropyrocatechol, and dinitrophenol. 5

References Cited

UNITED STATES PATENTS

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