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[54] **METHOD AND BATH FOR THE ELECTRODEPOSITION OF NICKEL**

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[58] **Field of Search** ..... 204/49, 43 T, 43 N, 43 P, 204/44; 106/1; 117/130 E

[56] **References Cited**

UNITED STATES PATENTS

3,264,200 8/1966 Clauss et al. 204/49

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[57] **ABSTRACT**

This invention relates to an improvement in the plating of ductile semi-bright nickel from aqueous acidic nickel electroplating solutions, by the addition of three conjunctive ingredients, i.e., an aryl sulfon, an acetylenic alcohol and an olefinic alcohol. The conjunctive use of these three types of compounds produce excellent semi-bright nickel deposits which are ductile, finegrained and which exhibit improved leveling characteristics. Specific compounds which can be utilized are (1) metasulfobenzoic acid or its salts; (2) butynediol or hexyne diol; and (3) butene diol and butenol alcohols. Aldehydes, such as chloral hydrate and formaldehyde, may be added to assist in grain refinement and in reducing the sulfur content of the bath.

4 Claims, No Drawings

METHOD AND BATH FOR THE ELECTRODEPOSITION OF NICKEL

BACKGROUND OF THE INVENTION

The present invention constitutes a specific improvement over the invention defined in U.S. Pat. No. 3,264,200 patented Aug. 2, 1966, and assigned to the Assignee of the present invention.

In U.S. Pat. No. 3,264,200, there is disclosed an improved method of and bath for the electrodeposition of ductile, lowstress nickel plate from an aqueous acidic nickel plating bath containing at least one nickel salt, which nickel salt is selected from the group consisting of nickel sulfate, nickel sulfamate, nickel fluoborate, nickel bromide and nickel chloride. The nickel salts are present in amounts conventional in the art, e.g., up to about 100 grams per liter of $NiCl_2.6H_2O$). The patent discloses the addition to such baths of a specific aryl sulfon compound, namely metasulfobenzoic acid or its derivatives, such as Ni-carboxy benzene sulfonic acid can be utilized.

An aldehyde, such as chloral hydrate or formaldehyde, may be added to the patented bath for grain refinement and to reduce the sulfur content of the bath.

The general purpose of nickel electroplating, of course, is to yield a semi-bright deposit having the desirable characteristics of ductility, uniformly fine grained appearance, and good leveling characteristics. Normally, these objectives are met by the use of coumarin and other additives. However, the deposit from a nickel solution containing coumarin generally deteriorates during use due to the gradual accumulation of the degradation products of the coumarin itself. These degradation products, such as melilotic acid and related compounds, are detrimental to the leveling and ductility of the deposit. As a result, these deposits must be removed by batch carbon treatments at periodic intervals, adding to the expense of the operation and normally resulting in time consuming, shortened scheduled production runs.

The bath of U.S. Pat. No. 3,264,200 was developed to reduce the problems encountered in the accumulation of coumarin degradation products. Generally, a bath containing metasulfobenzoic acid and its derivatives, particularly wherein aldehydes are incorporated, gives a fine lustrous nickel deposit which is ductile and of fine grained appearance. However, the leveling characteristics are substantially reduced. The presence of the aldehydes also appears to detract from the leveling characteristics of the nickel deposit.

If it were possible to develop a process and bath which is free of coumarin, thereby avoiding the accmulation of the coumarin degradation products, yet which yields the excellent leveling characteristics of coumarin-containing baths, an important forward step in the art of nickel electrodeposition could be made.

BRIEF SUMMARY OF THE PRESENT INVENTION

The present invention utilizes a specific combination of compounds which results in nickel deposits which are fine grained, lustrous, and ductile and which have markedly improved leveling characteristics. Although the leveling characteristics of the bath of the present invention are not quite as good as those obtained through the use of coumarin, the present invention does permit continuous use of the nickel solution without the accumulation of those deleterious degradation

products which are developed in coumarin solutions. The deposits from the solutions of the present invention generally contain less than about 0.005% sulfur.

More specifically, the present invention is directed to the addition to baths such as those defined in U.S. Pat. No. 3,264,200 of a combination of three specific compositions or compounds. The nickel-containing and pH-controlling elements of the bath are conventional and may be of any desired type, as defined in the noted patent.

The bath of the present invention may be of the Watts or modified Watts type containing nickel sulfate; of the sulfamate type; of the nickel fluoborate type; of the nickel bromide type; or of the nickel chloride type.

The pH of the bath is controlled by the use of boric acid (H_3BO_3); and an aldehyde, such as formaldehyde and/or chloral hydrate may be added, as above explained.

The specific addition agents of the present invention have a conjunctive affect and are used in combination. Specifically, these three ingredients include:

1. An aryl sulfon, specifically metsulfobenzoic acid or its nickel salts such as Ni-carboxy benzene sulfonic acid. This ingredient is present in an amount ranging from about 0.1 to about 10 grams per liter of the bath.
2. An alkyne diol, specifically butyne diol ($HOH_2CC \vdots CCH_2OH$) or 3-Hexyne 2, 5 diol $CH_3\ CH(OH)C \vdots C—CH(OH)\ CH_3$ being present in an amount ranging from about 0.05 to about 0.5 grams per liter of the bath; and
3. A butene alcohol, specifically butene diol ($HOCH_2CH{:}CHCH_2OH$) or butenol ($CH_3CH{:}CHCH_2OH$) or isomers of butenol, i.e. either 3 butene-1-ol $H_2C{=}CHCH_2CH_2OH$ or 3 butene-2-ol-$H_2C{=}CHCH(OH)CH_3$, this ingredient also being present in an amount ranging from about 0.05 to about 0.5 grams per liter of the bath.

It has been found that these three ingredients, used in conjunction with one another, exert a synergistic affect upon the bath in which they are incorporated so that the bath yields a nickel deposit which is semi-bright, ductile, of low-stress and of remarkably good leveling characteristics, the deposit generally containing a maximum sulfur content of about 0.005 percent, and the bath remaining free of those decomposition products, commonly encountered in the use of coumarin as a bath ingredient.

It is, therefore, an important object of the present invention to provide a bath for the electrodeposition of nickel plate from an aqueous acidic nickel plating bath containing dissolved therein an aryl sulfon, an alkyne diol and a short chain alkene alcohol.

Another important object of the present invention is the provision of a method of electrodeposition of ductile, low-stress nickel plate having good leveling characteristics and including the step of electrodepositing semi-bright ductile nickel from an aqueous acidic nickel plating bath containing metasulfobenzoic acid or its salts, and a combination of at least one alkyne diol and at least one alkene alcohol containing four carbon atoms.

It is a further important object of the present invention to provide an aqueous, nickel salt containing bath for the electrodeposition of semi-bright nickel plate

and having incorporated therein from about 0.1 to about 10 grams per liter of metasulfobenzoic acid or its nickel salts, from about 0.05 to about 0.5 grams per liter of an alkyne diol selected from the group consisting of butyne diol and hexyne diol, and from about 0.05 to about 0.5 grams per liter of an alkene alcohol selected from the group consisting of butene diol, butenol and isomeric forms of butenol.

Another object of the present invention is the provision of a method of electrodepositing ductile low-stress nickel plate from an aqueous acidic nickel plating bath containing at least one nickel salt and metasulfobenzoic acid or its salts, residing in the improvement of incorporating in the bath a mixture of an alkene diol selected from the group consisting of butyne diol and hexyne diol, and an alkene alcohol selected from the group consisting of butene diol, butenol, and isomeric forms of butenol.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

As above explained, the present invention constitutes an improvement upon the invention disclosed and claimed in U.S. Pat. No. 3,264,200, assigned to the assignee of the present invention. This improvement resides in the discovery of the synergistic effect which can be obtained from the incorporation of a specific mixture of specific unsaturated alcohols into the aqueous acidic nickel plating baths proposed in said earlier patent.

More specifically, the earlier patent proposes the incorporation of metasulfobenzoic acid or the nickel salt of the compound into a bath for the electrodeposition of ductile, semibright nickel plate. To reduce the internal tensile stress of nickel deposits, particularly those deposits obtained from Watts type and sulfamate type acidic nickel electroplating baths, the mentioned patent discloses the incorporation of from 0.1 to about 10 grams per liter of metasulfobenzoic acid.

Various other additions are proposed in the patent, particularly the addition of formaldehyde or chloral hydrate to the bath to assist in giving uniform grain refinement and low sulfur content. Additional additives are also disclosed, including the suggestion that other unsaturated compounds such as allyl alcohol and butyne diol may be added. It has now been determined that the addition of a combination of allyl alcohol and butyne diol is not completely effective to produce the desired and improved leveling characteristics of the present invention. Rather, the present invention is more particularly concerned with the conjunctive use of a combination of three specific compounds, namely the metasulfobenzoic acid which is the primary additive of U.S. Pat. No. 3,364,200, and a mixture of an acetylenic alcohol and an alkene alcohol containing four carbon atoms.

As is explained in U.S. Pat. No. 3,264,200, the metasulfobenzoic acid is usually neutralized with nickel hydroxide or nickel carbonate and is added to the bath as a nickel salt. It, however, can be added as the free acid, or as sodium or magnesium salt. If too high a concentration of the free acid is added to the nickel bath at one time, the pH of the bath will be substantially reduced. Therefore, the nickel salt of the acid is the preferred form, where additions of concentrations greater than about one gram per liter are added at one time. It should be understood that when metasulfobenzoic acid is referred to herein, this expression includes the nickel salt of the compound. Even where the free acid is added to the nickel bath, the metasulfobenzoic acid is generally in the form of the nickel salt, or the ionized nickel salt.

The acetylenic diols which are added are preferably in the simple unreacted diol form, since it has been found that the derivatives thereof, such as the epichlorohydrin adduct of butyne diol are not very effective. The two preferred alkyne diols are butyne 1, 4 diol, $HOCH_2CC \vdots CCH_2OH$ or 3-hexyne 2, 5 diol $CH_3CH(OH)C \vdots C—CH(OH)CH_3$. This ingredient is added in an amount ranging from about 0.05 to about 0.5 grams per liter of the solution. Short chained alkene alcohols are used in conjunction with the alkyne diols. Specific examples include butene diol, ($HOCH_2CH{:}CHCH_2OH$), butenol, ($CH_3CH{:}CHCH_2OH$) or the isomeric forms of butenol including 3-butene-2ol, $CH_3CHOHCH{:}CH_2$, or 3 butene-1-ol, ($H_2C{=}CHCH_2CH_2OH$). The alkene alcohols uniformly contain four carbon atoms and, as above noted, are effective whereas other specific unsaturated alcohols do not work in the combination, for example, allyl alcohol ($CH_2{:}CHCH_2OH$) is ineffective.

It will be noted that the concentration of the alkyne alcohol and the concentration of the alkene alcohol is defined as falling within the same broad range. It has been found that it is not necessary to use equal amounts of the two compounds, nor is the utilization of a specific combination of compounds within a defined group essential.

If desired, any suitable type of semi-bright nickel plating bath can be utilized, and the herein disclosed, three component combination is effective in sulfamate, fluoborate, bromide, and low chloride (less than 100 grams per liter $NiCl_2.6H_2O$) baths.

The following specific examples are submitted:

EXAMPLE I

	Concentration
$NiSO_4.6H_2O$	200–300 g/l
$NiCl_2.6H_2O$	15–50 g/l
H_3BO_3	30–50 g/l
Meta sulfobenzoic acid (Na salt)	0.2– 5 g/l
Chloral hydrate	0.03–0.2 g/l
Formaldehyde	0.01–0.1 g/l
Butyne diol	0.05–0.5 g/l
Butene diol	0.05–0.5 g/l

EXAMPLE II

$NiSO_4.6H_2O$	200–300	g/l
$NiCl_2.6H_2O$	15–50	g/l
H_3BO_3	30–50	g/l
Ni-carboxy benzene sulfonic acid	1–2	g/l
Butyne diol	50–150	mg/l
Butene diol	100–300	mg/l

EXAMPLE III

$Ni(SO_{Ni\ (STR)}NH_2)_2$ (nickel sulfamate)	250–500	g/l
$NiCl_2H_2O$	0–30	g/l
H_3BO_3	30–50	g/l
Butyne diol	75	mg/l
Butene diol	150	mg/l
Meta sulfobenzoic acid (Na salt)	1.5	g/l

EXAMPLE IV

	Concentration
$NiSO_4.6H_2O$	200–300 g/l
$NiCl_2.6H_2O$	30–60 g/l
H_3BO_3	30–50 g/l
Hexyne diol	150 mg/l
Butene diol	150 mg/l
Meta sulfobenzoic acid (Na salt)	2 g/l

The substitution of butenol, 3-butene-2ol, or 3-butene-1-ol for butene diol in Example II gave equivalent results.

In the above cited Examples, the preferred pH range is from about 2.8 to about 4.5, and the preferred bath temperature may range from 130° to 140°F. The cathode current density may be an average of 40 to 60 amps per square foot with air agitation.

In each instance, the Examples yielded lustrous, ductile, very low-stressed semi-bright nickel deposits which contain less than about 0.005% sulfur, and which have remarkedly good leveling characteristics. In each instance, the deposit which was obtained had improved leveling characteristics over the corresponding baths of U.S. Pat. No. 3,264,200.

What is claimed is:

1. A bath for the electrodeposition of ductile, low-stress nickel plate from an aqueous acidic nickel plating bath containing at least one nickel salt selected from the group consisting of nickel sulfate, nickel sulfamate, nickel fluoborate, nickel bromide and nickel chloride, and containing dissolved therein from about 0.1 to about 10 grams per liter of metsulfobenzoic acid, from about 0.05 to about 0.5 grams per liter of an alkyne diol selected from the group consisting of butyne diol and hexyne diol, and from about 0.05 to about 0.5 grams per liter of an alkene alcohol selected from the group consisting of butene diol, butenol and isomers of butenol.

2. In a bath for the electrodeposition of ductile low-stress nickel plate from an aqueous acidic nickel plating bath, said bath containing at least one nickel salt selected from the group consisting of nickel sulfate, nickel sulfamate, nickel fluoborate, nickel bromide and nickel chloride and containing dissolved therein from about 0.1 to about 10 grams per liter of metasulfobenzoic acid, the improvement of incorporating into said bath a combination of from about 0.05 to about 0.5 grams per liter of an alkyne diol and from about 0.05 to about 0.5 grams per liter of a butene alcohol.

3. A method for the electrodeposition of ductle low-stress nickel plate exhibiting improved leveling characteristics comprising the step of electrodepositing semi-bright ductile nickel from an aqueous acidic nickel plating bath containing at least one nickel salt selected from the group consisting of nickel sulfate, nickel sulfamate, nickel fluoborate, nickel bromide and nickel chloride and having dissolved therein from about 0.1 to about 10 grams per liter of metasulfobenzoic acid, from about 0.05 to about 0.5 grams per liter of an alkyne diol selected from the group consisting of butyne diol and hexyne diol, and from about 0.05 to about 0.5 grams per liter of an alkene alcohol selected from the group consisting of butyne diol, butenol and isomers of butenol.

4. In a method for the electrodeposition of ductile semi-bright nickel plate of low stress wherein semi-bright ductile nickel is electrodeposited from an aqueous acidic nickel plating bath containing at least one nickel salt selected from the group consisting of nickel sulfate, nickel sulfamate, nickel fluoborate, nickel bromide and nickel chloride and containing dissolved therein from about 0.1 to about 10 grams per liter of metasulfobenzoic acid, the improvement yielding improved leveling characteristics of incorporating into the bath from 0.05 to 0.5 grams per liter of an alkyne diol, and from 0.05 to 0.05 grams per liter of a butene alcohol.

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