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2,870,069

BATH FOR ELECTROPLATING NICKEL

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The present invention is directed to electroplating baths, more particularly to baths for depositing nickel from acid solutions of nickel salts such as sulphate and chloride.

This application is a continuation in part of co-pending application Serial No. 412,652, filed February 25, 1954, now abandoned.

In the plating of nickel, it is highly desirable that the bath have good leveling characteristics, good covering and throwing power, have a high tolerance for metallic impurities, and be adapted to provide a coating which shall be highly ductile, which is active and adapted to be chromium plated and in which the coating has good brightness or brilliance. In the past, attempts have been made to obtain these properties but up to the present time no prior bath was successful in obtaining all of the above characteristics. For instance, it had been proposed to add to the bath certain sulfonic acid compounds which gave a brightness but did not give a brilliance or a mirror brightness. It had also been proposed to add to the bath certain polyamines which give brightness to the coating, but the latter was brittle and tended to crack and peel off. Certain of the baths of the prior art gave a coating which was passive and which was not receptive to a chromium plate and an additional treatment of the nickel coating was necessary to overcome this defect. Other baths gave dullness in the low current density areas with small changes in brightener concentration.

The various nickel baths of the prior art showed various degrees of tolerance for metallic impurities such as zinc, copper, iron, chromium and lead. Such impurities accumulate in the bath during the operation thereof or are introduced into the bath by dissolving of the metal being plated. In particular, the coating of copper plated zinc die castings introduces zinc and copper into the solution and it is most desirable that the bath have a high tolerance thereto. Prior baths in general did not have good tolerance to these metals.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in prior nickel plating baths, it being among the objects thereof to provide a bath composition which is adapted to give a coating which is ductile, has a high degree of brightness or brilliance and to which a chromium plate will adhere firmly.

It is also among the objects of the present invention to provide a bath which will have high leveling and covering power, and which is active without the necessity of an additional treatment of the nickel coating.

It is further among the objects of the present invention to provide a bath which has a high degree of tolerance for metallic impurities, particularly for zinc and copper.

In practicing the present invention there is first provided an ordinary nickel plating bath such as a Watts type plating bath. Usually the composition has a pH of about 3.5 to 4.5 and contains a mixture of nickel sulphate and nickel chloride to which boric acid is added.

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In accordance with the present invention, the Watts bath is modified by increasing the boric acid concentration so that there is a minimum of 6 oz. thereof per gallon. The amount of boric acid may range up to the saturation point of the bath at the temperature of operation.

To this bath there is added a mixture of two types of substances. There is added thereto certain sulfonic acid compounds, together with extremely small amounts of certain reaction products of polyalkylene amines. It has been found that a bath containing the above substances combines all of the desirable and favorable characteristics noted above and which are present only in part in the prior commercial bright nickel baths.

Although unsaturated aldehydes and amines have been used prior to this discovery, they have never been combined in a single bath. Furthermore, unsaturated aldehydes alone have the disadvantage of poor stability; that is, there is a very definite tendency towards polymerization. The amines, on the other hand, will not produce maximum luster in the finished product and the bath containing such a compound is quite critical as to its tolerance for the amine compound. The use of polyamines at or near the optimum concentration for brightness tends to produce dull grey deposits in the low current areas.

On the other hand, the use of reaction products of unsaturated aldehydes and polyalkylene amines produces a nickel plate of maximum luster without greyness, and these compounds when used in the plating bath are quite stable and not at all critical.

More specifically, it has been found that the use of reaction products of polyalkylene amines with unsaturated aldehydes and unsaturated esters of lower fatty acids, preferably vinyl acetate, produces a highly desirable result. Such compounds used in conjunction with sulfonates of benzene, toluene or naphthalene or sulfonamids and sulfonimids thereof give even better characteristics than when the unreacted polyalkylene amines are used with the said sulfonic acid compounds. In particular the leveling characteristics of the bath become quite pronounced.

The polyalkylene amines adapted for the present invention contain alkylene groups having from 1 to 6 carbon atoms and there are present in the amines from 2 to 10 such alkylene groups. The aldehydes used have the formula $X-R-CHO$, in which R represents an unsaturated alkylene group having from 1 to 6 carbon atoms, phenyl and naphthyl groups which may have hydrocarbon substituents having 1 or 2 carbon atoms. X represents hydrogen or up to 3 halogens, OH or amino groups. Such amino groups may have one or more hydrogen atoms thereof substituted by methyl or ethyl groups.

The acid portion of the unsaturated esters is comprised of lower fatty acids having from 1 to 6 carbon atoms. They are reacted in a ratio of at least 1 mol. of the ester to 1 mol. of the amine. Usually there is 1 mol. of ester for two NH_2 groups. The reaction products are used in amounts of .001 to .01 g./liter of actual product.

The sulfonic acid compounds are those of benzene, toluene and naphthalene containing from 1 to 3 sulfonic groups having the following general formula: $-SO_2R$. In such compounds R represents H, OH, NH, NH_2 and alkali metal. Compounds of this type are known in the prior art and they include sulfonates, sulfonamids and sulfonimids, such as are described in Schlatter Patent No. 1,972,693, Brown No. 2,191,813 and Lind 2,238,861.

As stated above, the invention includes the use of the reaction products of polyamines and unsaturated esters of lower fatty acids in conjunction with the sulfonic com-

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pounds in the standard Watts nickel bath. The deposits obtained therefrom have excellent leveling and brightening characteristics. Leveling, as referred to in plating baths, is the characteristic which reduces the surface roughness of the basis metal by electrodeposition. The measurement of the surface roughness was obtained by the brush surface analyzer. This and other methods of measuring roughness are described by Kellner in the 37th Annual Proceedings of the American Electroplater's Society, pages 108-115. Such compounds are made by reacting the polyamine with the unsaturated ester. The molecular ratio of the amine to the ester ranges from 1 mol. of amine to 1-3 of the ester. In general, for two NH_2 groups present in the amine, 1 mol. of the ester is required and for each mol. of acid used, 2 mols. of water are eliminated.

The following are examples of the preparation of the reaction products of polyalkyleneamines and aldehydes coming within the scope of the present invention.

Example 1

One mol. of vinyl acetate (86 grams) is added gradually with cooling and stirring to 1 mol. of triethylene tetramine (148 grams). The reaction is exothermic and it must be cooled in order to prevent the reaction from proceeding violently. When the reaction is complete, the solution is a clear yellowish color. Then the product is refluxed gently at 100°C . for about one hour, after which the reaction mixture is acidified with hydrochloric acid to a pH of at least 3. The resulting product is dark brown in color, has a sweetish-fruity odor and no longer smells of vinyl acetate or the amine. The product is diluted with water to 100 liters and is added to the standard nickel bath as above described, in the amount of 2 cc. per liter.

Example 2

Two mols of cinnamic aldehyde (264 grams) are added to 1 mol. of tetramethylene pentamine (192 grams). The addition is made slowly with cooling and constant stirring. When all the aldehyde has been added, the reaction mixture is heated in a water bath for three hours. The reaction mixture is acidified with 1 to 1 hydrochloric acid to a pH of below 2 and is diluted to 100 liters. The reaction product is used in the standard nickel bath in concentrations of 0.5 to 6.0 ml. per liter.

Example 3

To 0.5 mol. of tetraethylene pentamine (96 grams) in 96 grams of water is added slowly with stirring, 2 mols. of acrolein (112 grams). Should the temperature of the reaction mixture rise above 80°C . while the acrolein is being added, the reaction mixture should be cooled. After the addition of the acrolein the reaction mixture is kept at 80°C . for one hour whereby a dark brown reaction product results. The pH is adjusted to approximately 2.0 with concentrated hydrochloric acid to completely solubilize the resin. It is then diluted with water to 50 liters and used in the nickel plating bath in a concentration of 0.5 to 10.0 ml. per liter.

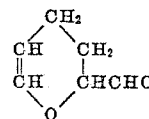
Example 4

To 0.25 mol. of crotonic aldehyde is added slowly with stirring 0.25 mol. of a 50% aqueous solution of diethylene triamine. After the reaction is completed, the mixture is maintained at 80°C . for one hour and diluted with 1 to 2 parts of water and acidified with concentrated hydrochloric acid to a pH of 2.0 or lower. The product is then diluted with water to a volume of 50 liters and is used in a nickel plating bath in a concentration of 1 to 8 ml. per liter.

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Example 5

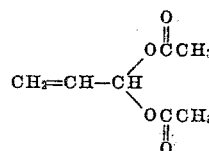
One mol. of acrolein dimer



is added slowly to 1 mol. of tetraethylene pentamine and the conditions of reaction are the same as in Example 3. After the reaction is complete, the product is acidified to a pH of 1.0 to 2.0 with hydrochloric acid and diluted with water to 100 liters. It is used in a nickel plating bath in a concentration of 0.25 to 10 ml. per liter.

Example 6

For the vinyl acetate in Example 1 is substituted 1 mol. of allylidene diacetate.



Example 7

For the vinyl acetate in Example 1 is substituted 2 chloroallylidene diacetate.

It is important that the reaction products of the polyalkylene amines with the unsaturated aldehydes and the unsaturated ester of the lower fatty acids should be soluble in the aqueous acid medium and should be stable in the pH range at which the nickel bath operates. In place of the unsaturated aldehyde an unsaturated ester of a lower fatty acid may be used as a reactant with the amino compound. It is the equivalent of an aldehyde in that in solution its structure is transformed to give an aldehyde temporarily and this reacts with the amino compound. While most unsaturated esters are satisfactory, vinyl acetate and allylidene acetate have been found particularly effective.

The following are specific examples showing various compositions of baths coming within the scope of the present invention. In said examples the pH of the solutions was 3.5 to 4.5 and the amounts of constituents set forth are in grams per liter of solution. The temperature on plating was 130° to 140°F . and the current density varied from 0 to 100 amperes per square foot.

Example 8

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	45
Boric acid-----	52.5
Na lauryl sulfate-----	.1 to .2
Na naphthalene trisulfonate-----	20
Vinyl acetate-triethylene tetramine reaction product-----	ml./liter-- 2

Example 9

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	g./l.-- 300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	g./l.-- 45
H_3BO_3 -----	g./l.-- 52.5
Na Naphthalene trisulfonate-----	g./l.-- 8.0
Vinyl acetate-triethylene tetramine reaction product-----	ml./l.-- 2.0
Sodium lauryl sulfate-----	g.-- 0.1-0.2

Example 10

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	g./l.-- 350
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	g./l.-- 45
Boric acid-----	g./l.-- 45
Sodium naphthalene trisulfonate-----	g./l.-- 16.0
Cinnamic aldehyde-tetraethylenepentamine reaction product-----	ml./l.-- 2.5

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Example 11

NiSO ₄ ·6H ₂ O	g./l.	300
NiCl ₂ ·6H ₂ O	g./l.	40
H ₃ BO ₃	g./l.	40
Acrolein-tetraethylene pentamine reaction product	ml./l.	4.0
Saccharin	g./l.	0.1
2,5 benzene disulfonic acid (sodium salt)	g./l.	8

Example 12

NiSO ₄ ·6H ₂ O	g./l.	300
NiCl ₂ ·6H ₂ O	g./l.	45
H ₃ BO ₃	g./l.	45
Benzene sulfonamide	g./l.	0.2
1,5 sodium naphthalene disulfonate	g./l.	10
Crotonic aldehyde diethylene triamine reaction product	ml./l.	2.5

Example 13

NiSO ₄ ·6H ₂ O	g./l.	350
NiCl ₂ ·6H ₂ O	g./l.	45
H ₃ BO ₃	g./l.	45
Ethylene sulfonic acid (sodium salt)	g./l.	1
Sodium naphthalene trisulfonate	g./l.	7
Acrolein dimer tetraethylene pentamine reaction product	ml./l.	3
Sodium lauryl sulfate	g./l.	0.2

Example 14

NiSO ₄ ·6H ₂ O	g./l.	300
NiCl ₂ ·6H ₂ O	g./l.	45
H ₃ BO ₃	g./l.	52
2,7 naphthalene sodium disulfonate	g./l.	4
Allylidene diacetate-tetraethylene pentamine reaction product	ml./l.	1.5

Example 15

NiSO ₄ ·6H ₂ O	g./l.	350
NiCl ₂ ·6H ₂ O	g./l.	45
H ₃ BO ₃	g./l.	45
1,3,6 sodium naphthalene trisulfate	g./l.	8
2 chloroallylidene diacetate-tetraethylene pentamine reaction product	ml./l.	2

The results obtained in accordance with Examples 8 to 15 were excellent in that all of the desirable properties of a nickel coating were obtained. For instance, a nickel deposit of .001" from the bath of Example 9 on a copper sheet having an initial R. M. S. of 23 micro-inches showed a reduction of R. M. S. of 11. The deposit was soft and did not emit any "cry" when bent to 180°. The nickel deposit was active and easily chromium plated without any activating treatment.

There are numerous advantages inherent in the present invention in that baths made in accordance therewith not only have a high tolerance for such metallic impurities as zinc and copper, but have good leveling characteristics, good covering power and the coatings are highly ductile. In addition the coatings have excellent brightness or brilliance.

One authority has mentioned the use of unsaturated aldehydes but he claims their practical usefulness is slight because of their great tendencies to form resins which interfere with the nickel deposition, causing what is customarily termed "skipping."

The reaction products of the polyamines with unsaturated aldehydes, unsaturated esters and the like, as described herein, constitute desirable addition agents to nickel baths provided that such products are acid soluble and provided that the products are used in conjunction with the sulfonates, sulfonamids and sulfonimids as set

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forth herein. These reaction products give a better level than the polyalkylene amines without any adverse effect on the ductility, activity and throwing power of the bath. For instance, in plating a copper panel with .001" nickel containing such reaction products as described in Example 9, a 30% improvement in level results over that obtained with a similarly plated panel from a bath containing a polyalkylene amine, as described in Example 6.

A number of variations in the details of the procedure may be made within the scope of the present invention. For instance, the temperature of operation may be varied and the pH of the bath may be altered to a substantial degree but optimum results are obtained at a temperature range of 130° to 140° F. and a pH of 3.5 to 4.5. The concentration of the salts may be varied, as for example, the nickel sulfate may vary from 100 to 400 g./liter, the nickel chloride from 15 to 100 g./liter and the boric acid from 10 g./liter to saturation. All or a part of the nickel may be present in the bath as a fluoborate or sulfamate.

These and other changes in the details may be made within the spirit of the invention, which is to be broadly construed and to be limited only by the character of the claims appended hereto.

What is claimed is:

1. In an acid nickel plating bath containing nickel sulfate, nickel chloride and boric acid, the improvement which comprises adding to said bath a mixture of a soluble and stable substance consisting of the reaction product of a polyalkylene amine, wherein the alkylene group has from 1 to 6 carbon atoms and 2 to 10 alkylene groups, with a compound taken from the class consisting of (a) compounds having the formula X—R—CHO wherein R represents an unsaturated group taken from the class consisting of alkylene groups having 1 to 6 carbon atoms, phenyl and naphthyl radicals having hydrocarbon substituents having 1 to 2 carbon atoms, and X represents 0 to 3 substituents taken from the class consisting of halogens, amino, H and OH, and (b) compounds comprising unsaturated esters of lower fatty acids wherein said acids have 1 to 6 carbon atoms, together with a sulfonic product of a material taken from the class consisting of benzene, toluene and naphthalene having from 1 to 3 sulfonic groups of the formula —SO₂R wherein R represents a substituent taken from the class consisting of OH, NH, NH₂, H and alkali metal.

2. In an acid nickel plating bath containing a nickel salt taken from the class consisting of nickel sulfate and nickel chloride, and boric acid, the improvement which comprises the addition to said bath of a mixture of a sulfonic product of a material taken from the class consisting of benzene, toluene and naphthalene having 1 to 3 sulfonic groups of the formula —SO₂R wherein R represents a substituent taken from the class consisting of OH, NH, NH₂, H and alkali metal, together with the reaction product of a polyalkylene amine, wherein the polyalkylene group has from 1 to 6 carbon atoms and 2 to 10 alkylene groups, with an unsaturated ester of a lower fatty acid having 1-6 carbon atoms.

3. A bath according to claim 1 containing also a wetting agent taken from the class consisting of tetradecyl, ethyldecyl, lauryl and octyl sulfates, isopropyl naphthalene sulfonate, and diisobutyl sulfosuccinate.

4. A bath according to claim 2 wherein the polyalkylene amine is reacted with vinyl acetate.

5. A bath according to claim 2 wherein the polyalkylene amine is reacted with allylidene diacetate.

References Cited in the file of this patent

UNITED STATES PATENTS

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