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ELECTRODEPOSITION OF NICKEL

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This invention relates to the electrodeposition of metals and an anode for eliminating the occurrence of pitting in the electrodeposited metal, and this application comprises a continuation in part of our copending application, Serial No. 50,566, filed November 19, 1935.

For many years little trouble was experienced in pitting during the electrodeposition of a metal, such as nickel, on steel, copper or brass at low temperature and at low current density and high pH, for in the early period of commercial plating, a nickel surface that would buff to a nickel color was all that the trade required. Recently, however, particularly since nickel has been extensively used as a protective coating for automotive parts, it has become necessary to plate heavier deposits to withstand corrosion over longer periods of time. This has necessitated an increase in current densities so as to facilitate the deposition of nickel in the least possible time.

For some time copper was thought to be necessary as a base on which nickel should be plated, but only recently experience has shown that copper as an alternate plate between nickel and steel did not offer any protection for the base metal, but instead, contributed to the corrosion of either the steel or iron on account of its position in the electromotive series with respect to iron. Consequently, copper has been eliminated and nickel has been plated directly upon the steel.

While pitting became readily apparent when the current densities were increased, it became a serious commercial problem as soon as the intermediate copper plate was discontinued. We have made extensive researches into the origin of pits and we have established that there are many types and kinds of pits. For example, we have found that if an article is not properly cleaned or rinsed, it will retain small particles of foreign matter which will cause the evolution of a steady stream of hydrogen, which will interfere with the deposition, and that pitting results whenever such particles of dirt interfere with the uniform release of hydrogen.

We have also found that pitting occurs when a deep abrasion or scratch is present on the surface of the base metal, as such occurrence also interferes with the normal evolution of hydrogen during plating. Obviously, pitting which resulted from the foregoing conditions could be controlled upon proper treatment of the base metal, but even when diligent efforts were made to correct such conditions, pitting was found to result when all of the other known causes were eliminated.

Microscopic studies of the nickel structure, even under the most favorable conditions of plating revealed startling facts. For example, it was found that nickel plated upon copper had a finer grained structure than that plated upon steel. Again, nickel plated at high temperature was coarser than that plated at low temperature, and moreover, nickel plated at high current densities was coarser than that plated at low current densities, but in every case it was found that a finer grained smoother surface would be substantially free from pits.

The kind of pitting with which we are concerned has not been a factor in electrodeposits of bright plate but it has been a serious problem in electrodeposits of gray plate. Bright plate, as used herein, means a plate which has a lustrous surface that reflects images with mirror-like fidelity and that requires no buffing or polishing after plating. Bright plate is usually brittle, and therefore not suited for plating automotive parts or any other article which may be subjected to impact while in use. Gray plate, on the other hand, has a dull, non-image producing surface when plated to a thickness required for commercial specifications and is ductile and therefore suited to a wide range of use. Bright plate has a grain size approximately one ten-thousandth of a millimeter, whereas the gray plate with which we are concerned has a grain size range between one-thousandth and five-thousandths of a millimeter. Plating, due to grain size, does not occur in the bright plate range, but it is a very serious problem in the gray plate range.

Commercial gray plating, as heretofore practiced, has generally included the use of an addition agent, such as hydrogen peroxide, to the nickel bath for the alleged purpose of preventing pitting; and under such practice, the operator has been compelled to add hydrogen peroxide to the bath, at intervals approximating every two hours, in quantities which had previously been discovered by the trial and error method, as being necessary to prevent pitting in any particular tank. The difficulty with such procedure, however, has been that the repeated replenishment has not only not prevented pitting, but that it has been expensive and has required attention at too frequent intervals for assurance of safety.

It has been assumed that hydrogen peroxide would eliminate the pitting at any depth of plate, but we have found that, regardless of the amount used, satisfactory commercial plating of nickel on steel beyond a depth of six ten-thousandths

of an inch could not be effected, and that satisfactory commercial plating of nickel on metals other than steel beyond a depth of one- and one-fourth-thousandths of an inch could not be obtained.

We have discovered that there is a definite relationship between pitting and grain size and that if the grain size is controlled, pitting can be eliminated. We have also discovered that when hydrogen peroxide is used, the grain structure assumes the shape of an inverted cone with the apex end in contact with the base metal, and that such formation necessarily limits the depth of the plate, because as the depth increases, the base of the cone, or the grain size at the surface, reaches a size that is beyond the limit of safe commercial plating. We have further discovered that by the use of certain addition agents, the shape of the grain structure can be modified so as to form a column of uniform cross-sectional shape throughout its length and that by reason of such formation, the depth to which the metal can be plated can be safely increased in production to one and one-half-thousandth of an inch. In fact, we have been able to plate nickel on steel to a depth of forty-five-thousandths of an inch and still maintain the desired grain size at the surface.

In our copending application, Serial No. 34,209, filed August 1, 1935, which matured into Patent Number 2,119,304, we described and claimed a method of plating by means of which pitting could be eliminated on gray plate, regardless of the depth of the plate that would be required for commercial production. Such method contemplated the introduction of certain chemicals into the plating bath as addition agents.

An object of the present invention is to accomplish substantially the same result in the control of the grain size, as defined in our aforesaid copending application, but without the use of addition agents to the bath. In this connection, we contemplate a grain size control by the use of addition agents which are incorporated in the anode. An advantage of such arrangement is that the material added to the anode will maintain a definite concentration in the solution after the proper concentration has once been established.

It is well known that certain addition agents produce advantageous results in electroplating, but the function of the agents has not been fully understood, and no general rule has been known that would enable one to predetermine the type of agent that would produce the most beneficial results for a given set of conditions.

So far as we know, no one, heretofore, has ascertained that a definite relationship exists between grain size and pitting; moreover, although addition agents have been used, they have not permitted nickel plating on steel to be accomplished at depths greater than six ten-thousandths of an inch. Furthermore, the addition agents have not eliminated the necessity for constant supervision of bath conditions, and where hydrogen peroxide has been used, the cost has been an important factor in the operation of a plating plant.

By way of illustration, a satisfactory aqueous nickel bath with which our invention may be used is as follows:

	Oz. per gal. of solution
$NiSO_4.7H_2O$	32
$NiCl_2.6H_2O$	6
H_3BO_3	4

We have further discovered that metals, such as zinc, cadmium, cobalt, tin and lead can be added to the anode in a nickel bath, and that such addition would not only control the grain size, but would eliminate the necessity of making constant additions to the bath during the plating operation.

In the above mentioned nickel bath, we have found that satisfactory results may be obtained by adding cobalt to a commercial nickel anode, in the proportion of not less than 0.05% by weight. The commercial nickel anode referred to is one that is at present on the market and which, upon analysis, shows a cobalt content of approximately 0.64%, so that the total proportion of cobalt should be not less than 0.69% of the total metal in the anode. The preferred percentage of cobalt, however, is one percent (1.0%) by weight of cobalt to the total metal in the anode. The upper limit of cobalt is approximately 3.0%, but for economic reasons it is preferable to keep the percentage of cobalt relatively low. The preferred proportion of cobalt will produce satisfactory results with a pH bath adjustment between 2 and 5.8 and at any current density between 5 and 400 amperes per square foot. The temperature of the bath may vary from room to boiling.

An anode made of commercial nickel as above specified, and cadmium should have a lower limit of cadmium of approximately 0.37% with a bath adjustment of 2 pH. The upper limit of cadmium is 1.6%. This anode is preferably operated at a temperature of 140 degrees F. and at current density of 75 amperes per square foot.

Where lead is added to a commercial nickel anode, the lower limit of lead with a bath adjustment of 2 pH is approximately 0.2%, while the upper limit is 0.7%. With a bath adjustment of 5.5 pH the lower limit of lead is approximately 0.1% and the upper limit is approximately 0.4%. In each bath, the current density is approximately 75 amperes per square foot at 120 degrees F.

A commercial nickel anode containing zinc when used in the above mentioned bath should have the lower limit approximating 0.22% with a bath adjustment of 2 pH and at a temperature of 140 degrees F. and a current density of 75 amperes per square foot. The upper limit of zinc is approximately 1.21%.

An anode containing tin when used in the above mentioned bath should have the lower limit approximating 0.15% with a bath adjustment of 2 pH, at a temperature of 140 degrees F., and at a current density of 75 amperes per square foot. The upper limit of tin is approximately 0.9%.

In preparing anodes referred to, the metal which is to be added is mixed with commercial nickel in the proportions desired prior to the casting operation.

We have found that if the above mentioned bath is operated, for example at room temperature, and with a current density of 5 amperes per square foot with a commercial nickel anode, but without the inclusion of grain size control agents, that the resulting grain size of the nickel deposit would approximate one thousandth (.001) of a millimeter, but satisfactory commercial plating in large scale production cannot be accomplished at such low current density. If the density were increased, however, to approximately 75 amperes per square foot the speed of depositing nickel would be increased to a sat-

isfactory rate, but the grain structure would increase in size to approximately eight thousandths (0.008) of a millimeter, under which conditions pitting would inevitably result: We have further found, however, that if the nickel anode used in the above mentioned bath had cadmium or any of the other metals mentioned added to it, within the range of percentage proportions heretofore set forth, and that if the high-current density were used, the resulting plate would have a grain size approximating one-thousandth (0.001) of a millimeter, and therefore, would be well within the range of commercial gray plating and free from pits.

The incorporation in the anode of a metal other than that to be plated has been very beneficial in large scale production of commercial plating, for it has not only resulted in the control of the grain size, but has eliminated the necessity for the addition of large quantities of hydrogen-peroxide. The cost of the metal added to the anode is extremely low in proportion to the cost of the peroxide, and therefore, the invention has been instrumental in materially reducing the cost of the plating operation. The metal added to the anode, as explained herein, is additionally advantageous in that it assists in obtaining a definite predetermined concentration in the solution.

As a result of our invention, we have established a definite predetermined means of regulation for maintaining the grain size of the electrodeposit under control, so that it may not approach a size at which pitting is apt to occur. The discovery enables articles to be plated in the grain size range of gray plate at high current densities, without the presence of pitting and eliminates the necessity for constant bath analysis by skilled operators. The resulting electrodeposit is exceedingly ductile and may be buffed more readily than deposits heretofore obtained in the gray plate range. Additionally, the electrodeposit is less porous, is denser and is therefore more resistant to corrosion. Experience has shown that the electrodeposit has an increase of salt spray resistance amounting to approximately 90% over that heretofore obtained.

The invention allows the use of a higher-current density than heretofore was regarded as practical for nickel plating purposes and hence with the same floor space and equipment has enabled the production to be approximately doubled. These advantages result from the fact that pitting can be eliminated at high current densities by the control of the grain size of the electrodeposit. By incorporating the grain size control agents in a soluble anode, we have obtained a bath which will operate satisfactorily insofar as freedom from pitting is concerned, without replenishment to the bath, except for supplying drag-out losses until the anode is dissolved.

We claim:

1. A soluble anode for the electrodeposition of nickel from an acid bath, comprising substantially 0.69% cobalt and the balance nickel, said anode being effective to produce a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch and having a grain size above that of bright nickel but below that at which pitting, due to grain size occurs.

2. A soluble anode for the electrodeposition of nickel from an acid bath, comprising cobalt between 0.69% and 3.0% and the balance nickel, said anode being effective to produce a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch and having a grain size above that of bright nickel but below that at which pitting, due to grain size occurs.

3. A soluble anode for the electrodeposition of nickel from an acid bath comprising lead between the proportion of 0.1% and .7% and the balance nickel, said anode being effective to produce a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch and having a grain size above that of bright nickel but below that at which pitting, due to grain size occurs.

4. A soluble anode for the electrodeposition of nickel from an acid bath comprising zinc between the proportions of 0.22% and 1.21% and the balance nickel, said anode being effective to produce a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch and having a grain size above that of bright nickel but below that at which pitting, due to grain size occurs.

5. A soluble anode for the electrodeposition of nickel from an acid bath comprising a major portion of nickel and a minor portion of cobalt, the proportion of cobalt being between approximately 0.69% and approximately 3.0%, so that when the anode is used in a bath containing nickel sulphate, nickel chloride and boric acid, the resulting grain size of the electrodeposited nickel is smaller than five-thousandths of a millimeter but larger than one-thousandth of a millimeter, said anode being effective to produce a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch.

6. A soluble anode for the electrodeposition of nickel from an acid bath comprising a major portion of nickel and a minor portion of lead, the proportion of lead being between approximately 0.1% and approximately 0.7%, so that when the anode is used into a bath containing nickel sulphate, nickel chloride and boric acid, the resulting grain size of the electrodeposited nickel is smaller than five-thousandths of a millimeter but larger than one-thousandth of a millimeter, said anode being effective to produce a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch.

7. A soluble anode for the electrodeposition of nickel from an acid bath comprising a major portion of nickel and a minor portion of zinc, the proportion of the zinc being between approximately 0.22% and 1.21% so that when the anode is used in a bath containing nickel sulphate, nickel chloride and boric acid, the resulting grain size of the electrodeposited nickel is smaller than five-thousandths of a millimeter, but larger than one-thousandth of a millimeter, said anode being effective to produce a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch.

8. A soluble anode for the electrodeposition of nickel from an acid bath comprising a relatively large percentage of nickel and a relatively small percentage of a dissimilar metal taken from the group consisting of cobalt, cadmium, lead, zinc and tin, wherein the dissimilar metals are in the following approximate proportions respectively: cobalt between 0.69% and 3.0%; cadmium between 0.37% and 1.6%; lead between 0.1% and 0.7%; zinc between 0.22% and 1.21%, and tin between 0.15% and 0.9%, whereby the resulting deposit comprises a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch, and having a grain size above that of bright nickel, but below that at which pitting, due to grain size, occurs.

9. The process of electrodepositing nickel from an acid bath which comprises passing a current between a cathode and an anode, wherein the anode comprises a relatively large percentage of nickel and a relatively small percentage of dissimilar metal taken from the group consisting of cobalt, cadmium, lead, zinc, and tin, and wherein the dissimilar metals are in the following approximate proportions respectively: cobalt between 0.69 and 3.0%; cadmium between 0.37% and 1.6%; lead between 0.1% and 0.7%; zinc between 0.22% and 1.21%; and tin between 0.15% and 0.9%, whereby the resulting deposit comprises a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch, and having a grain size above that of bright nickel, but below that at which pitting, due to grain size, occurs.

10. The process of electrodepositing nickel from an acid bath which comprises passing a current between a cathode and an anode, wherein the anode comprises a major portion of nickel and a minor portion of cobalt, the proportion of cobalt being between approximately 0.69% and approximately 3.0%, so that when the anode is used in a bath containing nickel sulphate, nickel chloride, and boric acid, and operated at a pH of substantially 2, the resulting deposit comprises a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch and having a grain size above that of bright nickel, but below that at which pitting, due to grain size, occurs.

11. The process of electrodepositing nickel from an acid bath which comprises passing a current between a cathode and an anode, wherein the anode comprises a major portion of nickel and a minor portion of lead, the proportion of lead being between approximately 0.1% and approximately 0.7%, so that when the anode is used in a bath containing nickel sulphate, nickel chloride, and boric acid, and operated at a pH of substantially 2, the resulting deposit comprises a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch, and having a grain size above that of bright nickel, but below that at which pitting, due to grain size, occurs.

12. The process of electrodepositing nickel from an acid bath which comprises passing a current between a cathode and an anode wherein the anode comprises a major portion of nickel and a minor portion of zinc, the proportion of zinc being between approximately 0.22% and 1.21%, so that when the anode is used in a bath containing nickel sulphate, nickel chloride, and boric acid, and operated at a pH of substantially 2, the resulting deposit comprises a pit-free gray plate having a thickness in excess of six ten-thousandths of an inch, and having a grain size above that of bright nickel, but below that at which pitting, due to grain size, occurs.

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