

[54] **STABILIZED, CHEMICAL NICKEL
PLATING BATH**

117/160 R

[72] Inventors: **Wolfgang Clauss; Dieter Menz**, both of
Berlin, Germany
[73] Assignee: **Schering AG**, Berlin, Germany
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May 22, 1969 Germany.....P 19 26 100.8
[52] **U.S. Cl.****106/1, 117/130 E, 117/130 B,**
117/160 R
[51] **Int. Cl.****C23c 3/02**
[58] **Field of Search****106/1; 117/130, 130 E, 130 B,**

[56] **References Cited**

UNITED STATES PATENTS			
2,762,723	9/1956	Talmey et al.	117/130
2,929,742	3/1960	De Minjer et al.	106/1 X
3,234,031	2/1966	Zirngiebl et al.	106/1
3,492,135	1/1970	Clauss.....	106/1

Primary Examiner—Lorenzo B. Hayes
Attorney—Joseph F. Padlon

[57] **ABSTRACT**
A stabilized chemical bath containing a solution of a nickel salt and selenium compounds as stabilizers.
5 Claims, No Drawings

STABILIZED, CHEMICAL NICKEL PLATING BATH

This invention relates to a stabilized reductive nickel bath containing at least one selenium compound as stabilizers.

For the application of metal layers on a variety of base materials, technical processes are being given more and more attention in which the metals are reductively deposited from baths without any external current source. Thus the deposition of nickel by reduction has in recent years found increasing importance, since reductive nickel precipitates are well suited as corrosion protection means or for the improvement of the surface properties of various materials, and also for the production of conductive layers on plastic plates or substrates.

These baths, which contain in solution a nickel salt, a reducing agent, complex formers and other additions, deposit nickel on the base metal or substrate upon contact of the bath with a catalytically active metal surface.

Not only catalytically active metals, but also many inactive metals and even non-conductors after activation, such as by palladium seeds, can be nickel-plated in this manner.

A disadvantage of the bath compositions or reductive nickel baths that have heretofore been known is their low stability, so that they are often discarded after the metal has been once spent.

Additives for the stabilization of these baths are known. Thus there are proposed in German Pat. No. 1,123,174, for this purpose, sulfur compounds, or if traces of sulfur are already present in the solution, compounds which are able to form sulfur compounds in any form with the sulfur present in the solution. These additives, however, may be added only in small quantities, since higher concentrations may greatly reduce the rate of deposition of the metal or even prevent the smooth deposition. Only in a very narrow concentration range, are xanthogenates and lead ions of the proposed stabilizers said to bring about, besides the stabilization, a slight increase of the rate of deposition, which however is not satisfactory for use in the art.

Also, it is known that in U.S. Pat. No. 2,929,742, selenious acid as an addition to reductive nickel baths is described, with which the rate of deposition of the nickel can be increased. These baths have the disadvantage, however, of decomposing more rapidly than baths which do not contain this addition.

The use of compounds characterized in the present application for the stabilization of reductive copper baths is also already known. French Pat. No. 1,545,227. However, because of the different behavior of these baths, a suggestion for the use of these compounds as stabilizers in reductive nickel baths could not be derived therefrom.

It has now been found that a reductive, aqueous, nickel bath containing a solution of nickel salt, complex formers, buffer substances, reducing agents and possibly wetting and brightening agents, bases or acids, characterized by a content of one or more selenium-containing compounds, in which the selenium has the degree of oxidation of "minus one" or "minus two," possesses a very good stability, which is greater than that of the known baths.

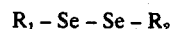
Other essential advantages of this bath consist in that the rate of deposition is very high and that regeneration with suitable concentrates or individual constituents can be effected for an almost unlimited length of time. Due to its good stability, this bath works without any special maintenance and need not be renewed after use.

Moreover, according to the invention, nickel layers of constant thickness can be deposited from the bath. These coatings

are very decorative and distinguish themselves by a bright metallic luster.

By the term, "degree of oxidation of the selenium" in the characterized selenium compounds is understood the so-called oxidation number or change value, i.e., the charge which an atom would possess in a molecule if the latter were composed only of ions.

Suitable selenium compounds with the degree of oxidation "minus one" are, for example, compounds of the general formula



wherein

R_1 and R_2 are identical or different and signify a univalent metal equivalent or an organic radical.

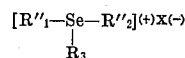
Suitable selenium compounds with the degree of oxidation "minus two" are, for example, compounds of the general formula



wherein

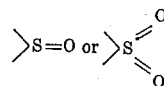
R'_1 and R'_2 are identical or different and have the same meaning as R_1 and R_2 , R'_1 representing in addition hydrogen, the radical $-CN$ or the radical $-SO_3Me$, where Me is a univalent metal equivalent.

Other suitable selenium compounds with the degree of oxidation "minus two" are, for example, the selenonium compounds of the general formula



wherein R''_1 , R''_2 and R_3 are identical or different and designate an organic radical and X designates an acid radical.

As univalent metal equivalents there enter into consideration, for example: Na , K , $Ca/2$ or $Al/3$, etc.; as organic radicals there may be mentioned, for example: aliphatic, cycloaliphatic, aromatic, and araliphatic radicals, which may possibly also be substituted and/or interrupted by one or more heteroatoms, such as oxygen or nitrogen and/or one or more heteroatom groups, such as



as well as the acryl radical and the CN group.

Substituents for the mentioned organic radicals are, for example, halogen atoms such as chlorine, bromine, etc., hydroxyl radicals, alkyl radicals, such as methyl and ethyl, etc., aryloxy radicals, such as phenoxy, etc., alkoxy radicals, such as methoxy and ethoxy etc., acyloxy radicals, such as acetoxyl etc., the nitro and cyano group, the carboxyl and the sulfonic acid group in free or functionally modified form; e.g., as esters, or as salts, heterocyclic radicals, such as tetrahydrofuryl, sulfolan, etc., as well as the radicals



or



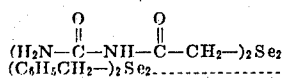
For the selenonium compounds there may be used the usual acid radicals of the onium compounds, e.g., those of the inorganic acids, advantageously of the halogen hydracids.

Compounds to be used according to the invention are, for example, the following (the compounds marked + can be used only in alkaline or neutral but not in acid baths):

A. Selenium compounds with the degree of oxidation "minus one":

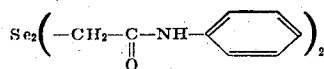
$K_2Se_2^{+}$	Potassiumdiselenide.
$(CH_3-CH_2-CH_2)_2Se_2$	Dipropyl-diselenide.
$(CH_3-CH_2-CH_2-CH_2)_2Se_2$	Di-n-butyl-diselenide.
$(CH_3-(CH_2)_4)_2Se_2$	Di-n-amyl-diselenide.
$(CH_3-(CH_2)_5)_2Se_2$	Di-n-hexyl-diselenide.
$(CH_3-(CH_2)_6)_2Se_2$	Di-n-heptyl-diselenide.
OH	
$(HOCH_2-CH-CH_2)_2Se_2$	Di-(2,3-dihydroxypropyl)-diselenide.
$(KO_3S-(CH_2)_3)_2Se_2$	Di-(potassiumsulfopropyl)-diselenide.
$(NaO_3S-(CH_2)_4)_2Se_2$	Di-(sodiumsulfobutyl)-diselenide.
CH_3	
$(NaO_3S-CH-(CH_2)_2)_2Se_2$	Di-(sodiumsulfo-methyl-propyl)-diselenide.
$(NaOOC-CH_2)_2Se_2$	Bis-(sodiumcarboxymethyl)-diselenide.

$(\text{KOOC}-\text{CH}_2-\text{CH}_2-)_2\text{Se}_2$	Bis-(potassiumcarboxyethyl)-diselenide.
$(\text{KOOC}-(\text{CH}_2)_5-)_2\text{Se}_2$	Bis-(potassiumcarboxypropyl)-diselenide.
$(\text{KOOC}-(\text{CH}_2)_{10}-)_2\text{Se}_2$	Bis-(potassiumcarboxydecyl)-diselenide.
$\text{C}_6\text{H}_5-\text{Se}-\text{Se}-\text{C}_6\text{H}_5$	Diphenyldiselenide.
$(p-\text{CH}_3\text{C}_6\text{H}_4-)_2\text{Se}_2$	Di-p-tolyl-diselenide.
$(p-\text{CH}_3\text{OC}_6\text{H}_4-)_2\text{Se}_2$	Di-(p-methoxyphenyl)-diselenide.
$(p-\text{NO}_2-\text{C}_6\text{H}_4-)_2\text{Se}_2$	Di-(p-nitrophenyl)-diselenide.
$(o-\text{CH}_3\text{CO}-\text{C}_6\text{H}_4-)_2\text{Se}_2$	Bis-(o-acetylphenyl)-diselenide.
$(2-\text{C}_6\text{H}_5-\text{C}_6\text{H}_4-)_2\text{Se}_2$	Di-2,2'-biphenyl-yl-diselenide.
$(p-\text{KO}_3\text{S}-\text{C}_6\text{H}_4-)_2\text{Se}_2$	Bis-(p-potassiumsulfofophenyl)-diselenide.
$(\text{KO}_3\text{S}-(\text{CH}_2)_2-)_2\text{Se}_2$	Di-(potassiumsulfoethyl)-diselenide.
$(p-\text{Cl}-\text{C}_6\text{H}_4-)_2\text{Se}_2$	Bis-(p-chlorophenyl)-diselenide.
$(p-\text{HOOC}-\text{C}_6\text{H}_4-)_2\text{Se}_2$	Bis-(p-carboxyphenyl)-diselenide.

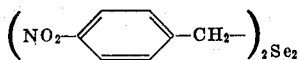


Diselendiacyetyl-urea.

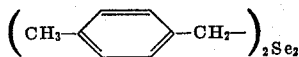
Dibensyldiselenide.



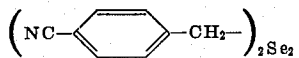
Di-(N-phenyl-carbamoylmethyl)-diselenide.



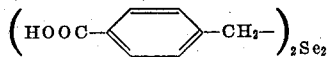
Bis-(p-nitrobenzyl)-diselenide.



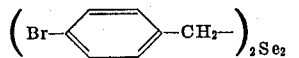
Bis-(p-methylbenzyl)-diselenide.



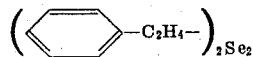
Bis-(p-cyan-benzyl)-diselenide.



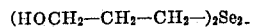
Bis-(p-carboxybenzyl)-diselenide.



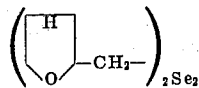
Bis-(p-brombenzyl)-diselenide.



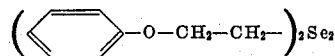
Bis-(β-phenylethyl)-diselenide.



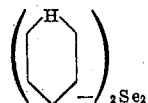
Bis-(3-hydroxypropyl)-diselenide.



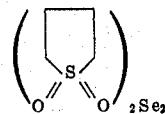
Bis-(α-tetrahydrofurylmethyl)-diselenide.



Bis-(β-phenoxyethyl)-diselenide.



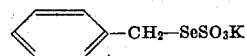
Bis-(cyclohexyl)-diselenide.



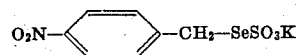
Di-(sulfolan)-diselenide.

B. Selenium compounds with the degree of oxidation "minus two":

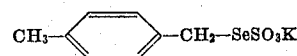
$\text{K}-\text{SeSO}_3\text{K}^+$ Potassiumselenosulfate.



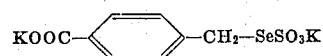
Potassium-benzylselenosulfate.



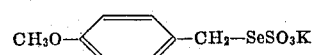
Potassium-p-nitrobenzyl-selenosulfate.



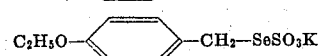
Potassium-(p-methylbenzyl)-selenosulfate.



Potassium-(p-potassium-carboxy-benzyl)-selenosulfate.



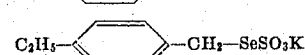
Potassium-(p-methoxybenzyl)-selenosulfate.



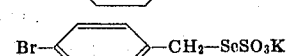
Potassium-(p-ethoxybenzyl)-selenosulfate.



Potassium-(p-cyanobenzyl)-selenosulfate.



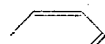
Potassium-(p-ethyl-benzyl)-selenosulfate.



Potassium-(p-brom-benzyl)-selenosulfate.

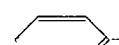
$C_2H_5SeSO_3K$	Potassium-ethylselenosulfate.
$C_4H_9SeSO_3K$	Potassium-butylselenosulfate.
$C_8H_{17}SeSO_3K$	Potassium-octylselenosulfate.
$C_{12}H_{25}SeSO_3K$	Potassium-dodecylselenosulfate.
$HOCH_2-CH(OH)-CH_2-SeSO_3K$	Potassium-(1,3-dihydroxypropyl)-selenosulfate.

$HOCH_2-CH_2-SeSO_3K$	Potassium-(hydroxyethyl)-selenosulfate.
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 -OCH ₂ -CH ₂ -SeSO ₃ K	Potassium-(phenoxyethyl)-selenosulfate.
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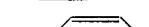
 -CH ₂ -SeSO ₃ K	Potassium-(tetrahydro-furfuryl)-selenosulfate.
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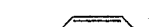
 -CH ₂ -CH ₂ -SeSO ₃ K	Potassium-(phenylethyl)-selenosulfate.
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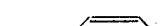
 -CH ₂ -CH ₂ -CH ₂ -SeSO ₃ K	Potassium-(phenylpropyl)-selenosulfate.
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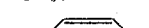
$HOCH_2-CH_2-CH_2-SeSO_3K$	Potassium-(3-hydroxypropyl)-selenosulfate.
$KOOC(CH_2)_2SeSO_3K$	Potassium-(potassium- ω -carboxyethyl)-selenosulfate.
$KOOC(CH_2)_3SeSO_3K$	Potassium-(potassium- ω -carboxybutyl)-selenosulfate.
$KOOC(CH_2)_4SeSO_3K$	Potassium-(potassium- ω -carboxypentyl)-selenosulfate.
$KOOC(CH_2)_5SeSO_3K$	Potassium-(potassium- ω -carboxyhexyl)-selenosulfate.
$KO_3S-CH_2-CH_2-SeSO_3K$	Potassium-(potassium- ω -sulfoethyl)-selenosulfate.
$KO_3S-(CH_2)_3-SeSO_3K$	Potassium-(potassium- ω -sulfopropyl)-selenosulfate.
K_2Se^{+}	Potassium selenide.

 -Se-CH ₂ -COOH	Phenylseleno-acetic acid.
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 -Se-CH ₂ -COOH	o-, m- or p-Nitrophenylselenoacetic acid.
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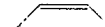
 -Se-CH ₂ -COOH	o-, m- or p-Methylphenylselenoacetic acid.
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 -Se-CH ₂ -COOH	o-, m- or p-Methoxyphenylselenoacetic acid.
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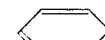
 -Se-CH ₂ -COOH	o-, m- or p-Chlorophenylselenoacetic acid.
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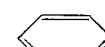
 -Se-CH ₂ -COOH	3,4-dimethylphenylseleno-acetic acid.
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 -Se-CH ₂ -COOH	2,4-dimethylphenylseleno-acetic acid.
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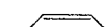
 -CH ₂ -Se-CH ₂ -COOH	Benzylseleno-acetic acid.
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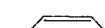
$C_2H_5-Se-CH_2COOH$	Ethylseleno-acetic acid.
$HOOCCH_2-Se-CH_2COOH$	Selendiacetic acid.
$HOOC(CH_2)_2-Se-(CH_2)_2COOH$	Selendipropionic acid.
$HOOC(CH_2)_3-Se-(CH_2)_3COOH$	Selendibutyric acid.

 -CH ₂ -Se-(CH ₂) ₃ COOH	Benzylselenobutyric acid.
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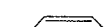
 -CH ₂ -Se-(CH ₂) ₁₀ COOH	Benzylselenundecanic acid.
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$C_2H_5-Se-CH_2-CH_2-CH_2SO_3Na$	Sodium ethylselenopropylsulfonate.
$C_3H_7-Se-CH_2-CH_2-CH_2SO_3K$	Potassium propylselenopropylsulfonate.
$(NaO_3S-CH_2-CH_2-CH_2)_2Se$	Bis-(Na-sulfopropyl)-selenide.

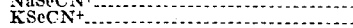
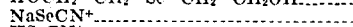
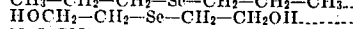
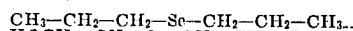
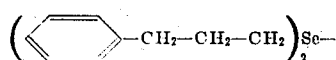
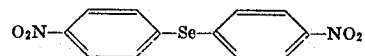
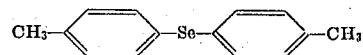
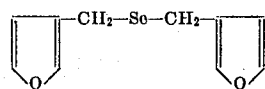
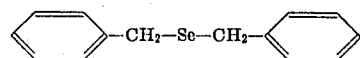
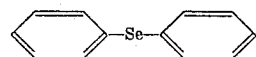
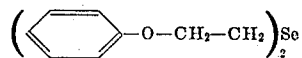
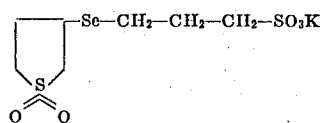
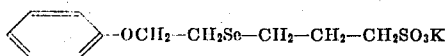
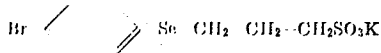
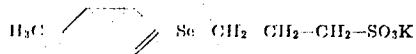
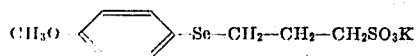
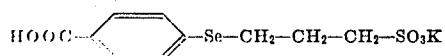
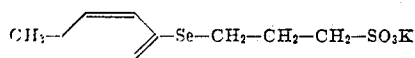
 -Se-CH ₂ -CH ₂ -CH ₂ -SO ₃ Na	Sodium phenylselenopropylsulfonate.
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 -CH ₂ -Se-CH ₂ -CH ₂ -CH ₂ -SO ₃ Na	Sodium benzylselenopropylsulfonate.
--	-------------------------------------

$C_2H_5-Se-CH_2-CH_2-CH_2SO_3K$	Potassium ethylselenopropylsulfonate.
$C_3H_7-Se-CH_2-CH_2-CH_2SO_3K$	Potassium propylselenopropylsulfonate.

 -O-CH ₂ -CH ₂ -Se-CH ₂ -CH ₂ -CH ₂ -SO ₃ K	Potassium phenoxyethylselenopropylsulfonate.
--	--

$HOOC-CH_2-CH_2-Se-CH_2-CH_2-CH_2SO_3K$	Potassium carboxyethylselenopropylsulfonate.
---	--



Potassium p-tolylselenopropylsulfonate.

Potassium carboxyphenylselenopropylsulfonate.

Potassium p-methoxyphenylselenopropylsulfonate.

Potassium p-methylphenylselenopropylsulfonate.

Potassium p-bromphenylselenopropylsulfonate.

Potassium phenoxyethylselenopropylsulfonate.

Potassium sulfolaniselenopropylsulfonate.

Bis-(phenoxyethyl)-selenide.

Diphenylselenide.

Dibenzylselenide.

Difurfuryselenide.

Bis-(p-methylphenyl)-selenide.

Bis-(p-nitrophenyl)-selenide.

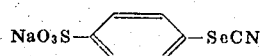
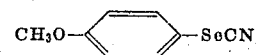
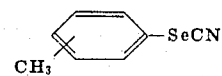
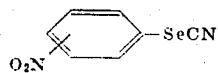
Bis-(3-phenylpropyl)-selenide.

Dipropyl-selenide.

Bis-(hydroxyethyl)-selenide.

Sodiumselenocyanate.

Potassiumselenocyanate.



o-, p- or m-Nitrophenylselenocyanate.

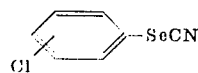
o, m- or p-Methylphenylselenocyanate.

p-Methoxyphenylselenocyanate.

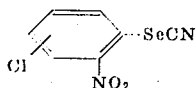
p-Ethylphenylselenocyanate.

p-Ethoxyphenylselenocyanate.

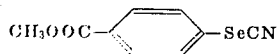
Sodium 4-cyanseleno-phenylsulfonate.



o-, m- or p-Chlorophenylselenocyanate.



2-nitro-4-chlorophenylselenocyanate.



p-Carbomethoxyphenylselenocyanate.



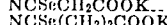
Ethylselenocyanate.



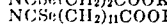
Butylselenocyanate.



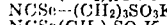
Decylselenocyanate.



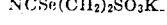
Potassium selencyanoacetate.



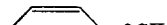
Potassium selencyanopropionic-acetate.



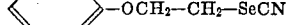
Potassium selencyanundecanic-acetate.



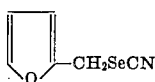
Potassium selencyanpropylsulfonic-acetate.



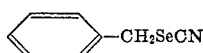
Potassium selencyanethylsulfonic-acetate.



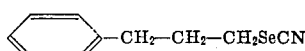
Phenoxyethylselenocyanate.



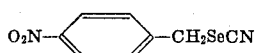
Furfurylselenocyanate.



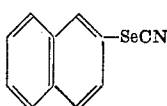
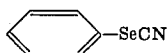
Benzylselenocyanate.



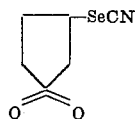
Phenylpropylselenocyanate.



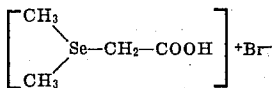
p-Nitrophenylselenocyanate.

 β -Naphthylselenocyanate.

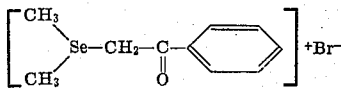
Phenylselenocyanate.



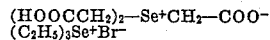
Sulfolanselenocyanate.



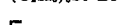
Carboxymethyl-dimethyl-selenonium-bromide.



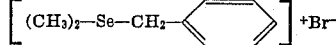
Phenacyl-dimethyl-selenonium-bromide.



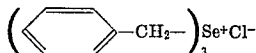
Dimethyl-selenotindicarboxylic acid.



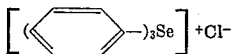
Triethylselenoniumbromide.



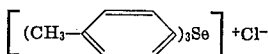
Dimethylbenzylselenonium-bromide.



Tribenzylselenoniumchloride.



Triphenylselenoniumchloride.



Tri-p-tolylselenoniumchloride.

Those compounds having a water-solubilizing group are particularly suitable, as they are easy to proportion and are able to produce prolonged stabilization. Reductive nickel baths containing one or more of these compounds are extremely stable for a relatively long period.

Effective stabilizers according to the present invention with the degree of oxidation "minus two" are also those selenium compounds which may be formed, for example, by hydrolysis of the selenocyanates or selenosulfates, i.e., the so-called selenols of the general formula



with R_2 having the meaning mentioned above, or their metal salts.

The compounds named are known and can be prepared by methods known in the art, such as described for the various compound classes in "Methods of Organic Chemistry," Houben-Weyl, volume 9 (1955), pages 937-947 (Preparation of selenocyanic acids), pages 972-1,002 (Preparation of selenides), page 1,034 (Preparation of selenonium compounds), pages 1,086-1,099 (Preparation of diselenides), pages 1,089-1,090 (Preparation of selenosulfates).

The additives for stabilizing reductive nickel baths or ordinary composition may be used in concentrations of about 0.0001 g/liter to 0.3 g/liter, preferably from 0.001 to 0.010 g/liter of bath liquid, the compounds being added either alone or mixed with one another. The nickel baths stabilized accord-

ing to the present invention contain in addition the usual constituents i.e., nickel salts, reducing agents, buffer substances, complex formers as well as wetting and brightening agents, etc.

The pH value of the baths stabilized according to the invention may be in the acid, neutral, or alkaline range.

The acid baths work preferably in a pH range of 5 to 6, the alkaline in a preferred pH range of 8 to 9.5. Depending on the reducing agent used, lower or higher pH values may be selected.

The adjustment of the desired pH value is effected, if desired, by the addition of suitable bases or acids, such as soda lye or hydrochloric acid. To maintain the adjusted pH value, common buffer substances, e.g., $\text{Na}_2\text{B}_4\text{O}_7$, are also added to the bath.

For the reductive deposition of the nickel, reducing agents are used, such as, alkali metal hypophosphite, such as sodium hypophosphite in the acid and alkaline range, or hydrazine, the salts thereof, borazanes or alkali borohydride, preferably sodium borohydride, in the alkaline range. The concentration of the reducing agent used is about 0.01 to 0.5 mol/liter.

As nickel salts, nickel chloride, nickel sulfate and nickel acetate, etc., are used in concentrations of about 0.01 to 0.5 mol/liter.

In alkaline medium, nickel salts can, as is known, be maintained in solution only by complex formers. For this there enter into consideration, for example, lactic acid, glycolol, sodium acetate, trisodium citrate and triethanolamine, etc. Depending on whether 1:1 or 1:2 complexes are formed, suitable concentrations for this are 0.01 to 0.5 mol/liter respectively 0.02 mol/liter to 1.0 mol/liter. Higher concentrations are readily possible, the maximum concentration being the effect of the solubility of the complex former.

According to another embodiment of the invention, the bath may additionally contain salts of alloy metals, such as water-soluble salts of cobalt. Also, such a bath distinguishes itself by the described advantageous properties and can be used for the reductive deposition of nickel alloys. With the nickel baths stabilized according to the invention, it is possible to nickel-plate objects of metals, plastics or other materials in a well known manner.

For this purpose, the materials to be nickel-plated are introduced into the designated baths. The deposition is carried out at a bath temperature of about 20° to 95° C until the desired layer thickness is obtained. For the nickel-plating of plastics one selects, advantageously, temperatures below 65° C. To obtain uniform nickel layers on the materials to be nickel-plated, it is advisable to agitate the bath vigorously.

Non-conductive materials, such as, plastic parts, require pretreatment of their surfaces. This is done in a manner known in itself, such as by chemical roughening with a heated chromic acid-containing sulfuric acid and chemical activation with a tin-II chloride and a palladium-II chloride solution or with a modified palladium solution.

A condition for the stability of the baths is, of course, the absence of metals in whose presence the precipitation of the desired nickel layer occurs. For the bottling and storage of the baths, therefore, vessels of plastics are suitable, such as of polyvinyl chloride, polyethylene or polypropylene, or vessels lined with these plastics.

Not until the solutions are brought into contact with metals or metal seeds does the desired deposition of the nickel layers on the metal surface or on the properly prepared surfaces of otherwise non-conductive materials begin.

The following illustrative examples describe some of the nickel baths stabilized according to the invention.

EXAMPLE 1

0.1 mol/liter	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
0.25 mol/liter	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
0.25 Mol/liter	trisodium citrate
0.1 mol/liter	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
2 mg/liter	di-(butyl)-diselenide
pH: 5.0	

EXAMPLE 2

0.1 mol/liter	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
0.25 mol/liter	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
0.25 mol/liter	trisodium citrate
0.1 mol/liter	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
4 mg/liter	bis-(4-nitrobenzyl)-diselenide
pH: 5.5	

EXAMPLE 3

0.130 mol/liter	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
0.10 mol/liter	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
0.30 mol/liter	trisodium citrate
0.90 mol/liter	NH_4Cl
3 mg/liter	dibenzyl-diselenide
pH: 9.0	

EXAMPLE 4

0.1 mol/liter	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
0.25 mol/liter	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
0.20 mol/liter	succinic acid
0.1 mol/liter	$\text{Na}_2\text{B}_4\text{O}_7$
4mg/liter	benzylseleno-acetic acid
pH: 5.0	

EXAMPLE 5

0.1 mol/liter	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
0.15 mol/liter	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
0.25 mol/liter	succinic acid
1 mg/liter	diseleno-dipropionic acid
pH: 5.5	

EXAMPLE 6

0.1 mol/liter	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
0.15 mol/liter	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
0.05 mol/liter	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
4 mg/liter	diseleno-diacetic acid
pH: 5.5	

EXAMPLE 7

0.1 mol/liter	$\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$
0.25 mol/liter	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
0.3 mol/liter	sodium acetate
0.1 mol/liter	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
2mg/liter	dibenzyl-selenide
pH: 5.5	

EXAMPLE 8

0.1 mol/liter	$\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$
0.1 mol/liter	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
0.35 mol/liter	trisodium citrate
1.00 mol/liter	NH_4Cl
5 mg/liter	potassium 4-nitrobenzyl-seleno-sulfate
pH: 8.5	

EXAMPLE 9

0.1 mol/liter	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
0.15 mol/liter	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
0.25 mol/liter	trisodium acetate
0.5 mol/liter	NH_4Cl
2mg/liter	potassium benzylseleno-sulfate
pH: 9.0	

EXAMPLE 10

0.1 mol/liter	NiCl ₂ ·6 H ₂ O
0.20 mol/liter	NaH ₂ PO ₄ ·H ₂ O
0.25 mol/liter	succinic acid
0.05 mol/liter	Na ₂ B ₄ O ₇
0.5 mg/liter	phenylacetyl-phenyl-selenide
pH: 5.5	

EXAMPLE 11

0.05 mol/liter	NiSO ₄ ·7 H ₂ O
0.2 mol/liter	Na ₂ P ₂ O ₇ ·10 H ₂ O
0.6 mol/liter	N ₂ H ₄
0.2 mol/liter	K ₂ HPO ₄
0.2 mg/liter	phenylacetyl-benzyl selenide
pH: 12.0	

EXAMPLE 12

0.05 mol/liter	NiSO ₄ ·7 H ₂ O
0.3 mol/liter	Na ₂ P ₂ O ₇ ·10 H ₂ O
0.4 mol/liter	N ₂ H ₄
0.4 mol/liter	K ₂ HPO ₄
15 mg/liter	bis-(-potassium sulfopropyl)-selenide
pH: 12.5	

EXAMPLE 13

0.1 mol/liter	NiSO ₄ ·6 H ₂ O
0.15 mol/liter	NaH ₂ PO ₄ ·H ₂ O
0.15 mol/liter	lactic acid
2 mg/liter	dimethyl-carboxy-methyl-selenium bromide
pH: 6.0	

EXAMPLE 14

0.15 mol/liter	NiCl ₂ ·7 H ₂ O
0.15 mol/liter	lactic acid
0.1 mol/liter	NaH ₂ PO ₄ ·H ₂ O
2 mg/liter	potassium butylselenosulfate
pH: 5.5	

EXAMPLE 15

0.2 mol/liter	NiCl ₂ ·7 H ₂ O
0.15 mol/liter	NaH ₂ PO ₄ ·H ₂ O
0.4 mol/liter	sodium acetate
1 mg/liter	sodium phenyl-seleno-propylsulfonate
pH: 5.0	

EXAMPLE 16

0.15 mol/liter	NiSO ₄ ·6 H ₂ O
0.15 mol/liter	NaH ₂ PO ₄ ·H ₂ O
0.4 mol/liter	sodium acetate
4 mg/liter	sodium ethyl-selenopropyl-sulfonate
pH: 5.5	

EXAMPLE 17

0.15 mol/liter	NiSO ₄ ·6 H ₂ O
0.1 mol/liter	NaH ₂ PO ₄ ·H ₂ O
0.35 mol/liter	trisodium citrate
0.5 mol/liter	NH ₄ Cl
5 mg/liter	dimethyl-phenyl-acetyl-selenium-bromide
pH: 8.0	

EXAMPLE 18

0.1 mol/liter	NiSO ₄ ·6 H ₂ O
0.25 mol/liter	NaH ₂ PO ₄ ·H ₂ O
0.25 mol/liter	trisodium citrate
0.1 mol/liter	Na ₂ B ₄ O ₇ ·10 H ₂ O
1 mg/liter	dimethyl-carboxy-methyl-selenium-bromide
pH: 5.0	

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EXAMPLE 19

0.1 mol/liter	NiSO ₄ ·6 H ₂ O
0.20 mol/liter	NaH ₂ PO ₄ ·H ₂ O
0.2 mol/liter	glycocoll
0.1 mol/liter	Na ₂ B ₄ O ₇ ·10 H ₂ O
4 mg/liter	phenylacetyl-beta-chlorophenyl-selenide
pH: 8.0	

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EXAMPLE 20

0.1 mol/liter	NiCl ₂ ·7 H ₂ O
0.15 mol/liter	NaH ₂ PO ₄ ·H ₂ O
0.3 mol/liter	sodium acetate
5 mg/liter	methyl-phenyl-acetylene-selenide
pH 5.5	

30

EXAMPLE 21

0.15 mol/liter	NiSO ₄ ·6H ₂ O
0.15 mol/liter	NaH ₂ PO ₄ ·H ₂ O
0.4 mol/liter	sodium acetate
1 mg/liter	di-(potassium sulfopropyl)-diselenide
pH: 6.0	

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What is claimed is:

1. In an aqueous electroless nickel plating bath containing a source of nickel ions, a complexing agent and a reducing agent capable of reducing said ions to metallic nickel on the surface of an object immersed in said bath, the improvement which comprises a stabilizing agent in said bath in an amount sufficient to substantially prevent spontaneous precipitation of nickel in the absence of said immersed object, said stabilizer being selected from the group consisting of organic selenium compounds and the selenides, diselenides, selenosulfate and selenocyanates of an alkali metal, the oxidation state of the selenium being -1 or -2.

2. A nickel-plating bath according to claim 1 wherein said stabilizer is present at a concentration of about 0.0001 to 0.3 gram per liter.

3. A nickel-plating bath according to claim 1 wherein said stabilizer is selected from the group consisting of:

- potassium-diselenide;
- dipropyl diselenide;
- di-n-butyl diselenide;
- di-n-amyl diselenide;
- di-n-hexyl diselenide;
- di-n-heptyl diselenide;
- di-(2-3-dihydroxypropyl)diselenide;
- di-(potassiumsulfopropyl)diselenide;
- di-(potassiumsulfoethyl)diselenide;
- di-(sodiumsulfobutyl)diselenide;
- bis-(sodiumcarboxymethyl)diselenide;
- bis-(potassiumcarboxylethyl)diselenide;
- bis-(potassiumcarboxypropyl)diselenide;
- bis-(potassiumcarboxydecyl)diselenide;
- diphenyl diselenide;
- di-p-tolyl diselenide;
- di-(p-methoxyphenyl)diselenide;
- di-(p-nitrophenyl)diselenide;
- bis-(o-acetylphenyl)diselenide;

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di-2,2'-biphenyl diselenide;
 bis-(p-potassiumsulfophenyl)diselenide;
 bis-(p-chlorophenyl)diselenide;
 bis-(p-carboxyphenyl)diselenide;
 diseleniumdiacetylurea;
 dibenzyl diselenide;
 di-(N-phenyl-carbamoylmethyl)-diselenide;
 bis-(p-nitrobenzyl)diselenide;
 bis-(p-methylbenzyl)diselenide;
 bis-(p-cyanobenzyl)diselenide;
 bis-(p-carboxybenzyl)diselenide;
 bis-(B-bromobenzyl)diselenide;
 bis-(β-phenylethyl)diselenide;
 bis-(3-hydroxypropyl)diselenide;
 bis-(α-tetrahydrofurylmethyl)diselenide;
 bis-(β-phenoxyethyl)diselenide;
 bis-(cyclohexyl)diselenide;
 bis-(cyclopentyl)diselenide;
 potassiumselenosulfate;
 potassiumbenzylselenosulfate;
 potassium p-nitrobenzylselenosulfate;
 potassium p-methylbenzylselenosulfate;
 potassium p-potassium-carboxybenzylselenosulfate;
 potassium p-methoxybenzylselenosulfate;
 potassium p-ethoxybenzylselenosulfate;
 potassium p-cyanobenzylselenosulfate;
 potassium p-ethyl-benzylselenosulfate;
 potassium p-bromobenzylselenosulfate;
 potassium ethylselenosulfate;
 potassium butylselenosulfate;
 potassium octylselenosulfate;
 potassium dodecylselenosulfate;
 potassium 1,3-dihydroxypropylselenosulfate;
 potassium hydroxyethylselenosulfate;
 potassium phenoxyethylselenosulfate;
 potassium tetrahydrofurylselenosulfate;
 potassium phenylethylselenosulfate;
 potassium phenylpropylselenosulfate;
 potassium 3-hydroxypropylselenosulfate;
 dipotassium w-carboxyethylselenosulfate;
 dipotassium w-carboxybutylselenosulfate;
 dipotassium w-carboxydecylselenosulfate;
 dipotassium w-sulfoethylselenosulfate;
 dipotassium w-sulfopropylselenosulfate;
 potassium cyclopentylselenosulfate;
 potassium selenide;
 phenylseleniumacetic acid;
 o-, m- or p-nitrophenylseleniumacetic acid;
 o-, m- or p-methoxyphenylseleniumacetic acid;
 o-, m- or p-chlorophenylseleniumacetic acid;
 3,4-dimethylphenylseleniumacetic acid;
 2,4-dimethylphenylseleniumacetic acid;
 benzylseleniumacetic acid;
 ethylseleniumacetic acid;
 seleniumdiacetic acid;
 seleniumdipropionic acid;
 seleniumdibutyric acid;
 benzylseleniumbutyric acid;
 benzylseleniumundecanoic acid;
 sodium ethylseleniumpropanesulfonate;

bis-(sodium sulfopropyl)selenide;
 phenylseleniumglycolic acid;
 sodium phenylseleniumpropanesulfonate;
 sodium benzylseleniumpropane sulfonate;
 5 bis-(phenoxyethyl)selenide;
 diphenylselenide;
 dibenzylselenide;
 difurfurylselenide;
 10 bis-p-methylphenylselenide;
 bis-p-nitrophenylselenide;
 bis-3-phenylpropylselenide;
 dipropylselenide;
 bis-(hydroxyethyl)selenide;
 sodiumselenocyanate;
 15 potassiumselenocyanate;
 o-, p- or m-nitrophenylselenocyanate;
 o-, m- or p-methylphenylselenocyanate;
 p-methoxyphenylselenocyanate;
 p-ethylphenylselenocyanate;
 20 p-ethoxyphenylselenocyanate;
 sodium 4-cyanoseleno-phenylsulfonate;
 o-, m- or p-chlorophenylselenocyanate;
 2-nitro-4-chlorophenylselenocyanate;
 p-carbmethoxyphenylselenocyanate;
 25 ethylselenocyanate;
 butylselenocyanate;
 decylselenocyanate;
 potassium selenocynoacetate;
 potassium selenocyanopropionate;
 30 potassium selenocyanoundecanoate;
 potassium selenocyanopropanesulfonate;
 potassium selenocyanooethanesulfonate;
 phenoxyethylselenocyanate;
 35 furfurylselenocyanate;
 benzylselenocyanate;
 phenylpropylselenocyanate;
 p-nitrophenylselenocyanate;
 β-naphthylselenocyanate;
 40 phenylselenocyanate;
 carboxymethyldimethyl-selenoniumbromide;
 phenacyl-dimethyl-selenoniumbromide;
 dimethyl-selenetin dicarboxylic acid;
 triethylselenonium iodide;
 45 tribenzylselenoniumchloride;
 dimethyl-benzyl-selenoniumbromide;
 triphenylselenoniumchloride;
 tri-p-tolylselenoniumchloride.
 4 In the method of depositing nickel on a conductive sur-
 50 face or an activated nonconductive surface by immersing said
 surface in a bath containing a source of nickel ions, a com-
 plexing agent and a reducing agent capable of reducing said
 ions on a surface, the improvement which comprises im-
 mersing said surface in a bath according to claim 1.
 55 5. In the method of depositing nickel on a conductive sur-
 face or an activated nonconductive surface by immersing said
 surface in a bath containing a source of nickel ions, a com-
 plexing agent and a reducing agent capable of reducing said
 ions on a surface, the improvement which comprises im-
 60 mersing said surface in a bath according to claim 2.
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