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ELECTRODEPOSITION OF NICKEL

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This invention relates to new and useful improvements in the electrodeposition of nickel or combinations of nickel and cobalt.

This application is a continuuation-in-part of my application Ser. No. 764,897 filed July 30, 1947, now abandoned.

Many attempts have been made to produce nickel deposits that do not require buffing after plating. When the metal surface on which the nickel is deposited has a smooth enough finish, it is sufficient to put on a nickel deposit producing good specular reflection. This is the type of deposit that the plater calls "bright nickel." Its field of application is chiefly on buffed brass and copper.

If the metal surface on which bright nickel is deposited is not free from scratches and die marks, these may show up in the bright nickel deposit; in fact, contrast with the surrounding bright surface may make such imperfections stand out even more than they do in the unplated surface. Scratches and die marks are more likely to be found on steel because they are more difficult to polish out on steel than on brass or copper. The use of bright nickel on steel is therefore less advantageous than it is on brass or copper. Buffing the bright nickel does not help matters much because bright nickel deposits do not flow readily under the pressure exerted in the buffing operation and therefore buffing the bright nickel does not satisfactorily cover up scratches and die marks.

Even when bright nickel is applied over brass or copper, buffing lines may show through on careful examination. This is especially the case when the finishing operations have been performed by careless or unskilled workmen or when an essential step in finishing is omitted for the sake of economy.

Thus, whether the deposit is to be buffed or not, it is desirable to produce deposits, if possible, which cover up lines, scratches and marks of any description that are present in the surface to be plated. If the deposit is to be buffed, furthermore, it is desirable to produce deposits with characteristics which make for easy buffing.

One object of the present invention is a method of producing electrodeposits containing nickel or an alloy of cobalt and nickel that is more readily buffed than ordinary deposits of the same metal.

Another object of the present invention is a method of producing electrodeposits containing nickel or an alloy of cobalt and nickel that diminish the roughness of the starting surface and

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reduce the amount of buffing required after plating.

Another object of the present invention is a method of producing either bright or gray electrodeposits containing nickel or an alloy of cobalt and nickel that diminish the roughness of the starting surface and reduce the amount of polishing or finishing required preparatory to plating.

Still further objects and advantages will appear from the more detailed description given below.

I have found that the bright nickel plating solution described by Weisberg and Stoddard in U. S. Patent No. 2,026,718 can be modified to give deposits with superior buffing characteristics and with ability to smooth out lines, scratches, die marks and various other defects in the surfaces over which they are applied. This improved type of deposit lends itself to a variety of applications.

For example, the cost of polishing steel, nickel plating in this improved solution, and then buffing the nickel is lower than that of any alternative procedure of which I am aware. There is a two-fold advantage: first, a large proportion of the polishing lines in the steel are smoothed out or erased, thus reducing the amount of nickel buffing required; and in the second place, the nickel deposit itself is easier to buff than ordinary electrodeposited nickel. Thus savings in the over-all cost of producing acceptable nickel plated steel can be brought about by utilizing the present invention.

In the foregoing example, the plating conditions are usually chosen so as to give a deposit that is not bright, because that type of deposit has other properties which make it especially suitable for certain applications, such as automobile bumpers. For plating on brass or copper, a bright deposit would generally be preferred. The use of my improved solution for producing a bright deposit on brass or copper would make it possible to reduce the finishing work done preparatory to plating, because the plating operation itself would smooth out certain lines and defects that would otherwise have to be taken out before plating.

Normally a nickel deposit may cause some increase in the roughness of the surface treated and does not generally improve the smoothness of the surface to which it is applied. The smoothness before and after treatment can be determined by use of the brush "Surface Analyzer" or a "Profilometer." The brush surface analyzer produces a chart which shows graphically the

peaks and valleys on the surface. Hence by application of this device to the original and plated surfaces a quantitative comparison of the smoothness of the surfaces can be obtained.

On examining numerous samples of surfaces of the improved deposits above referred to by means of a brush surface analyzer and comparing them with the original steel surfaces before plating, I have found that the nickel deposit tends to cover up or smooth out scratches and other imperfections in the original surface. Furthermore, I have found that this improved coating produces a far greater smoothing action than ordinary coatings of gray nickel or bright nickel. This deposit therefore shows a double advantage. It is not only easier to buff, but less buffing is required than with ordinary nickel.

I have also found that the smoothing action can be further increased by the addition of certain substances, as hereinafter described, and that the smoothing action may be adversely affected by failure to exclude certain other substances. Some of these addition agents, when used by themselves, produce brittle deposits which are often pitted, but when used in conjunction with my modified solution, excellent physical properties are obtained along with the desired smoothing action and no pitting.

The preferred composition of a water solution for producing semi-bright deposits in accordance with this invention is given as Example I.

Example I

	Grams per liter
Nickel sulphate.....	360
Nickel chloride.....	30
Formic acid.....	15
Boric acid.....	40
Cobalt sulphate.....	3
Formaldehyde (anhydrous).....	0.0-0.5

The preferred operating conditions are:

Temperature.....	70-75 degrees centigrade
pH (electrometric).....	2.3
Current density.....	40 amperes per square foot
Agitation.....	Vigorous

The conditions above set forth represent the optimum for producing nickel, or rather cobalt-nickel, deposits that are easy to buff and have a powerful smoothing action so that the total amount of work required to buff the plated deposit to a high lustre is less than for ordinary nickel. The deposits so obtained, moreover, are extremely ductile and free from pits.

The preferred composition of a water solution for producing bright deposits in accordance with this invention is given as Example II.

Example II

	Grams per liter
Nickel sulphate.....	360
Nickel chloride.....	30
Formic acid.....	20
Boric acid.....	40
Cobalt sulphate.....	3
Formaldehyde (anhydrous).....	1

The preferred operating conditions are:

Temperature.....	70-75 degrees centigrade
pH (electrometric).....	3.7
Current density.....	40 amperes per square foot
Agitation.....	Vigorous

In both examples, the content of nickel sulphate may be varied over a wide range, say from 120 to 400 grams per liter. A relatively high

value is preferred, because the results obtained are somewhat better and because solutions with high nickel sulphate content are more strongly buffered against pH change.

The principal function of the chloride is to promote good anode corrosion. The amount stated is sufficient. Considerably more or less may be used without particular effect, for example, from 15 to 60 grams per liter.

Boric acid may vary from 30 to 40 grams per liter.

Formic acid may vary from 5 to 30 grams per liter. The lower amount is essential for good smoothing action. Any increase beyond that has little effect on the smoothing action, but is desirable where brightness is required.

The cobalt content is kept at the lowest figure practicable in order to keep the cost down. The quantity indicated corresponds to a cobalt content of about one per cent in the deposit. A small amount of cobalt has considerable smoothing action; large amounts produce additional smoothing but not in proportion. Larger amounts of cobalt are therefore not economical. Somewhat less desirable results are obtained if no cobalt is present. Thus the content of cobalt compounds may vary from no cobalt to any amount which is economically justifiable. The quantity of cobalt indicated in Example II is sufficient to produce bright deposits when the solution is reasonably free from impurities. Somewhat greater tolerance for impurities may be gained by increasing the cobalt.

Formaldehyde does not have any marked effect on the smoothing action. It is helpful in controlling pitting and is necessary for brightness, as in Example II. The amount required to control pitting depends on the condition of the solution with respect to impurities and other operating conditions. The preferred amount required for bright deposits is 1 gram of anhydrous material per liter but may vary from about 0.7 to 1.5 grams per liter. The amount of formaldehyde used may therefore vary all the way from none up to about 1.5 grams per liter according to the purpose for which the solution is operated.

In comparing the composition of the foregoing solutions with that in the Weisberg and Stoddard patent previously referred to, it is to be noted that formaldehyde, which is the primary brightening agent in the patent, is not a factor in producing smoothing action and may or may not be used in the practice of my new invention. A further difference is that ammonium sulphate, which is recommended as an auxiliary brightening agent in the Weisberg and Stoddard patent, is omitted altogether. Since even small amounts of ammonium sulphate have been found to exert an unfavorable effect on the smoothing action, the solution should be free from ammonia and ammonium salts in amounts which will deleteriously affect the smoothing action of the deposited nickel. Moreover, I have also found, so far as brightness is concerned, that ammonium sulphate is not required if the solution is sufficiently free from impurities.

In regard to operating conditions, the temperature may vary from about 60 to 80 degrees centigrade. Below 60 the smoothing action is diminished; above 80 the smoothing action continues to improve, but the deposit tends to become hard and brittle. It is believed that the impairment in physical properties is due to the fact that formic acid becomes rather volatile under these extreme conditions and is lost from the solution.

The pH range may vary from about 2.0 to 4. The best range for semi-bright plate is 2.1 to 2.5; for bright plate 3.5 to 3.7 is preferable. The smoothing action has been found to be substantially independent of whether the higher or lower pH range is employed.

In general, the smoothing action decreases with increased current density, other conditions remaining the same. An average of 40 to 50 amperes per square foot may be used on most kinds of work with suitable agitation. Under favorable conditions, good smoothing action has been obtained at current densities as high as 100 amperes per square foot.

The addition of magnesium sulphate to the preferred solution up to 150 grams per liter or more improves the electrical conductivity of the solution and is useful in lowering power consumption where higher current densities are employed. Addition of magnesium sulphate for this purpose is not detrimental to the smoothing action and buffability nor to the physical properties of the deposit. The following examples illustrate preferred compositions containing magnesium sulphate, III being a solution that gives semi-bright deposits and IV a solution that gives bright deposits.

Example III

Nickel sulphate.....	360 grams per liter
Nickel chloride.....	30 grams per liter
Formic acid.....	15 grams per liter
Boric acid.....	40 grams per liter
Cobalt sulphate.....	3 grams per liter
Magnesium sulphate.....	120 grams per liter
Formaldehyde	
(anhydrous).....	0.0-0.5 gram per liter
Temperature.....	70-75 degrees centigrade
pH (electrometric) ..	2.3
Current density.....	60 amperes per square foot
Agitation.....	Vigorous

Example IV

Nickel sulphate.....	360 grams per liter
Nickel chloride.....	30 grams per liter
Formic acid.....	15 grams per liter
Boric acid.....	40 grams per liter
Cobalt sulphate.....	3 grams per liter
Magnesium sulphate.....	120 grams per liter
Formaldehyde	
(anhydrous).....	1 gram per liter
Temperature.....	70-75 degrees centigrade
pH (electrometric) ..	3.5
Current density.....	60 amperes per square foot
Agitation.....	Vigorous

Preceding comments concerning ranges of proportions of various constituents of the bath and operating conditions apply to Examples III and IV.

Agitation of the solution or moving the work with respect to the solution has an appreciable effect on the smoothing action and buffability of the deposit. Vigorous agitation is desirable for best results.

The presence of dissolved impurities in the solution may interfere with the smoothing action of the solution or make the deposits harder to buff, besides possibly impairing other desirable qualities of the deposit. Suspended impurities should likewise be avoided. The solution must therefore be purified and filtered with scrupulous care for best results. Methods for purifying nickel plating solutions are well known to those skilled in the art.

The following table gives some idea of the tolerance for various metallic impurities.

	Milligrams per liter
Aluminum.....	5
Chromium.....	1
Copper.....	20
Iron (ferrous).....	1

The tolerance for ferric iron is about one hundred times higher than for ferrous iron. Lead, zinc and cadmium are somewhat beneficial at certain concentrations, but their effect on other properties makes it desirable to exclude them.

The effects of organic impurities are more difficult to describe specifically because there are so many possible impurities to consider. As an example, it may be mentioned that a trace of oil is sufficient to cause complete loss of smoothing effect. Care is necessary to avoid contaminating the solution, in the first place. Besides this, periodic or continuous treatment with activated carbon is necessary to maintain favorable conditions for operation. In general, good smoothing action is obtained only when careful attention is given to all operating requirements as described herein.

The smoothing action of the nickel deposit herein referred to can be obtained by adding certain other substances, notably coumarin, to a typical Watts nickel plating solution having the following composition:

	Grams per liter
Nickel sulphate.....	240
Nickel chloride.....	45
Boric acid.....	30

However, under the most favorable conditions of operation, the deposit obtained from this solution is so hard and brittle as to be undesirable for most purposes where nickel is applied. I have found, though, that the addition of coumarin to the improved solution as hereinbefore described enhances the smoothing action of the deposits produced therefrom. If the amount of coumarin added is not excessive, the deposits obtained in this way have good physical properties as well as superior smoothness.

Example V

50 Nickel sulphate.....	360 grams per liter
Nickel chloride.....	30 grams per liter
Nickel formate.....	20 grams per liter
Boric acid.....	40 grams per liter
Cobalt sulphate.....	3 grams per liter
55 Formaldehyde	
(anhydrous).....	0.5 gram per liter
Coumarin.....	1.0 gram per liter
Temperature.....	60 degrees centigrade
Current density.....	40 amperes per sq. foot
60 pH (electrometric) ..	2.3
Agitation.....	Vigorous

Example VI

Nickel sulphate.....	360 grams per liter
65 Nickel chloride.....	30 grams per liter
Nickel formate.....	30 grams per liter
Boric acid.....	40 grams per liter
Cobalt sulphate.....	3 grams per liter
Formaldehyde	
70 (anhydrous).....	1.0 gram per liter
Coumarin.....	1.0 gram per liter
Temperature.....	60 degrees centigrade
Current density.....	40 amperes per sq. foot
pH (electrometric) ..	3.7
75 Agitation.....	Vigorous

Preceding comments concerning ranges of proportions of the various constituents of the bath and operating conditions apply to Examples V and VI.

The solubility of coumarin in the nickel plating solution is low but increases rapidly with the temperature. Coumarin is plated out of the solution fairly rapidly so that it must be replaced regularly, or better still continuously, as the solution is used. This may be done by circulating the solution, or part of it, through a filter charged with coumarin. The content of coumarin can be controlled at the desired point by saturating the solution at any desired temperature and circulating as much of the solution through the filter as may be necessary.

The amount of coumarin required in the solution is small. The optimum content of coumarin for the purpose of this invention is in the neighborhood of one gram per liter or even less.

A noteworthy feature in regard to the smoothing action of the nickel and cobalt-nickel deposits herein described is the fact that the smoothing action increases with increasing thickness of deposit, at least over the range I have investigated. If the nickel thickness is 0.002 inch, the smoothing action is more pronounced than if the thickness is only 0.001 inch. If the thickness of the deposit is increased to 0.003 inch, there is a further gain in smoothness.

The term "nickel" in the accompanying claims includes the possible presence of small amounts of cobalt. The term "smooth" as used in the claims refers to a deposit the surface of which is smoother than the surface on which the deposit is applied, the specific test being made by means of a brush surface analyzer.

The foregoing description is given by way of explanation and illustration only, and not by way of limitation. Various changes may be made by those skilled in the art without departing from the scope and spirit of the present invention.

I claim:

1. The method of electrodepositing nickel to produce smooth, ductile, easy-buffing deposits which comprises electrolyzing a body of a solution containing as essential constituents nickel sulphate 120 to 400 grams per liter, nickel chloride 15 to 60 grams per liter, formic acid 5 to 30 grams per liter, and boric acid from 30 to 40 grams per liter, the solution being free of ammonia and ammonium salts in amount which will deleteriously affect the smoothing action of the deposited nickel, and free from impurities in amounts of not more than 5 milligrams per liter of aluminum, nor more than 1 milligram per liter of chromium, not more than 20 milligrams per liter of copper, and not more than 1 milligram per liter of ferrous iron, purifying said body of solution with respect to said impurities, the frequency of said purification and the extent thereof being such as to maintain the purity of the solution, during electrolysis, within said limits, maintaining the pH of the solution, during electrolysis, between 2 and 4, and discontinuing the electrolysis before the electrodeposited nickel has exceeded a thickness substantially greater than 0.003 inch, whereby deposits are obtained which are ductile, easily buffed, and have a surface substantially smoother than the surface of the cathode on which they are deposited.

2. The method of claim 1 in which the solution is electrolyzed at a temperature between 60° C. and 80° C.

3. The method of claim 1 in which the solu-

tion contains formaldehyde up to 1.5 grams per liter, and in amount sufficient to impart increased brightness to the deposited nickel.

4. The method of claim 3 in which the solution is electrolyzed at a temperature between 60° C. and 80° C.

5. The method of claim 1 in which the solution contains cobalt sulphate up to 3 grams per liter, and in amount sufficient to further enhance the smoothing action of the deposited nickel.

6. The method of claim 1 in which the solution contains magnesium sulphate up to 150 grams per liter, and in amount effective to improve the electrical conductivity of the solution.

7. The method of claim 1 in which the solution contains approximately 1 gram per liter of coumarin.

8. An electrolyte for depositing a smooth, ductile, easy-buffing coating of nickel which comprises as essential constituents nickel sulphate 120 to 400 grams per liter, nickel chloride 15 to 60 grams per liter, formic acid 5 to 30 grams per liter, boric acid 30 to 40 grams per liter and formaldehyde up to 1.5 grams per liter and in amount effective to impart increased brightness to nickel electrolytically deposited from the electrolyte, the pH of the electrolyte being between 2 and 4, said electrolyte being free of ammonia and ammonium salts in amount which will deleteriously affect the smoothing action of nickel electrolytically deposited therefrom and free from impurities in amount of more than 5 milligrams per liter of aluminum, more than 1 milligram per liter of chromium, more than 20 milligrams per liter of copper and more than 1 milligram per liter of ferrous iron.

9. An electrolyte for depositing a smooth, ductile, easy-buffing coating of nickel which comprises as essential constituents nickel sulphate 120 to 400 grams per liter, nickel chloride 15 to 60 grams per liter, formic acid 5 to 30 grams per liter, boric acid 30 to 40 grams per liter and cobalt sulphate up to 3 grams per liter and in amount effective to further enhance the smoothing action of nickel electrolytically deposited from the electrolyte, the pH of the electrolyte being between 2 and 4, said electrolyte being free of ammonia and ammonium salts in amount which will deleteriously affect the smoothing action of nickel electrolytically deposited therefrom and free from impurities in amounts of more than 5 milligrams per liter of aluminum, more than 1 milligram per liter of chromium, more than 20 milligrams per liter of copper and more than 1 milligram per liter of ferrous iron.

10. An electrolyte for depositing a smooth, ductile, easy-buffing coating of nickel which comprises as essential constituents nickel sulphate 120 to 400 grams per liter, nickel chloride 15 to 60 grams per liter, formic acid 5 to 30 grams per liter, boric acid 30 to 40 grams per liter and approximately 1 gram per liter of coumarin, the pH of the electrolyte being between 2 and 4, said electrolyte being free of ammonia and ammonium salts in amount which will deleteriously affect the smoothing action of nickel electrolytically deposited therefrom and free from impurities in amounts of more than 5 milligrams per liter of aluminum, more than 1 milligram per liter of chromium, more than 20 milligrams per liter of copper and more than 1 milligram per liter of ferrous iron.

11. An electrolyte as defined in claim 10 which also contains formaldehyde up to 1.5 grams per liter and in amount effective to impart increased

brightness to nickel electrolytically deposited
from the electrolyte.

LOUIS WEISBERG.

REFERENCES CITED

The following references are of record in the
file of this patent:

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Number	Name	Date
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