

UNITED STATES PATENT OFFICE

2,315,802

NICKEL PLATING

Rudolf Lind, Euclid, William J. Harshaw, Shaker Heights, and Kenneth E. Long, South Euclid, Ohio, assignors to The Harshaw Chemical Company, Elyria, Ohio, a corporation of Ohio

No Drawing. Application April 20, 1940,
Serial No. 330,696

11 Claims. (Cl. 204—49)

This invention relates as indicated to electrodeposition of metals and more specifically, to a process of and materials for use in the process of electrodepositing nickel characterized in that the resultant nickel plate, as deposited, is both bright and ductile. More particularly, the present invention has to do with new addition agents for producing the above-named desirable characteristics in the nickel plate and which may be used with acid nickel baths of usual composition operating under usual conditions.

In order to properly evaluate the present invention, it is necessary to define brightness and ductility or brittleness, terms used in the old art, but used loosely to describe all degrees of brightness or brittleness.

Brightness

It is obvious that an extremely thin deposit of nickel over a highly buffed surface will appear bright. Bright plates of this type have been made for years and are well recognized in the art. Their limitations are that if the plated article is exposed to the atmosphere or to wear, the plate soon disappears or wears off. A plate thin enough so that it will retain substantially the full brightness of the polished base metal is impractical for use even as a base for the electrodeposition thereover of a protective coating of other metals such as chromium. If a heavier deposit is plated out, the brightness of the highly buffed surface diminishes and a gray or white dull deposit is obtained.

A nickel plate which is thick enough to be practical for use and which is bright without buffing is not only desirable per se, but it is particularly advantageous where it is destined for use as the base for an electrolytically deposited chromium plate, since, if the nickel plate does not require to be polished and buffed, a relatively thin plate gives the same protection as the necessarily heavier gray plate, some of which must be taken off in the polishing to secure the desired brightness. Furthermore, a very considerable saving in time and in cost on the production of plated articles becomes possible, whether with nickel plate per se or with additional chromium finish.

Various so-called addition agents have been proposed from time to time for inclusion in nickel plating baths in order to control or affect the character of the electrolytically deposited metal. One principal objective in such modification of the plating bath has been to increase the brightness or luster of the deposited metal.

Many of these previous nickel plating addition agents have allowed a much heavier deposit of nickel to be built up before the brightness of the base metal was materially diminished. When polished articles are plated in such baths, the

deposit is not truly bright but merely, at best, has the same character as the base metal. The brightness produced by such addition agents may, therefore, be characterized as "brightness diminishing with increased thickness of plate on a polished surface."

Others of these previous nickel plating addition agents have produced a plate which would maintain the brightness of the polished base surface, even though the plate was built up to a substantial thickness. They would not build up any substantial brightness on an unpolished surface and, at best, would only very slowly build up brightness on an unpolished surface when plates of extreme thickness were made. The brightness produced by such addition agents may, therefore, be characterized as "brightness maintaining itself with increased thickness of plate on a polished surface."

The addition agents of the present invention produce a plate that not only maintains the brightness of the most highly polished base metal, irrespective of the thickness of the plate within practical limits, but also increases in brightness with increase in thickness of the plate on an unpolished surface. The brightness produced by such addition agents may, therefore, be characterized as "brightness increasing with thickness of plate on an unpolished surface."

Ductility

The question of ductility is one of vital concern to the plater. In general, all bright plates are harder and, therefore, more brittle than ordinary dull nickel. When enough of many of the previously employed addition agents was added to a bath to produce a bright plate, the plate was often too brittle for commercial use and yet if less addition agent was used, the plate would not be fully bright.

A test for ductility may be made by plating on a non-adherent surface and stripping off the foil and bending it double on itself. A plate .001" thick which will pass this test without breaking is considered to have good ductility. A plate .0005" thick which will just pass this test is considered to have passable ductility. A plate .0002" thick which will not pass this test without breaking is considered to have poor ductility.

The addition agents of the present invention not only produce plates with the highest order of brightness, but also with a high order of ductility as defined by the above scale. This is desirable and essential to the practical use of bright nickel plating.

The principal object of the present invention, therefore, broadly stated, is to provide an improved process of and materials for use in the process of electrodepositing nickel which will not only render the nickel plate desirably bright but

which will also preserve or render the plate desirably ductile.

Other objects of our invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter more particularly pointed out in the claims, the following description setting forth in detail certain approved modes of operation of our process and combination of ingredients embodying our invention, such disclosure constituting, however, but certain of various forms in which the principles of our invention may be used.

Broadly stated, our invention comprises the discovery that by the use in acid nickel electrolytes of a plurality of addition agents respectively selected from certain different classes of compounds, we are able to produce deposits which are superior to those obtainable by the use of addition agents from either one of such classes alone. We find that the addition agents from one of said classes, although characterized by an embrittling tendency, are productive of extreme brightness when used in combination with addition agents from the other class and that addition agents from said other class not only cooperate in the production of brightness but also exert a ductilizing effect in the combination. The use of one addition agent from each class is preferable but a plurality from each class can be used successfully. Our cooperating addition agents are suitable for use in a wide variety of nickel electroplating solutions. We have found them to be very effective in aqueous acid nickel sulfate solutions and aqueous acid nickel chloride solutions. Among the nickel sulfate solutions in which they are effective are aqueous acid solutions of nickel sulfate, nickel sulfate and nickel chloride, nickel sulfate and sodium chloride, nickel sulfate and hydrochloric acid, nickel sulfate and ammonium chloride, nickel sulfate and alkali metal chlorides other than sodium chloride, the chlorides serving to produce good anode corrosion. Our addition agents are effective in nickel chloride solutions with and without nickel sulfate. In each of said solutions it is desirable, although not necessary, to employ boric acid or another suitable buffering agent. We prefer to employ a bath containing nickel sulfate together with a suitable chloride, preferably nickel chloride and a suitable buffer, preferably boric acid. We prefer to employ one or more addition agents from one of said classes in quantity to produce the desired brightness and one or more from the other class in quantity to overcome to a substantial extent the resulting embrittling tendency.

As representative of separate classes of compounds which, when used in combination as above stated, produce improved results, are those classes of compounds which may be respectively identified as (1) alkaloids of cyclic structure, soluble in the bath to the extent of at least .001 gram per liter and (2) aromatic sulfonates, sulfonamides and sulfimides soluble in the bath to the extent of at least $\frac{1}{2}$ gram per liter. Since these two classes of addition agents are distinct, they will be discussed separately

Alkaloids

The alkaloids of cyclic structure are complex basic compounds originally discovered in plants and animals but now often synthesized. Most of them are tertiary amines characterized by a heterocyclic ring containing nitrogen in the

ring. It is immaterial for our purpose whether the compound is extracted from vegetable or animal sources or synthesized providing the product is fairly pure.

The salts of the compounds of the above described class, for example, the chlorides, hydrochlorides, acetates, sulfates and bisulfates are suitable and often to be preferred to the compounds themselves because of their greater solubility. It is essential that these compounds, a single one or a mixture of two or more thereof, be present in the solution to an extent to exert their brightening effect, preferably at least two milligrams per liter.

Some specific examples of compounds suitable for our purpose are as follows:

Table I

Apomorphine	Cinchonine
Caffeine	Quinine
Aspidospermine	Narcotine
Atropine	Hydrastine
Papaverine	Morphine
Cocaine	Theobromine
Codeine	Colchicine
Ephedrine	Ethyl morphine
Strychnine	Aconitine
Nicotine	Brucine
Tropacocaine	Piperine
Adrenaline	

Of the foregoing materials, caffeine, theobromine, nicotine, quinine and cinchonine are to be preferred as being readily available, comparatively cheap, relatively free from danger to workmen and not subject to the difficulties surrounding industrial uses of materials such as morphine.

While the quantity of these substances employed is not sharply critical, they are used in small amounts, that is, amounts of the order of 2 to 100 milligrams per liter, the upper limit being determined by their embrittling effect and, in some cases, by their solubility.

The specific examples of Table I are commercial products. There are many other alkaloids which will be found suitable for our purpose. Many of these, however, are not available because they are not commercial products or are difficult to make.

The second class of materials, representative particular ones of which are employed in combination with one or more substances of the first class of compounds above identified, may be and for the purposes of this specification are designated as aromatic sulfon-compounds. These materials are capable of cooperating with the materials of the first class to produce nickel deposits having a high order of brightness accompanied by commercial ductility.

Particular examples which we have found to give excellent results are as follows:

Table II

1. Alpha-naphthalene mono-sulfonate.
2. Beta-naphthalene mono-sulfonate.
3. Naphthalene disulfonates.
4. Naphthalene trisulfonates.
5. Sulfonated naphthalene.
6. o-Benzic sulfimide (saccharin, preferably as sodium salt).
7. Benzene sulfonamide.
8. Benzene sulfohydroxamic acid.
9. p-Toluene sulfonamide.
10. o-Toluene sulfonamide.

The above named addition agents of this second class, suitably in the form of the sodium or

the nickel salt, may be used in various quantities upwards from 0.2 g./l., however, 5 g./l. or less is usually sufficient concentration for best results. Larger quantities, within the limits of solubility, do no harm.

Specific example 5 of Table II above is such as may be produced by reacting 2 parts of 20% oleum on one part of naphthalene at 160° C. for two hours, neutralizing the resulting mixture with nickel carbonate, filtering and diluting to 25° Bé. Where quantities of "sulfonated naphthalene" are referred to hereinafter, it is to be understood that the quantity specified represents roughly the nickel-naphthalene-mixed-sulfonate content of the mixture. Five cc. of the nickel neutralized reaction mixture is taken as equivalent to one gram of nickel-naphthalene-mixed sulfonates. Other mixtures of compounds of the second class of materials also are satisfactory.

A conventional aqueous acid nickel bath in which the combined use of the two classes of addition agents will be found to give improved results, as above indicated, consists of:

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ¹ 120-450 grams per liter.
 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 15-75 grams per liter.
 H_3BO_3 15 grams per liter to saturation.
 Sodium lauryl sulfate ¹ 0-1.0 gram per liter.
 Current density. Up to 60 amperes per sq. ft.
 pH 1.5-5.5.
 Temperature Room to 170° F.

¹ Where this compound is referred to, the material sold under the trade name of "Duponol M. E. Dry" is to be understood. It is sold as the technical compound. Other equivalent surface tension reducing agents may be used instead of Duponol. Preparations known as Fergitol 7 and Tergitol 08, sold by Carbide & Carbon Chemicals Co. and said to be sodium secondary alcohol sulfates, may be used instead of Duponol. The quantities required are of the same order.

² Some heptahydrate is usually present. Where nickel sulfate is used herein in specific examples, this mixture of hydrates is to be understood.

In the above table giving the composition of a conventional bath, sodium lauryl sulfate is added for the purpose of reducing the surface tension in order to prevent pitting of the plate. The sulfates of normal primary aliphatic alcohols, having from 8 to 18 carbon atoms, are a class of compounds preferred for use for this purpose.

Example I

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	grams	240
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	do	37.5
H_3BO_3	do	37.5
Sulfonated naphthalene	do	4.0
Sodium lauryl sulfate	do	0.25
Quinine bisulfate	do	0.010
H_2O to make	cc	1000
Temperature	°C	50
Current density	amps./sq.ft.	40
pH		3.0

Example II

Same as Example I except that for the quinine bisulfate was substituted 0.004 gram of nicotine.

Example III

Same as Example I except that for the quinine bisulfate was substituted 0.005 gram of brucine sulfate.

Example IV

Same as Example I except that for the quinine bisulfate was substituted 0.010 gram of cinchonine.

In each of the foregoing examples, the sodium lauryl sulfate may be omitted or substituted by equivalent anti-pit agent, boric acid may be substituted by another buffer and proportions

may vary as in the conventional bath limits above set forth.

This application is a continuation-in-part of our co-pending application, Serial No. 217,774, filed July 6, 1938, now Patent No. 2,238,861.

This application is also a continuation-in-part of our co-pending applications, Serial Nos. 309,232 and 309,233, filed December 14, 1939, now Patents No. 2,198,267 and No. 2,198,268, respectively, which were continuations-in-part respectively of our applications, Serial Nos. 200,120 and 200,121, filed April 5, 1938.

Having thus described our invention, what we claim is:

1. An electroplating solution comprising an aqueous, acid solution of a nickel electrolyte of the class consisting of a nickel sulfate and nickel chloride, said solution having the capability of producing bright and ductile deposits of nickel, such capability having been imparted thereto by the inclusion therein of cooperating addition agents, one said addition agents comprising an alkaloid of cyclic structure and soluble in the bath to the extent of at least 0.002 gram per liter and mixtures of such alkaloids, said addition agents being present in the solution to an extent to exert their brightening effect and the other of said addition agents being selected from the group consisting of naphthalene sulfonates, the single ring aryl sulfonamides and single ring aryl sulfonimides and mixtures thereof, said second type being present in solution in the bath to the extent of at least 0.2 gram per liter.

2. An electroplating bath comprising an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate and nickel chloride, said solution having the capability of producing bright and ductile deposits of nickel, such capability having been imparted thereto by the inclusion therein of cooperating addition agents, one of said addition agents being present in the bath in concentration of from 2 to 100 milligrams per liter and comprising an alkaloid of cyclic structure and mixtures of such alkaloids, and the other of said addition agents being present in concentration of at least one-half gram per liter and being selected from the group consisting of naphthalene sulfonates, the single ring aryl sulfonamides and single ring aryl sulfonimides and mixtures thereof, said second type being present in solution in the bath to the extent of at least 0.2 gram per liter.

3. An electroplating solution as claimed in claim 1, further characterized in that said solution contains both nickel sulfate and nickel chloride.

4. An electroplating solution as claimed in claim 1, further characterized in that said solution contains both nickel sulfate and nickel chloride, said nickel sulfate being present in greater quantity than said nickel chloride.

5. An electroplating solution as claimed in claim 1, further characterized in that said solution contains both nickel sulfate and nickel chloride and a buffer comprising boric acid.

6. An electroplating solution consisting essentially of an aqueous acid solution of a substance of the class consisting of nickel sulfate, nickel chloride and mixtures thereof, said solution having the capability of producing bright and ductile deposits of nickel, such capability having been imparted thereto by the inclusion therein of cooperating addition agents, one of said addition agents being selected from the group consisting of apomorphine, caffeine, aspidospermine,

atropine, papaverine, cocaine, codeine, ephedrine, strychnine, nicotine, tropacocaine, adrenaline, cinchonine, quinine, narcotine, hydrastine, morphine, theobromine, colchicine, ethylmorphine, aconitine, brucine and piperine and mixtures of such substances and salts thereof, and being present to the extent of from 0.002 to 0.10 gram per liter, and the other of said addition agents being selected from the group consisting of naphthalene sulfonates, the single ring aryl sulfonamides and single ring aryl sulfonimides and mixtures thereof and being present to the extent of at least one-half gram per liter.

7. An electroplating solution as defined in claim 6 further characterized in that said solution also contains a buffer comprising boric acid.

8. An electroplating solution as defined in claim 6 further characterized in that said solution also contains an aliphatic alcohol sulfate of from 8 to 18 carbon atoms.

9. An electroplating solution consisting essentially of an aqueous acid solution of a substance of the class consisting of nickel sulfate, nickel chloride and mixtures thereof, said solution having the capability of producing bright and ductile deposits of nickel, such capability having been imparted thereto by the inclusion therein of cooperating addition agents, one of said addition agents being an alkaloid of cyclic structure soluble in the said solution to the extent of at least 0.002 gram per liter and mixtures of such alkaloids, said addition agents being present in the solution to an extent to exert their brightening effect and the other of said addition agents being selected from the group consisting of naphthalene sulfonates, the single ring aryl sulfonamides and single ring aryl sulfonimides and mixtures thereof, said second type being present in solution in the bath to the extent of at least 0.2 gram per liter.

10. An electroplating solution consisting es-

5
10
15
20
25
30
35
40
sentially of an aqueous acid solution of a substance of the class consisting of nickel sulfate, nickel chloride and mixtures thereof, said solution having the capability of producing bright and ductile deposits of nickel, such capability having been imparted thereto by the inclusion therein of cooperating addition agents, one of said addition agents being selected from the group consisting of apomorphine, caffeine, aspidospermine, atropine, papaverine, cocaine, codeine, ephedrine, strychnine, nicotine, tropacocaine, adrenaline, cinchonine, quinine, narcotine, hydrastine, morphine, theobromine, colchicine, ethylmorphine, aconitine, brucine and piperine and mixtures of such substances and salts thereof, and being present to the extent of from 0.002 to 0.10 gram per liter, and the other of said addition agents being a naphthalene sulfonate.

11. An electroplating solution consisting essentially of an aqueous acid solution of a substance of the class consisting of nickel sulfate, nickel chloride and mixtures thereof, said solution having the capability of producing bright and ductile deposits of nickel, such capability having been imparted thereto by the inclusion therein of cooperating addition agents, one of said addition agents being selected from the group consisting of apomorphine, caffeine, aspidospermine, atropine, papaverine, cocaine, codeine, ephedrine, strychnine, nicotine, tropacocaine, adrenaline, cinchonine, quinine, narcotine, hydrastine, morphine, theobromine, colchicine, ethylmorphine, aconitine, brucine and piperine and mixtures of such substances and salts thereof, and being present to the extent of from 0.002 to 0.10 gram per liter, and the other of said addition agents being saccharine.

RUDOLF LIND.
WILLIAM J. HARSHAW.
KENNETH E. LONG.