ELECTROLYTIC STRIPPING OF NICKEL COATINGS FROM FERROUS METALS

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1. This invention relates to stripping nickel coatings; and it comprises a process wherein a ferrous metal article having a nickel coating is immersed in a stripping bath, comprising an ammonium or nitrogen base salt of nitric acid or chromic acid in a concentration advantageously ranging from about 50 to 300 grams of said salt per liter; said bath operating usually at a temperature within the range of about 25° to 55° C. and having a pH within the range of about 3 to 6; followed by passing through said bath from said metal article to a suitable cathode a direct current having a current density within the range of about 20 to 400 amperes per square foot, whereby the nickel coating is stripped without damage to the ferrous base; all as more fully hereinafter set forth and as claimed.

It is frequently necessary in the plating art to strip defective metal coatings from ferrous metal bases. While several stripping methods are known, which give more or less satisfaction in the case of other metals, the stripping of nickel has always presented great difficulties. Three methods have hitherto been used for this purpose. One of these makes use of a stripping bath containing sulfuric acid at a density ranging from about 52° to 56° Bé. The nickel plated parts are made anodes in this stripping bath. A second method makes use of a concentrated neutral solution of sodium nitrate, this bath being operated in the same manner except for the use of higher current densities. The third method makes use of fuming nitric acid without the aid of the electric current. All of these methods have serious technical and economic disadvantages and are hazardous in operation.

The sulfuric acid bath has found the widest use up to this time. However the operation of this bath is much slower than is desired. For example, a nickel deposit that has required from 10 to 40 minutes for its application will need from 30 to 120 minutes for its removal by this bath. The action of this bath can be accelerated by dilution but, if this is done, the attack of the acid upon the base metal is aggravated. This is a step in the wrong direction, for, notwithstanding the use of addition agents to inhibit the etching action of the acid, light gauge cold rolled steels are generally etched to a degree which makes it impossible to repolish and satisfactorily replate them. Furthermore, an insoluble nickel sludge is formed which must be removed, resulting in large and uneconomic losses of the stripping bath. The disadvantages of the sulfuric acid bath are found also in the sodium nitrate bath, which is even slower in operation. While the tendency to etch is likewise reduced, the work must nevertheless generally be polished before replating.

2. The fuming nitric acid bath has not been widely used because of the obvious health hazards and the dangers involved in using so corrosive an acid.

It is an object of the present invention to provide a stripping bath containing an electrolyte which will remove nickel coatings of commercial thickness within practical time limits. It is a further object to provide an electrolyte which will remove defective nickel coatings from all types of ferrous base metals without necessitating repolishing of the metal before replating. Yet another object is to provide an electrolyte for stripping of defective nickel coatings which is free of hazard in its use and operation. It is a still further object to provide a stripping composition which upon solution in water is ready for use without the necessity of any adjustment.

We have discovered that the foregoing and other objects of our invention can be attained by the use of an aqueous stripping bath comprising a nitrogen base salt of nitric acid or chromic acid, sufficient acid being present in said bath to produce a pH of about 6.0 or below. The ferrous metal article whose nickel coating is to be stripped is dipped into said bath and its coating removed by the passage of a direct current from the article to a suitable cathode. We have found that it is necessary to have present in our stripping bath the nitrate or chromate anion in a concentration not substantially less than about 10 grams per liter. Other acids may be present whose anodic decomposition products are relatively inert or non-activating towards ferrous metals. For example we have found that sulfates and acetates do not unfavorably affect the operation of our baths, while chlorides cause the etching of the ferrous metal, owing to the activating effect of their anode decomposition product, i.e. chlorine. Chromates and nitrates of nitrogen bases selected from a class consisting of ammonium hydroxide, guanidine, diethanolamine, triethanolamine, trimethyl amine, ethylene diamine, urea, benzyl amine, aniline, methylphenyl amine, dimethylphenyl amine, diphenylmethyl amine etc. are suitable.

Our stripping baths can be made by mixing the amine or ammonia with nitric or chromic acid
in an aqueous medium. For example, a bath can be made by adding nitric or chromic acid and ammonia or an amine to water, to form the corresponding ammonium or substituted ammonium salt. It is also possible and usually more advantageous in cases where the salts are commercially available, to add these salts directly to the bath rather than adding their reactive components. The resulting baths are operative over a wide range of concentrations and temperatures but for best results the concentrations, temperatures and pH values must be held within relatively close limits.

We have found that if the concentration of the salt is held within the range of from about 10 g./L. (1.3 oz./gal.) to saturation, good stripping results may be obtained. However, if the concentration is below about 50 g./L. (67.7 oz./gal.) the conductivity of the solution is so low that unduly high voltages are required. On the other hand solutions more concentrated than about 300 g./L. (40 oz./gal.), while operating quite well, do not exhibit sufficiently greater conductivity or stripping speed to justify the additional cost of preparation and maintenance. In the preferred range, it will be found that a bath containing about 200 g./L. (26.6 oz./gal.) of the salt will most generally prove satisfactory.

In the preferred concentration range, the speed at which the deposit is removed depends upon the temperature and pH of the bath and the anode current density. If the bath temperature is above about 130° F.—this limit varying somewhat with type and quantity of salt and with acidity—there may be some tendency for anode steel to etch on prolonged immersion. It is not desirable to chill the bath, as its resistivity at low temperatures is high enough to require uneconomically high voltages. As a result of these factors temperatures between 80° F. and 130° F. are most suitable.

We have discovered that, in order to avoid etching of the ferrous base metal, it is essential that the stripping bath be maintained at least slightly on the acid side of the neutral point. Thus, we have found that a neutral stripping bath containing ammonium nitrate causes some etching of steel when the latter is merely immersed in the bath for any length of time. But surprisingly we have discovered that this etching is eliminated by slightly acidifying the bath and passing an electric current therethrough from the steel to a suitable cathode. It would have been expected that either or both of these changes would have accelerated the etching. The fact is, however, that the combined effect of the electric current and a slightly acid bath sharply diminishes the etching effect. At pH values only slightly on the acid side of the neutral point, that is, at a pH of 6.0 or above, we have found that the stripping rate is quite slow. At low pH values in the neighborhood of a pH of 1, on the other hand, the stripping rate is high but in this region there is some danger of etching the base metal, particularly in areas where the thermal deposit is thin and where therefore the base metal is laid bare early in the stripping operation. We therefore operate our process within a pH range of about 3.0 to 6.0. This avoids both difficulties.

In operation the pH of the stripping bath tends to increase; hence, occasional replenishment of time to time is necessary. The pH can be controlled within the desired limits by occasional addition of an acid or an acid salt. It is usually advisable to add in this manner the acid whose salt is present in the bath in order to be certain that the passivating character of the bath shall be preserved. But we have found that it is also feasible to adjust the pH, especially the initial pH, by the addition of sulfuric acid or sodium acid sulfate. This reduces the operating cost but, if such an acid is used during operation of the bath, tests should be made from time to time to be certain that the concentration of the passivating anion in the bath does not fall substantially below about 10 g./L. since the passivating acid is used up in the process. When the passivating acid is added to control the pH, however, usually it is not necessary to test the concentration of this acid.

A very convenient way of starting the operation of one of our stripping baths is to use a mixture of dry chemicals which when dissolved in water in a predetermined quantity will produce a stripping bath of the correct pH and concentration. The acid constituent employed in such compositions must, of course, be dry. Chromic acid and sodium acid sulfate are the most convenient to use. Thus a mixture of ammonium nitrate with either chromic acid or sodium acid sulfate can be employed and a mixture of ammonium or a substituted ammonium chrome with potassium bisulfate or chromic acid is equally satisfactory.

We have found no upper limit to the current density that may be used. Densities as high as 528 a./sq. ft. (58.7 a./sq. dm.) work quite as well as densities as low as 20 a./sq. ft. (2.1 a./sq. dm.). Very high current densities will of course demand high voltages and the spray from the cathodes is likely to be excessive, with loss of stripping solution. On the other hand, too low an anode current density results in an unduly extended stripping time. Moreover, very low current densities, or no current density at all may result in etching of the work. Suitable current densities may be obtained from customary direct current sources, operating at voltages between 4 and 18. These current densities may run from about 20 a./sq. ft. (2.1 a./sq. dm.) up to 400 a./sq. ft. (42 a./sq. dm.)

To summarize the above, the preferred operating conditions for our stripping bath may be tabulated as follows:

- Concentration of Salt, 50 g./L. (6.7 oz./gal.) to 300 g./L. (40 oz./gal.)
- pH, 3.0 to 6.0
- Temperature, 25° C. (77° F.) to 55° C. (131° F.)
- Current densities, 20 a./sq. ft. to 400 a./sq. ft. (2.0 a./sq. dm. to 40 a./sq. dm.)

A tank made of corrosion-resistant material or lined with such material is required. Among suitable materials are synthetic resins of the vinyl or vinylidene groups, polyethylene, polyacrylonitrile or other plastics, and glass. It is necessary merely to dissolve the salts in water in such a tank, connect the work to be stripped to the positive pole of a generator or other source of current, and immerse it in the solution, the negative pole of the current source being connected to an inert cathode, of steel or nickel, for example, immersed in the solution.

Our invention can be explained more fully by reference to the illustrative examples which represent illustrative embodiments of our process with which we have had practical operating suc-
Example 1

A solution is made up containing:

\[
\begin{align*}
\text{NH}_4\text{NO}_3 & \quad 100 \text{ g./l.} \\
\text{NaHSO}_4 & \quad \text{enough to lower the pH to 4.0}
\end{align*}
\]

In this solution nickel having a thickness of 0.0016 inch was completely stripped in 9 minutes at 3.3 a./sq. in. current density from polished steel, leaving it bright, and in condition to be replaced without rebuffing.

Example 2

Triethanolamine \quad 90 g./l. \\
\text{HNO}_3 \quad \text{enough to lower the pH to 4.0}

In this solution, nickel having a thickness of 0.0016 inch was completely stripped in 20 minutes at 1.3 a./sq. in. current density from polished steel, leaving it bright, and in condition to be replaced without rebuffing.

Example 3

\[
\begin{align*}
\text{Cr}_2\text{O}_3 & \quad 80 \text{ g./l.} \\
\text{NH}_2\text{OH} & \quad \text{enough to raise the pH to 4.0} \\
\text{HNO}_3 & \quad \text{adding during stripping to maintain pH}
\end{align*}
\]

In this solution, nickel having a thickness of 0.0016 inch was completely stripped in 40 minutes at a current density of 1.5 a./sq. in. from polished steel, leaving it covered with a glossy adherent black film. This film was dissolved off by a 10 second dip in dilute HCl, and the piece was immediately replated with bright nickel with completely satisfactory luster.

Example 4

\[
\begin{align*}
\text{NH}_4\text{NO}_3 & \quad 100 \text{ g./l.} \\
\text{HNO}_3 & \quad \text{enough to lower the pH to 4.0}
\end{align*}
\]

In this solution, nickel having a thickness of 0.00125 inch was completely stripped in 40 minutes at a current density of 0.75 a./sq. in. from polished steel, leaving it bright, and in condition to be replaced without repolishing.

Example 5

\[
\begin{align*}
\text{NH}_4\text{NO}_3 & \quad 200 \text{ g./l.} \\
\text{NaHSO}_4 & \quad 0.6 \text{ g./l.}
\end{align*}
\]

This solution had a pH of 3.1. During the stripping, \(\text{H}_2\text{SO}_4\) was added at intervals to keep the pH between 3.0 and 4.0. In this solution, nickel having a thickness of 0.0015 inch was completely stripped in 9 minutes at a current density of 1.5 a./sq. in. from polished steel, leaving it bright and in condition to be replaced without repolishing.

Example 6

\[
\begin{align*}
\text{Urea} & \quad 150 \text{ g./l.} \\
\text{CrO}_3 & \quad 7 \text{ g./l.} \\
\text{HNO}_3 & \quad \text{enough to lower the pH to 5.0}
\end{align*}
\]

In this solution, nickel having a thickness of 0.00185 inch was completely stripped in 14 minutes at a current density of 1.3 a./sq. in. from polished steel, leaving it bright and in condition to be replaced without repolishing.

Example 7

\[
\begin{align*}
\text{Guanidine carbonate} & \quad 110 \text{ g./l.} \\
\text{HNO}_3 (70\%) & \quad 80 \text{ ml./l.}
\end{align*}
\]

This is equivalent to a 150 g./l. solution of guanidine nitrate. Because of the lesser solubility of guanidine nitrate at lower temperatures, the bath was maintained at 125°-130° F. The pH was kept between 3.5 and 6.0 by occasional additions of HNO₃. In this solution, nickel having a thick-
but holes are eaten into it, stopping at the steel, and these holes expand, eating away at the edges of the remaining nickel.

It will be appreciated that the chief merits of our process are (1) that it will rapidly dissolve nickel and (2) that iron can be subjected to it for extended periods of time without damage. We know of no other stripping process that possesses both advantages.

While we have described what we consider to be the most advantageous embodiments of our process, it is evident, of course, that various specific details which have been described can be varied without departing from the purview of our invention. The procedure to be used in making up our stripping baths will depend, of course, upon the relative cost and availability of the ingredients. If an amine salt is to be used, for example, and the cost of the oxidizing acid is lower than the cost of the amine salt, it would be preferable to make the stripping baths by adding the amine and the oxidizing acid separately to the water thus forming the amine salt in situ. This is a very satisfactory way to proceed since, if the amine is added first, the oxidizing acid can be added until the pH of the bath is within the desired range. On the other hand, if the amine salt is added to the water, it is then usually necessary to adjust the pH by the addition of an acid or acid salt. Any conventional type of electroplating or electrostripping apparatus can be used in our process and conventional stripping procedures can be used. Other modifications of our invention which fall within the scope of the following claims will be immediately evident to those skilled in this art.

What we claim:

1. 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 substantially of an aqueous solution of ammonium nitrate having a concentration ranging from about 50 to 300 grams per liter and a pH of about 3.0 to 6.0.

2. 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 a direct current from said article, serving as anode, to a cathode; said stripping bath consisting substantially of an aqueous solution of a salt whose anion is that of an oxidizing-passivating acid selected from a class consisting of nitric and chromic acids and whose cation is that of a nitrogen base selected from a class consisting of ammonium hydroxide, guanidine, diethanolamine, triethanolamine, trimethyl amine, ethylene diamine, urea, benzyl amine, aniline, methylphenyl amine, dimethylphenyl amine and diphenylmethyl amine, said bath having a concentration of said salt ranging from about 50 to 300 grams per liter and a pH within the range of from about 3.0 to 6.0.

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 substantially of an aqueous solution of ammonium chromate having a concentration ranging from about 50 to 300 grams per liter and a pH of from about 3.0 to 6.0.

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