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ELECTRODEPOSITION OF METALS

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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 unpolished 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 de-

sirable 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 may employ soluble or insoluble anodes. 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) the amino poly aryl methane compounds in which at least one amino group is connected to an aryl group; and (2) the benzene sulfonamides, benzene sulfimides and substitution products of such compounds. Since these classes of compounds are in themselves distinct, it is believed advisable to deal with them separately in more specifically identifying them and in pointing out specific examples which will be found to be particularly suitable for use.

Amino compounds

While this class of compounds has been identified above as the amino aryl methanes, nevertheless, our invention contemplates for use as this group of addition agents compounds characterized by the presence of the primary, secondary or tertiary amino group, a large cyclic molecule and the dominance of the amino group or groups over other antagonistic groups.

A representative class of the above identified amino compounds are the amino substituted poly aryl methanes. The various substitution products of the poly aryl methanes which are within the contemplation of the invention may be classified as follows, viz.:

1. Amino compounds with at least one alkyl substituent group.
2. Amino compounds with at least one aryl substituent group on one of said aryl groups.
3. Amino compounds with at least one alkyl and at least one aryl substituent group on one of said aryl groups.
4. Amino compounds with at least one hydroxyl group.
5. Amino compounds with at least one sulphonic group.

The alkyl groups may be present in certain of the above classes of compounds include methyl, ethyl, etc. The additional aryl groups which may characterize certain of the above mentioned subclasses of compounds are the benzyl, phenyl, tolyl, etc.

The salts of the above referred to types of compounds, such as chloride, hydrochloride, acetate and sulfate, are preferable to the referred to type of compounds themselves because of their greater solubility. The reduction products and carbitols of such compounds are also suitable and, in some cases, somewhat superior to the compounds themselves.

Specific examples which have been found to give good results are as follows, the common name and the chemical name from "Farbstoff Tabelen" by Gustav Schulz, 7th edition, vol. 1 (1931), being given, where possible, as more specific, the particular salt employed being indicated in the following table:

TABLE I

Triphenylmethane derivatives

1. p.p'-Diamino-m-methyl fuchsonimonium chloride (Fuchsin).
2. Triaminotolyl diphenyl methane hydrochloride (reduction product of Fuchsin).
3. Triaminotolyl phenyl carbitol hydrochloride (carbitol product of Fuchsin).
4. Mixture of reduction products and carbitol of Fuchsin prepared as hereinafter explained.
5. Symmetric tetramethyl-p-aminofuchsonimonium chloride (Malachite Green).
6. Symmetric diethyl-di-p-sulfobenzyl-p-aminofuchsonimonium (sodium salt of internal sulfonate, Pontacyl Green B).
7. Pentamethyltriaminotriphenyl methane acetate (reduction product of Methyl Violet).
8. Pentamethyl - p . p' - diaminofuchsonimonium chloride (Gentian Violet).
9. Hexamethyl-p.p' - diaminofuchsonimonium chloride (Crystal Violet).

Diphenylmethane derivatives

10. 2.2',4.4',-tetramino - 5.5' - dimethyl diphenyl methane-sulphate.
11. Tetramethyldiaminobenzophenonimium chlorhydrate (Auramine O).
12. Tetramethyl diamino diphenyl methane hydrochloride.

It will be observed that all of the specific examples of triphenylmethane derivatives given above are fuchsonimonium compounds, thus more specifically identifying a class of compounds which has been found to produce remarkably improved plates when employed as a constituent in the bath comprising our invention.

We have found it most practical to prepare specific Example 4 given above in the following way: Fifty parts of the dye, 1,000 parts of water, 100 parts of granular nickel and 100 parts of hydrochloric acid are heated and mechanically stirred until the magenta color of fuchsin has practically disappeared. The mixture is then stirred with a small amount of activated carbon and filtered. The filtrate is made up to one liter and contains the equivalent of five grams of the original fuchsin per 100 cc.

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

Most of the specific examples given in Table I are commercial products. There are many other members of the same groups, mostly not commercial products or not obtainable in pure form, which we believe would, if available and sufficiently pure, have the same effect. In general, impurities are undesirable. Fuchsin and its carbitol and reduction products, prepared as above indicated and 2.2',4.4'-tetramino 5.5'-dimethyl diphenyl methane produce plate of outstanding quality as compared with any of the other compounds listed. The presence of the primary, secondary or tertiary amino group, the large cyclic molecule and the dominance of the amino group or groups over any antagonistic groups are believed to be the significant factors which account for the improved results.

The benzene sulfonamides and substituted benzene sulfonamides

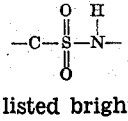
The second class of materials, representative specific examples of which are employed in combination with one or more specific examples of the first class of compounds above identified, i. e., the amino compounds, may be, as indicated, chemically identified as aryl sulfonamides, aryl sulfimides, and substitution products thereof.

Particular examples are:

TABLE II

1. o-Benzoic sulfimide (saccharin, preferably as sodium salt).
2. Benzene sulfonamide.
3. Benzene sulfohydroxamic acid.
4. p-Toluene sulfonamide.
5. o-Toluene sulfonamide.

The common grouping characterizing each of these specific examples is as follows:



With the above listed brightening agents, this group, which for convenience may be termed a "sulfonamide group," even though one of the amino hydrogens has been replaced, appears to be, in the case of the single aryl ring compounds, superior to the sulfonate group. In the case of naphthalene compounds, the sulfonate group appears to be superior to the "sulfonamide group."

The above-named addition agents of this second class may be used in various quantities preferably upwards from ½ gram per liter, however, 5 grams per liter or less is usually a sufficient concentration for best results. Larger quantities, within the limits of solubility, do no harm.

A conventional 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:

$NiSO_4 \cdot 6H_2O$**	120–450 grams per liter
$NiCl \cdot 6H_2O$**	15–75 grams per liter
H_3BO_3	15 grams per liter to saturation
Sodium lauryl sulfate*	0–1.0 gram per liter
Current density	Up to 60 amperes per sq. ft.
pH	1.5–3.0
Temperature	Room—170° F.

*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 Tergitol 4 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.

**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 of the bath to below 50 dynes per cm., in order to prevent pitting of the plate. Our invention contemplates the use of any surface tension-reducing agent effective to reduce the surface tension of the bath to below 50 dynes per cm. The sulfates of normal primary aliphatic alcohols, having at least six carbon atoms, are a class of compounds suitable for use for this purpose.

PARTICULAR EXAMPLES

Example No. 1

Nickel sulfate	grams per liter	240
Nickel chloride	do	37.5
Boric acid	do	37.5
2.2', 4.4'-tetramino-5.5'-dimethyl diphenyl-methane sulfate	grams per liter	0.010
o-Benzoic sulfimide (saccharin) (sodium salt)	grams per liter	1.0
Sodium lauryl sulfate (technical)	do	0.25
pH		3–4.5
Temperature	°C	45–55
Current density	amp./sq. ft.	30–40

Example No. 2

Nickel sulfate	grams per liter	240
Nickel chloride	do	37.5
Boric acid	do	37.5
Reduced fuchsin	do	*0.025
Benzene sulfonamide	do	4.0
Sodium lauryl sulfate (technical)	do	0.25
pH		3.0
Temperature	°C	50–55
Current density	amp./sq. ft.	40

*That is, the reduction product of .025 g. of the unreduced dye.

Example No. 3

Nickel sulfate	grams per liter	240
Nickel chloride	do	37.5
Boric acid	do	37.5
Reduced fuchsin	do	*0.005
Benzene sulfohydroxamic acid	do	2.0
pH		3.5
Temperature	°C	45–50
Current density	amp./sq. ft.	40

*That is, the reduction product of .005 g. of the unreduced dye.

Example No. 4

Nickel sulfate	grams per liter	240
Nickel chloride	do	37.5
Boric acid	do	37.5
Reduced fuchsin	do	*0.005
p-Toluene sulfonamide	do	1.0
pH		4.0
Temperature	°C	50–55
Current density	amp./sq. ft.	40

*That is, the reduction product of .005 g. of the unreduced dye.

Example No. 5

Nickel sulfate	grams per liter	240
Nickel chloride	do	37.5
Boric acid	do	37.5
Reduced fuchsin	do	*0.005
o-Toluene sulfonamide	do	1.0
pH		4.0
Temperature	°C	50–55
Current density	amp./sq. ft.	40

*That is, the reduction product of .005 g. of the unreduced dye.

Example No. 6

Nickel sulfate	grams per liter	240
Nickel chloride	do	37.5
Boric acid	do	37.5
Fuchsin	do	0.015
o-Benzoic sulfimide	do	3.0
Sodium lauryl sulfate (technical)	do	0.25
pH		3.0
Temperature	°C	55–60
Current density	amp./sq. ft.	60

This application is a continuation-in-part of Lind et al., application, Ser. No. 200,121, filed April 5, 1938, which is now abandoned.

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 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 an amino poly aryl methane compound in which at least one amino group is attached to an aryl group and the other of said addition agents being a substance of the class consisting of single ring aryl sulfonamides and sulfimides.

2. An electroplating solution comprising an aqueous, acid nickel sulfate 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 amino poly aryl methane compound in which at least one amino group is attached to an aryl group and the other of said addition agents being a substance of the class consisting of single ring aryl sulfonamides and sulfimides soluble in the bath to the extent of at least ½ gram per liter.

3. An electroplating solution as defined in claim 2, such solution also having the capability of producing good anode corrosion, this latter capability having been imparted thereto by the inclusion therein of one or more substances of the class consisting of nickel chloride, ammonium chloride, hydrochloric acid and alkali metal chlorides.

4. An electroplating solution as defined in claim 2, such solution also having the capability of producing good anode corrosion, this latter capability having been imparted thereto by the inclusion therein of one or more substances of the class consisting of nickel chloride, ammonium chloride, hydrochloric acid and alkali metal chlorides, said solution also containing boric acid.

5. An electrodeposition bath comprising an aqueous acid solution containing nickel sulfate, nickel chloride and cooperating addition agents, one of said addition agents being an amino poly aryl methane compound in which at least one amino group is connected to an aryl group, soluble in the bath to the extent of at least two milligrams per liter and characterized by a brightening and embrittling tendency, and the other of said addition agents being a substance of the class consisting of single ring aryl sulfonamides and sulfimides soluble in the bath to the extent of at least ½ gram per liter.

6. An electrodeposition bath comprising an aqueous acid solution containing nickel sulfate, nickel chloride and cooperating addition agents of two classes, one of said classes consisting of carbitol of fuchsin, fuchsin, reduced fuchsin, 2.2′, 4.4′-tetramino 5.5′-dimethyl-diphenyl methane, and the chlorides, hydrochlorides, acetates and sulfates thereof and the other of said classes consisting of single ring aryl sulfonamides and sulfimides soluble in the bath to the extent of at least ½ gram per liter.

7. An electrodeposition bath as defined in claim 5 further characterized in that the first mentioned addition agent is present in the bath in quantity from 2 to 100 milligrams per liter and the second mentioned addition agent is present in quantity sufficient to render the deposit ductile.

8. An electrodeposition bath as defined in claim 6 further characterized in that the first mentioned addition agent is present in solution in quantity from 2 to 100 milligrams per liter and the second mentioned addition agent is present in solution in quantity from ½ gram per liter to saturation.

9. An electrodeposition bath as defined in claim 6 further characterized in that the first mentioned addition agent is present in the bath in quantity from 2 to 10 milligrams per liter and the second mentioned addition agent is present in quantity from ½ gram to 5 grams per liter.

10. An electrodeposition bath comprising an aqueous acid solution containing nickel sulfate, nickel chloride and cooperating addition agents effective to produce bright and ductile deposits, one of said addition agents being an amino poly aryl methane compound in which at least one amino group is connected to an aryl group, soluble in the bath to the extent of at least two milligrams per liter and characterized by a brightening and embrittling tendency, the other of said addition agents being a substance of the class consisting of single ring aryl sulfonamides and

sulfimides soluble in the bath to the extent of at least ½ gram per liter.

11. An electrodeposition bath as recited in claim 5 wherein the second mentioned addition agent is saccharine.

12. An electrodeposition bath as recited in claim 6 wherein said second mentioned addition agent is saccharine.

13. An electrodeposition bath as recited in claim 10 wherein said second mentioned addition agent is saccharine.

14. An electrodeposition bath as recited in claim 6 wherein said first mentioned addition agent is reduced fuchsin employed in quantity from 2 to 100 milligrams per liter and said second mentioned addition agent is saccharine employed in quantity from ½ gram per liter to saturation.

15. An electrodeposition bath as recited in claim 6 wherein said first mentioned addition agent is reduced fuchsin employed in quantity from 2 to 10 milligrams per liter and said second mentioned addition agent is saccharine employed in quantity from ½ gram to 5 grams per liter.

16. An electrodeposition bath as recited in claim 6 wherein said first mentioned addition agent is fuchsin employed in quantity from 2 to 100 milligrams per liter and said second mentioned addition agent is saccharine employed in quantity from ½ gram per liter to saturation.

17. An electrodeposition bath as recited in claim 6 wherein said first mentioned addition agent is carbitol of fuchsin employed in quantity from 2 to 100 milligrams per liter and said second mentioned addition agent is saccharine employed in quantity from ½ gram per liter to saturation.

18. An electrodeposition bath comprising an aqueous acid solution of nickel sulfate, nickel chloride, boric acid and cooperating addition agents effective to produce bright and ductile deposits, one of said addition agents being an amino poly aryl methane compound in which at least one amino group is connected to an aryl group, soluble in the bath to the extent of at least two milligrams per liter and characterized by a brightening and embrittling tendency, the other of said addition agents being a substance of the class consisting of single ring aryl sulfonamides and sulfimides soluble in the bath to the extent of at least ½ gram per liter.

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