This invention relates to the art of electroplating, and more particularly to the electrodeposition of nickel upon steel, or other surfaces, for the purpose of providing such surfaces with an ornamental and rust-protecting covering.

An example of the type of articles to which such coatings have been applied, reference is made to the bars from which bumpers are made, it being understood that such reference is merely illustrative and that our invention is applicable to various other and different articles than the specific ones selected.

As articles of the type referred to have been plated heretofore, the same are usually provided with a thin or "flash" coating of nickel, then with a coating of copper, and finally with a heavier coating of nickel.

With the processes heretofore in general use, it has been found impracticable to provide a coating of nickel which does not require a large and expensive amount of buffing in order to impart sufficient brightness to the nickel coating. While attempts have been made to produce a coating of sufficient brightness to reduce the expense due to buffing, these attempts have not met with commercial success. Furthermore, so far as we are aware, it has been impossible to obtain a bright nickel deposit upon other than a polished surface, as distinguished from a matte surface, and, with other than an extremely thin surface plate. Also in such processes it has only been practical to deposit the metal at low current densities while with our process the deposition may be made with high current densities.

We have discovered that, by using a material quantity of lead in solution in the electroplating bath and by so preparing the bath and operating the process as to insure the presence in the nickel deposit of a much higher proportion of lead than has been contemplated heretofore, we are enabled to produce a coating which possesses the brightness referred to hereinafter and which will possess also all of the good qualities of the best nickel-plated coatings or deposits hitherto obtained.

We obtain the foregoing general advantages, as well as others and more specific advantages to be referred to hereinafter, in and through the electroplating solution and the process of conducting the plating operation which will now be set forth.

Our bath and process may be conveniently employed in connection with articles which have been given a coating of copper, either with or without a preliminary "flash" coating of nickel. If, however, a high resistance to rusting or corrosion of the base metal is not required, our bath and process may be applied to the metal without a preliminary coating of any sort.

The plating bath or solution is prepared by dissolving the following constituents in the respective proportions mentioned per gallon of the desired volume of bath or solution:

- 1.75 lbs. nickel sulphate
- 0.208 lb. nickel chloride
- 0.238 lb. boric acid
- 0.437 lb. citric acid
- 0.067 oz. basic lead carbonate

The solution of the foregoing ingredients will be hastened by heat, and agitation.

After all of the aforesaid ingredients have been completely dissolved and lead is shown to be present in solution by testing with sulphuric acid in a test tube, the bath or solution is substantially neutralized with nickel carbonate so that the pH value will have been increased to about 6. This will require approximately 0.41 lb. of dry nickel carbonate per gallon of such bath or solution.

In lieu of making a single solution of the first five ingredients and neutralizing such solution later with nickel carbonate, it may be more economical to prepare the solution for a few articles in the manner indicated and then to add nickel carbonate until the desired pH is obtained.
be found to be advantageous to prepare two solutions, each containing certain of the ingredients, in the proportions per gallon of desired solution specified hereinafore, and to add one solution to the other. For instance, good results have been obtained by making a solution of the nickel sulphate, nickel chloride, and boric acid and by making a separate solution of the citric acid and basic lead carbonate, neutralizing this latter solution with nickel carbonate to the aforesaid pH value. Then, by mixing the solutions, the final bath will be identical in composition with the bath prepared from a single solution neutralized with nickel carbonate. After solution of the ingredients and as a result of chemical recombinations therebetween, the bath in either instance will contain the following ingredients or substances in the respective proportions and normalities shown below:

<table>
<thead>
<tr>
<th>Substances used</th>
<th>Normality</th>
<th>Grams per liter of sol.</th>
<th>Oal. sol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulphate</td>
<td>1.94</td>
<td>210</td>
<td>28.0</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>0.72</td>
<td>25</td>
<td>3.34</td>
</tr>
<tr>
<td>Nickel citrate</td>
<td>0.75</td>
<td>70</td>
<td>6.3</td>
</tr>
<tr>
<td>Boric acid</td>
<td>0.45</td>
<td>28</td>
<td>3.22</td>
</tr>
<tr>
<td>Lead (probably citrate)</td>
<td>0.0088</td>
<td>0.4</td>
<td>0.03</td>
</tr>
</tbody>
</table>

We have described two methods for preparing the above solution but it is obvious to one skilled in the art that a solution containing the above constituents in the proportions given may be prepared by other methods. Substantially pure salts for the bath and substantially pure anodes should be used. This will reduce to a minimum the amount of iron and other impurities in the bath. Iron is especially undesirable, and may be removed by adding hydrogen peroxide to the bath in the proportion of approximately one gallon of peroxide to four hundred gallons of bath. Suitable proportions of other oxidizing agents may be substituted for hydrogen peroxide. The oxidizing agent will convert any ferrous iron to ferric iron, which will precipitate as ferric hydroxide in a bath in which the acidity has been neutralized with an excess of nickel carbonate or other suitable basic compounds. The precipitated ferric hydroxide, together with other insoluble impurities, and any excess of nickel carbonate, may be removed by filtering the bath. The addition of the oxidizing agent also has the advantage of overcoming a tendency to produce pits in the plate, which may be caused by organic materials, particularly those of glue-like nature, which may be present in the bath. After filtration, or before use in case the bath is not filtered, the solution should be acidified until the pH value equals 5.2 to 5.6, after which it is ready for use.

The articles to be plated are suspended in the bath in the usual manner. The current is passed through nickel anodes, the solutions, and the articles which serve as anodes, the cathodic current density being preferably from 35 to 50 amperes per square foot of surface to be coated, and the bath being maintained at a temperature of from 110° F. to 120° F.

The plating solution should be tested from time to time (preferably twice daily) in order that the acidity should be maintained substantially between pH 5.2 and 5.6. If the acidity is high, nickel carbonate (or lead carbonate if the solution is low in lead) should be added to neutralize the acid. If the solution is too alkaline, citric or sulphuric acid should be added to lower the pH value.

If the solution shows the correct acidity, but is low in lead, more lead may be added by dissolving the required amount of basic lead carbonate in a small excess of citric acid, neutralizing the excess acid with nickel carbonate, and adding to the solution, the required amount of lead citrate, containing nickel citrate.

Should nickel be low, nickel sulphate should be added, but only after the chloride and citrate have been brought to the required concentrations. If the chloride is low, this should be brought up by adding nickel chloride or a solution containing the desired amount of nickel chloride.

If the solution is low in citrate, it may be brought up to standard by adding a prepared solution of nickel citrate which, however, is not conveniently prepared of a strength greater than 2.5 normal.

Reference has been made hereinafore to the operating temperatures. It is advisable not to operate the bath at a temperature materially below 110° F., as such lower temperatures favor the passage of current, with a resultant evolution of chlorine and increase in the acidity of the solution. The best operating temperatures so far discovered are those specified, namely: 110° F. to 120° F.

While a current density of 35 to 50 amperes per square foot of surface coated has been found to be very satisfactory, bright deposits have been produced at current densities varying from 5 and 70 amperes per square foot. Also, while the plating solution works best at an acidity of pH 5.2 to 5.6, good deposits have been obtained outside this range. However, with a solution of higher pH value, there is a tendency toward brittleness in the deposit and a liability to peel—at least under the current densities mentioned hereinbefore. Furthermore, with higher acidities, there is a likelihood of the deposit becoming pitted.

While the nickel concentration preferred...
is 2.5 normal, we have obtained bright nickel deposits in baths wherein the nickel concentrations vary from .32 normal to 3.32 normal.

As to the chloride and boric acid concentrations, the concentrations set forth herein are those which have been found to be effective in operation, but these concentrations may be varied considerably by varying other conditions. It is desirable, however, to have sufficient chloride in solution so that the nickel anode used will not become passive at the temperature of the bath and at the current density employed. The remaining nickel is obviously present as sulphate or citrate. Excess chloride does no harm but is more expensive than the sulphate.

The preferred citric acid concentration has been hereinbefore described as 0.75 normal. The function of the citric acid, which is present in the plating solution not as the free acid but as nickel citrate, is most important; it serves as “carrier” for the lead, maintaining it in solution and preventing its precipitation as lead sulphate by the nickel sulphate bath. However, good results have been obtained with rather wide variations from the citric acid concentration referred to, the 0.75 normal representing a condition wherein approximately 30% of the nickel is present as citrate. Good deposits, however, have been obtained with citric acid concentrations of less than .50 normal.

The preferred lead concentration as set out herein is .003 oz. of metallic lead per gallon, which is not much less than the solubility of lead in the solution. However, bright deposits have been obtained with about one-fourth this concentration of lead. As the brightness of the deposits appears to vary with the concentration of the lead, it is desirable that this concentration be maintained near the maximum value indicated.

For the anodes, as pure nickel as possible should be employed, it being particularly desirable that the presence of iron should be avoided, since its co-deposition is likely to result in a deposit of inferior quality.

By preparing the bath and conducting the process in the manner described hereinbefore, we are able to produce a coating or deposit of nickel which is so bright, as compared with coatings heretofore produced, that the time required for the buffing operation is reduced to not over half of that previously required and under very favorable conditions the buffing may be altogether eliminated.

It has been found that the coating or deposit thus produced is not pure nickel but an alloy of nickel and lead. Although good results have been obtained in cases where the lead constitutes only 1 1/2% of the alloy, it is preferred that the concentration on the solution be such that a deposit containing one or two percent of lead will be obtained. Satisfactory deposits, containing higher percentages of lead may, however, be had.

At lower current densities (say under 20 amperes per square foot of surface plated) we have found that sodium citrate can be used as a substitute for nickel citrate. However, without the use of a special carrier, such as nickel citrate or sodium citrate, it has been found impossible to secure a sufficiently high proportion of lead in the deposit or plating to produce a bright effect at all comparable with that produced by the use of such a carrier. Furthermore, it has been impossible heretofore to produce such bright deposits on top of a matte deposit.

As substitutes for lead, zinc or cadmium may be used, but while these are capable of imparting brightness to the nickel deposits, they are much more difficult to control than lead.

It should be understood that, whereas we prefer to use nickel carbonate for neutralizing acidity, other compounds, such as ammonium hydroxide, sodium hydroxide, or sodium carbonate may be used. These materials will give the desired result, and the resulting ammonium or sodium salts are not harmful in small concentrations, but they do have the disadvantage of making the bath composition more complicated and less easy to control. It will also be apparent to one skilled in the art that nickel hydrate may be substituted for an equivalent quantity of nickel carbonate.

Crystallizing of nickel citrate, and a consequent decrease of the nickel concentration, is minimized by maintaining the solution uniformly at its operating temperature, and by avoiding higher concentrations of nickel citrate than those herein mentioned as preferred. Crystallized nickel citrate may be removed by filtering these solutions, and the citrate so removed may be replaced by the addition of a freshly prepared solution of nickel citrate, which may be prepared by neutralizing citric acid with nickel carbonate.

Whereas a total nickel deposit of .0002 inch is representative of the average thickness of commercial nickel plating, we have found it possible to produce bright deposits not only of this thickness, but even to thicknesses ten times as great. But the thickness to which our bright nickel may be deposited does not appear to be limited, and we have, in fact, produced bright nickel plates in excess of .002 inch thick.

The bright nickel deposits which have been heretofore made are extremely thin deposits upon highly polished surfaces. This is in marked contrast to the behavior of our bright nickel plating solution, for we are able to plate upon a matte surface, and by continuing the deposition sufficiently long, to obtain, finally, a bright and lustrous surface. It is apparent that our process is particularly ad.
vantageous for the plating of surfaces which may be polished, but which are buffed only with difficulty. These surfaces may be first plated if desired with nickel and copper from ordinary solutions and may then be finished by plating by our process, thus avoiding the necessity of buffing, or at least producing a surface which requires very little buffing.

Having thus described our invention, what we claim is:

1. The process of nickel plating which comprises immersing the articles to be plated in a nickel-plating bath containing at least .01 ounce of lead in each gallon of solution and a carrier for maintaining the lead in such solution, and employing with bath and articles a current having a density of from 5 to 70 amperes per square foot of surface coated.

2. The process of nickel plating which comprises immersing the articles to be coated in a nickel-plating bath containing lead and a citrate in solution, employing for the plating operation a current having a density of from 5 to 70 amperes per square foot of surface coated, and maintaining the bath at a temperature of not materially less than 110° F.

3. An electroplating bath for depositing bright nickel, the same containing lead in solution and a carrier serving to maintain the lead in solution in the presence of sulphate to the extent of at least .01 ounce per gallon of such solution.

4. An electroplating bath for depositing bright nickel, the same containing lead and nickel in solution with substantially one-third of the nickel present as citrate.

5. An electroplating bath for depositing bright nickel, the same containing nickel sulphate, nickel chloride, nickel citrate, boric acid and lead citrate, the citrates being present in such proportion as to constitute a carrier preventing the precipitation of the lead in the presence of the sulphate.

6. An electroplating bath for depositing bright nickel, the same containing nickel sulphate, nickel chloride, nickel citrate, boric acid and lead citrate, the citrates being present in proportion to constitute a carrier preventing the precipitation of the lead in the presence of the sulphate, and an oxidizing agent.

7. An electroplating bath for depositing bright nickel, the same being formed by solution and admixture of nickel sulphate, nickel chloride, nickel citrate, boric acid and basic lead carbonate, the bath thus formed being subsequently adjusted to a pH value of about 5.4 by the addition of a basic nickel compound.

8. An electroplating bath for depositing bright nickel comprising a solution of the following ingredients in the proportions mentioned per gallon of water:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulphate</td>
<td>1.75 lbs.</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>0.209 lbs.</td>
</tr>
<tr>
<td>Boric acid</td>
<td>0.238 lbs.</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.437 lb.</td>
</tr>
<tr>
<td>Basic lead carbonate</td>
<td>0.067 oz.</td>
</tr>
</tbody>
</table>

The bath, after complete solution of the foregoing constituents being neutralized to a pH value of 5.2 to 5.6.

9. An electroplating bath for depositing bright nickel comprising a solution of the following ingredients in the proportions mentioned per gallon of water:

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<td>0.437 lb.</td>
</tr>
<tr>
<td>Basic lead carbonate</td>
<td>0.067 oz.</td>
</tr>
</tbody>
</table>

The bath, after complete solution of the foregoing constituents being neutralized to a pH value of 6 by adding thereto approximately 0.41 lb. of dry nickel carbonate per gallon and, after such neutralization, there being added to the bath hydrogen peroxide in sufficient quantity to oxidize any ferrous iron that may be present to ferric iron, and the resultant solution being filtered and acidified to a pH value of 4.2–5.6.

10. The process of nickel plating which comprises immersing the articles to be plated in a nickel-plating bath containing from .01 to approximately .053 ounce of lead in solution per gallon of bath and a carrier for maintaining said amount of lead in solution, and employing with the bath and articles a current density of from 5 to 70 amperes per square foot of surface to be coated.

11. The process of nickel plating which comprises immersing the articles to be plated in a nickel-plating bath containing from .01 to approximately .053 ounce of lead in solution per gallon of bath and a carrier for maintaining said amount of lead in solution, and employing with the bath and articles a current density of from 5 to 70 amperes per square foot of surface to be coated, said carrier being nickel citrate.

In testimony whereof, we hereunto affix our signatures.

WALTER L. PINNER
CLYDE C. DE WITT.