

UNITED STATES PATENT OFFICE

2,026,718

ELECTRODEPOSITION OF METALS

Louis Weisberg and William B. Stoddard, Jr., New York, N. Y., assignors to Weisberg & Greenwald, Inc., New York, N. Y., a corporation of New York

No Drawing. Application March 30, 1935,
Serial No. 13,922

22 Claims. (Cl. 204—14)

This invention relates to new and useful improvements in methods for producing electrodeposits of nickel, cobalt, or combinations of nickel and cobalt.

5 Ordinary electrodeposits of nickel, cobalt, and nickel-cobalt alloys are dull when they are brought out of the plating solution, unless they are very thin, and require buffing or polishing to produce a satisfactory appearance. Since the buffing or
10 polishing operation is usually more costly than the operation of electroplating itself, many attempts have been made to develop plating solutions which would produce deposits that do not require polishing or buffing. This has resulted
15 in the appearance of many so-called "bright nickel" plating solutions. These solutions differ from one another, but all of them are subject to the objection that the deposits produced are brittle and prone to crack.

20 It may be well at this point to state that there are various ways of testing an electrodeposit for brittleness. In the case of some of the addition agents that have been proposed, the only test necessary is to plate a piece long enough to put on a substantial thickness of plate (for example, 0.0005 inch or upward); when the piece is removed from the plating solution, there are cracks in the deposit visible to the naked eye. Sometimes the plate is subject to so much tension that
30 the deposit cracks and curls up, leaving patches entirely uncovered. Where the deposit is apparently sound, one method of testing it for cracks is to examine the surface by means of a microscope. Another method is to bring the piece near the ear and bend it. If the plate is brittle, the sound of its tearing can be heard. Different deposits can be compared by observing the angle to which the bend can be carried before a sound is heard. Still another method is to strip the deposit and test it directly. A good deposit, say
40 one that is 0.001 inch thick, can be bent sharply on itself and handled quite roughly without damaging it; a brittle deposit on the other hand can be broken apart between the fingers with
45 ease.

50 One object of the present invention is a method of producing lustrous electrodeposits containing nickel, cobalt, or alloys of nickel and cobalt, and possessing little or no tendency towards brittleness and cracking. By lustrous we mean that the surfaces require no buffing or polishing after plating, and when the underlying surface is smooth, reflect images with mirror-like fidelity. These deposits are also free from cracks and
55 other evidence of brittleness.

Another object of this invention is an efficient depolarizer for nickel and/or cobalt plating solutions whereby pitting and other defects in the deposits can be eliminated.

Still further objects and advantages will appear from the more detailed description given below, it being understood, however, that this more detailed description is given by way of explanation and illustration only, and not by way of limitation, since various changes therein may be made
10 by those skilled in the art without departing from the scope and spirit of the present invention.

The nature and scope of our invention will appear from the following account of the investigation which led up to it. Our original purpose
15 was to develop a bright nickel plating solution and after many experiments and trials, we reached a point where we were able to obtain bright deposits, free from cracks and brittleness, from a solution containing nickel sulphate, cobalt sulphate, and sodium formate, nickel sulphate being the predominant constituent. This solution gave
20 reproducible results at room temperatures and low current densities (about 10-15 amperes per square foot) but when the temperature and current density were raised to the usual range employed for rapid commercial plating, it gave
25 bright deposits for a while and then the deposits became cloudy. After that no more bright deposits could be obtained from the solution. Numerous attempts were made to resuscitate the solution, but all of them failed until it was discovered that a comparatively small addition of formaldehyde caused the solution to give bright plate again and that the solution continued to give
30 bright plate as long as small additions of formaldehyde were made from time to time.

Nevertheless, on attempting to convert an old nickel plating solution by adding the necessary ingredients to give the desired composition, bright
40 plate was not obtained. A careful check-up revealed that the only difference between the previous solution and this one was in the amount of ammonium salts present. Ammonium sulphate was present in both solutions, because both ammonia and sulphuric acid had been used in adjusting the hydrogen ion concentration in the solutions. Further experiments showed that there was an optimum amount of ammonium sulphate which should be present to give the best results.
50 Finally, by adjusting the ammonium sulphate content to the proper point in the old nickel plating solution that we were trying to convert into a bright plating solution, we obtained excellent bright plate.

Having thus found a means of obtaining lustrous electrodeposits consisting of an alloy of nickel and cobalt in which nickel is the major constituent, we next set about investigating the effect of varying separately each constituent in the plating solution and each variable such as temperature and current density. As a convenient means of making such studies, the deposits were made on bent cathodes. The technic of using the bent cathode is well known to those skilled in the plating art. The bent cathodes employed in this investigation were pieces of nickel-silver about $2\frac{1}{2}$ inches long and slightly under $\frac{3}{4}$ of an inch wide, bent at right angles 1 inch from the bottom. The bent portion extended towards the anode when the cathode was in position for plating. The advantage of using a bent cathode is that it gives in one operation a picture of the effect of varying the current density over wide limits.

Because of the excellent throwing power and wide operating range of these solutions, most of the bent cathodes were plated at a current density corresponding to an average of one hundred amperes per square foot. For solutions within the working limits which are hereinafter described, the bent cathodes were bright all over at this current density. As the limits for good plating were exceeded, dull or cloudy spots appeared, sometimes first in the recessed portions and sometimes at the tip and edges of the horizontal part of the cathode, according as the current density was then too low or too high for bright plating. In some cases, passing of the limits for good plating was evidenced by darkening or burning of the deposit.

On some of the solutions the composition of which was such that they did not give the best results, bent cathodes were also tried at a current density corresponding to an average of sixty amperes per square foot. In some of these cases perfectly bright plate and good throwing power were obtained at an average current density of sixty amperes per square foot when it could not be obtained at one hundred amperes per square foot. In general, however, as the throwing power improved the permissible current density increased.

Bent cathode experiments were made varying separately each of the following components of the solution, while the others were kept constant:

- 1—Cobalt content; ratio of cobalt to nickel
- 2—Formate radical content
- 3—Hydrogen ion concentration (measured colorimetrically)
- 4—Ammonium sulphate or ammonia content
- 5—Formaldehyde content

In addition, the effects of adding boric acid and chloride, in the form of nickel chloride, were investigated to the extent that was necessary for determining whether or not their use was advisable. It was found that neither boric acid nor chloride appears to have any appreciable effect on the brightness of the deposit.

The cobalt content of the deposit increases with the cobalt content of the solution. As long as the cobalt content of the solution is not too high, the relationship remains approximately linear. For a solution containing approximately 240 grams of nickel sulphate and 45 grams of nickel chloride per liter, we have found that the lower limit for cobalt, expressed in terms of cobalt sulphate, is in the neighborhood of 10 to 12 grams per liter. As the amount of cobalt sulphate is further increased, the deposit becomes whiter all

over the cathode, but particularly in the recessed portions, which with lower cobalt content in the solution have a darker color in comparison with the remainder of the surface.

A satisfactory working concentration in the above mentioned solution is obtained with 15 grams of cobalt sulphate per liter. The cobalt content of a deposit made from a solution of this composition at an average current density of 60 amperes per square foot and at a temperature of 60 degrees Centigrade is approximately fifteen per cent. As the cobalt content is raised beyond 15 grams per liter of cobalt sulphate, the solution continues to give bright deposits, and we have observed no upper limit to the amount of cobalt that may be employed, short of plating practically pure cobalt. Of course, with the price of cobalt higher than that of nickel, as it is at present, there is a practical reason for operating with the lowest possible proportion of cobalt.

Working with solutions of the composition described, we have found that good bright plate may be obtained on flat surfaces with inclusions of formate radical as low as 20 grams of nickel formate per liter. Other equivalent soluble formates such as sodium formate, or cobalt formate may be used in place of nickel formate. Ammonium formate, if used, should be added only with due consideration for the specific effects exerted by ammonium salts. The amounts of formate set forth in the claims are expressed in terms of nickel formate, $\text{Ni}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$, but it is to be understood that the scope of our invention includes the use of other salts containing equivalent amounts of formate radical in place or instead of nickel formate.

With the bent cathode, the lower range for good throwing power is found to be around 30–40 grams of nickel formate per liter. We have found it convenient to employ a working concentration of 45 grams per liter, although we have operated satisfactorily solutions containing as high as 100 grams per liter. The formate content of the solution appears to exert a considerable influence and to be critical at the lower end of the range. However, once the formate content is brought above the critical range for good throwing power, a substantial further increase has little effect.

The formate has a two-fold effect. In the first place, it acts as an excellent buffer for control of hydrogen ion concentration near the optimum point. In addition to this, however, it has a specific action as a brightening agent when present in combination with certain of the other ingredients of the solution. This action is definite and pronounced, for a solution made up without formate and adjusted to the same hydrogen ion concentration does not give as good results as a solution containing nickel or equivalent formate.

The optimum value of the hydrogen ion concentration, measured colorimetrically and expressed in terms of pH, is 4.2–4.3 for the solutions above considered. The position of the optimum varies somewhat as the concentration of the different components is varied, but remains within a range of about 4 to 4.4. As the pH falls below 3.9, we have found that the solution no longer produces bright plate unless the current density is decreased. The solution then begins to smell like a formic acid solution. Bright deposits have been obtained at a pH as low as 2 with reduced current densities. On neutralizing the formic acid, good bright plate is once more obtained at the original current density. It is desirable not

to use ammonia for neutralizing the acid, since, as has already been mentioned, a change in the ammonia content of the solution produces a considerable effect on the plate. When the pH is raised much above 4.5, the plate becomes dull and pitted. On bringing the pH back within the working range by addition of sulphuric acid, the pitting disappears and the plate becomes bright again. Increasing the pH beyond the upper working range causes a precipitate to separate out when the solution is cooled. This precipitate, we believe, consists of nickel and/or cobalt formate.

We have found that the addition of ammonium salts not only affects the brightness of the plate, but also has a marked effect on the physical properties of the plate itself. Successive increases in the amount of ammonium salts present with other components constant produce first a brightening of the deposit, and then after the optimum has been passed, a very decided darkening, until finally the deposit becomes gray-black. With lower ammonium salt content, the plate is soft and ductile; as the ammonium salt content is increased, the deposits become harder, and when the point is reached where the deposit becomes dark or black as has just been described, the deposit has also become brittle. It is important, therefore, to avoid getting too much ammonia or ammonium salts in the solution.

Starting with a solution containing no ammonium salts, we find that addition of even one or two tenths of a gram per liter produces an immediate brightening effect. A solution containing even this amount of ammonium salts is more stable and permanent in operation than a solution in which ammonium salts are not present. Ammonium sulphate, ammonium chloride, and ammonium borate are convenient salts to use. Apparently the effect of different salts is in proportion to their ammonia content, or at least approximately so. The quantities of ammonium salts are expressed here and in the claims in terms of ammonium sulfate, but it is to be understood that equivalent amounts of other ammonium salts may be used in place or instead of ammonium sulfate. A good working concentration is obtained when the ammonium sulphate content exceeds 0.5 or preferably 0.7 grams per liter, but does not exceed 5 grams per liter. The higher concentrations of ammonium sulphate produce much harder deposits. If the deposits are to be subjected to any kind of mechanical working, it is desirable to work near the lower end of the range, say at about 1 gram per liter of ammonium sulphate. However, for most purposes, a working concentration of two to three grams per liter of ammonium sulfate is preferable, because with this composition the solution has a broader working range. When the ammonium sulphate exceeds 5 grams per liter, the deposits begin to lose in brightness and show a tendency towards brittleness. Above 15 grams per liter, the deposits become so brittle that they crack and crumble to pieces. When the ammonium salt content of the solution approaches the upper working limit, its dulling effect may be counteracted in part by lowering the pH. We have also found that increasing the formaldehyde content has some beneficial effect in this situation.

With ammonium borate, for example, instead of ammonium sulphate, a recommended concentration would be in the neighborhood of 4 grams per liter. A solution containing 3.6 grams per

liter has been found to give excellent results with respect to brightness of the deposit and to possess good throwing power at an average current density of 100 amperes per square foot.

When formaldehyde is added in successive small amounts to a plating solution such as has been described, keeping all other factors constant, there is an immediate brightening effect at first; finally a point is reached where further additions cause the brightness to diminish. At the upper limit, the odor of formaldehyde becomes so pronounced that it would not be convenient to use such high concentrations. The lower limit for the recommended working concentration is about 0.5 gram per liter of actual formaldehyde. The upper limit is about 7.5 grams per liter. Since commercial solutions of formaldehyde contain approximately 40% by weight of formaldehyde, the recommended minimum is equivalent to about 1.25 cubic centimeters of commercial formaldehyde solution per liter.

We have found that paraformaldehyde can be used in place of formaldehyde. The beneficial effect of formaldehyde and certain of its immediate derivatives such as paraformaldehyde is a specific one. Certain other aldehydes such as benzaldehyde and furfuraldehyde, on the contrary, produce black deposits that are utterly useless. We have found that while hexamethylene tetramine causes brightening of the deposit, it also causes severe embrittlement.

In general, we prefer to use a solution having the following composition, although variations within the limits hereinbefore mentioned afford satisfactory results:

	Grams per liter	
Nickel sulphate	240	
Nickel chloride	45	
Nickel formate	45	
Cobalt sulphate	15	40
Ammonium sulphate	1	
Formaldehyde	0.5-1.0	

A solution having the following composition produces a deposit somewhat less ductile, but this solution has a broader plating range:

	Grams per liter	
Nickel sulphate	240	
Nickel chloride	45	
Sodium formate	35	50
Cobalt sulphate	15	
Ammonium sulphate	2.5	
Formaldehyde	1.0	

The total metal content (nickel plus cobalt), expressed as the sulphates, may be varied from 120 to 400 grams per liter, so long as the ratio between the nickel and the cobalt is kept within suitable limits. These limits are wide. A ratio of 20 nickel to 1 cobalt gives excellent results; so does 10 nickel to 1 cobalt. On the other hand, fair results have been obtained with a ratio of 20 cobalt to 1 nickel. The chloride expressed as metal chloride may vary all the way from 0 to 60 grams or more per liter. The purpose of the chloride is to produce adequate anode corrosion. For high purity nickel anodes 45 grams per liter or more are recommended. Cobalt anodes or anodes containing cobalt may be operated with a lower chloride content. The formate radical may be varied from about 20 to 100 grams, in terms of nickel formate, per liter; at the upper limit the viscosity of the solution begins to become noticeably affected, although there is apparently no deleterious effect otherwise. The ammonium sulphate may vary from about 0.5 to 5 grams or

more per liter, the upper limit increasing with the ratio of cobalt to nickel. The amount of formaldehyde may be varied from about 0.5 gram per liter to about 7.5 grams per liter.

- 5 While it is convenient to employ anodes containing the proper ratio of cobalt and nickel to maintain the solution at a proper working composition, we have found that it is not difficult to use straight nickel anodes and add cobalt sulphate as required from time to time. Only occasional analyses are needed for checking the cobalt content. Additions of cobalt sulphate can be made with sufficient accuracy over long periods of time by calculation from the number of ampere hours passed through the plating solution. The current efficiency is almost one hundred per cent.

In plating with the preferred solutions above described, we prefer to maintain the pH value between 4.2 and 4.3, the temperature between 50 and 65 degrees centigrade, and the current density between 50 and 150 amperes per square foot. The solution must be filtered regularly to keep it free from suspended matter. The solution should be agitated or the work to be plated should be moved as is usually done in plating with warm nicked solutions.

The deposits obtained under these conditions have a brilliant lustre. As the thickness of the deposit is increased, the lustre increases. Even when the underlying metal has a surface which is not smooth or well polished to begin with, the surface becomes more and more lustrous as the plating proceeds and the final appearance is greatly improved if sufficient thickness of deposit is applied. This contrasts with the usual result, in which surface marks and defects are accentuated.

Boric acid in varying amounts is present in most nickel plating solutions. Such solutions can usually be converted into a solution having the above stated composition by proper adjustment and additions. The boric acid present in such cases is not harmful and can be disregarded.

45 When cobalt sulphate is omitted, the nickel plating solution which remains gives nickel deposits which are somewhat cloudy. The results can be improved by adjusting the concentration of the various components, as for example, by increasing the nickel formate to 100 grams per liter and decreasing the ammonium sulphate to 0.5 gram per liter, but the best straight nickel deposits that we have obtained do not compare in brilliance with the results that are obtained on the addition of cobalt. It is noteworthy, nevertheless, that such nickel deposits are unusually smooth and free from elevations or depressions of any kind. They show at most a haze or cloud, and are remarkably free from any tendency towards pitting. We have found that nickel plating solutions containing formaldehyde and ammonium salts in proper amounts, with or without formate, are to be preferred to the old style nickel plating solution even when the plate is not required to be bright. Similar results are obtained from solutions containing cobalt without nickel. On adding nickel to such solutions, greater brightness is obtained.

The action of formaldehyde is evidently a depolarizing action, for it has been observed that in its presence hydrogen evolution is apparently completely stopped. This is in accord with the fact that pitting is known to be connected with hydrogen evolution and that preventing hydrogen evolution reduces pitting.

While we do not wish to be bound by any theory as to what takes place in these solutions, we believe that the key to an explanation of the production of bright plate is to be found in this depolarizing action, and the consequent absence of elevations or depressions in the plated surface. It is well known that if a surface is perfectly plane, mirror-like reflection is obtained. According to the wave theory of light, a surface reflects like a plane surface as long as there are no elevations or depressions in it which have dimensions exceeding a small fraction of the wave length of light. For a given degree of roughness, it also follows that the regularity of the reflection depends not only on the wave length of the light but also on the angle of incidence. The smoothness of the surface is therefore best tested with light falling on it at nearly grazing incidence. This may be seen by examining a plate which is just on the border line of being fully bright. When looked at in the usual way, it seems bright, but if it is held so that it can be viewed by light falling on it at nearly grazing incidence, it shows a faint haziness or cloud. Perfectly bright plate, though, does not show this cloud.

All the observed facts are consistent with the hypothesis that the mechanism, by which bright plate is produced is simply that which is involved in the elimination of pitting and treeing, carried out more perfectly, of course, than is the case in ordinary plating.

We claim:

1. The method of electrodepositing nickel which comprises electrolyzing a solution containing a nickel salt from the group consisting of sulphates and chlorides, in the presence of an ammonium salt, a formate and formaldehyde.
2. The method of electrodepositing nickel which comprises electrolyzing a solution containing a nickel salt from the group consisting of sulphates and chlorides, in the presence of an ammonium salt, a formate, and formaldehyde, and having a pH of about 4 to 4.4.
3. The method of electrodepositing a nickel-cobalt alloy which comprises electrolyzing a solution containing nickel and cobalt salts from the group consisting of sulphates and chlorides, in the presence of an ammonium salt, a formate and formaldehyde.
4. The method of electrodepositing a nickel cobalt alloy which comprises electrolyzing a solution containing nickel and cobalt salts from the group consisting of sulphates and chlorides, in the presence of an ammonium salt, a formate, and formaldehyde, and having a pH of about 4 to 4.4.
5. The method of electrodepositing nickel which comprises electrolyzing a solution containing a nickel salt in the presence of 0.5 to 5 grams per liter of an ammonium salt, 20 to 100 grams per liter of a formate, and 0.5 to 7.5 grams per liter of formaldehyde.
6. The method of electrodepositing nickel which comprises electrolyzing a solution containing a nickel salt in the presence of 0.5 to 5 grams per liter of an ammonium salt, 20 to 100 grams per liter of a formate, and 0.5 to 7.5 grams per liter of formaldehyde, the pH of the solution being about 4 to 4.4.
7. The method of electrodepositing a nickel-cobalt alloy which comprises electrolyzing a solution containing nickel and cobalt salts in the presence of 0.5 to 5 grams per liter of an ammonium salt, 20 to 100 grams per liter of a formate, and 0.5 to 7.5 grams per liter of formaldehyde.

8. The method of electrodepositing a nickel-cobalt alloy which comprises electrolyzing a solution containing nickel and cobalt salts in the presence of 0.5 to 5 grams per liter of an ammonium salt, 20 to 100 grams per liter of a formate, and 0.5 to 7.5 grams per liter of formaldehyde, the pH of the solution being about 4 to 4.4.

9. The method of electrodepositing nickel which comprises electrolyzing a solution containing a nickel salt from the group consisting of sulphates and chlorides, in the presence of an ammonium salt and formaldehyde.

10. The method of electrodepositing a nickel-cobalt alloy which comprises electrolyzing a solution containing nickel and cobalt salts from the group consisting of sulphates and chlorides, in the presence of an ammonium salt and formaldehyde.

11. The method of electrodepositing nickel which comprises electrolyzing an acid solution containing a nickel salt from the group consisting of sulphates and chlorides, in the presence of formaldehyde.

12. The method of electrodepositing a nickel-cobalt alloy which comprises electrolyzing an acid solution containing nickel and cobalt salts from the group consisting of sulphates and chlorides, in the presence of formaldehyde.

13. An electrolyte for depositing bright metal coatings consisting of a water solution containing salts of the metals nickel and cobalt in the proportion expressed in terms of sulphate of 120 to 400 grams per liter, a formate in the proportion of 20 to 100 grams per liter, an ammonium salt in the proportion of 0.5 to 5 grams per liter, and formaldehyde in the proportion of 0.5 to 7.5 grams per liter.

14. An electrolyte for depositing bright metal coatings consisting of a water solution containing salts of the metals nickel and cobalt in the proportion expressed in terms of sulphate of 120 to 400 grams per liter, a formate in the proportion of 20 to 100 grams per liter, an ammonium salt in the proportion of 0.5 to 5 grams per liter, and formaldehyde in the proportion of 0.5 to 7.5 grams per liter, the pH being adjusted to about 4 to 4.4.

15. An electrolyte for depositing bright metal coatings consisting of a water solution containing 240 grams per liter of nickel sulphate, 45 grams per liter of nickel chloride, 15 grams per liter of

cobalt sulphate, 45 grams per liter of nickel formate, 1 gram per liter of ammonium sulphate, and 0.5-1.0 gram per liter of formaldehyde.

16. An electrolyte for depositing bright metal coatings consisting of a water solution containing 240 grams per liter of nickel sulphate, 45 grams per liter of nickel chloride, 15 grams per liter of cobalt sulphate, 45 grams per liter of nickel formate, 1 gram per liter of ammonium sulphate, and 0.5-1.0 gram per liter of formaldehyde, the solution having a pH of 4.2 to 4.3.

17. The method of electrodepositing a metal from the class consisting of nickel and cobalt, which comprises electrolyzing an acid solution containing a salt from the class consisting of the sulphates and chlorides of the metals of said group, in the presence of formaldehyde.

18. The method of electrodepositing a metal from the class consisting of nickel and cobalt, which comprises electrolyzing an acid solution containing a salt from the class consisting of the sulphates and chlorides of the metals of said group, in the presence of an ammonium salt and formaldehyde.

19. The method of electrodepositing a metal from the class consisting of nickel and cobalt which comprises electrolyzing an acid solution containing a salt from the class consisting of the sulphates and chlorides of the metals of said group, in the presence of a formate, an ammonium salt and formaldehyde.

20. An electrolyte for depositing a coating of a metal from the class consisting of nickel and cobalt, which consists of a water solution containing a salt from the class consisting of the sulphates and chlorides of the metals of said group, and formaldehyde.

21. An electrolyte for depositing a coating of a metal from the class consisting of nickel and cobalt, which consists of a water solution containing a salt from the class consisting of the sulphates and chlorides of the metals of said group, an ammonium salt and formaldehyde.

22. An electrolyte for depositing a coating of a metal from the class consisting of nickel and cobalt, which consists of a water solution containing a salt from the class consisting of the sulphates and chlorides of the metals of said group, a formate, an ammonium salt and formaldehyde.

LOUIS WEISBERG.

WILLIAM B. STODDARD, Jr.