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ELECTRODEPOSITION OF NICKEL

Milton Kosmin, Dayton, Ohio, assignor to Monsanto Chemical Company, a corporation of Delaware

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This invention relates to a process and composition for use in electrodepositing nickel characterized in that the resultant nickel plate, as deposited, is highly lustrous, dense and uniform; it is highly adherent and of improved ductility. More particularly, the present invention relates to new compositions for producing electrodeposits of nickel possessing the above-mentioned characteristics.

I have found that improved results are obtained in the electrodeposition of nickel by having present in the electrolytic bath alkali metal or nickel salts of the polysulfonates of the high-boiling product secured in the cracking of benzene into biphenyl or of a like high-boiling product which has been subsequently partially hydrogenated.

In the cracking of benzene to biphenyl there is obtained as by-product a high-boiling material distilling as follows:

	°C.
°C at 1st drop	370
5%	373
10%	374
50%	382
60%	384
70%	387
80%	393
90%	Approx. 400

The chemical composition of the material boiling above 369° C. and obtained as by-product in the cracking of benzene to biphenyl is approximately:

	Per cent
m-Diphenylbenzene	50–60
p-Diphenylbenzene	About 20
o-Diphenylbenzene	About 10
Triphenylene	3–4

and may therefore be characterized as a composition comprising approximately 83% to 93% of mixed isomeric diphenyl benzenes. Such a composition will be hereinafter referred to as biphenyl high-boiler. Nickel plating baths containing small amounts, preferably 3.5 percent, by weight (based upon the volume of solution) of nickel or alkali metal polysulfonates of biphenyl high-boiler yield adherent and ductile deposits of nickel which are characterized by high luster, density and uniformity.

The addition to nickel plating baths of small amounts, say 3.5 percent, of the nickel or alkali metal polysulfonates of partially hydrogenated biphenyl high-boiler likewise yields electrodeposits of nickel possessing the above-mentioned desirable characteristics. Thus, the biphenyl high-boiler may be caused to react with hydrogen or an agent yielding hydrogen until from 40% to 60% or 70% of the double bonds have been saturated, and the partially hydrogenated biphenyl high-boilers obtained in this manner are subsequently converted into their alkali metal or nickel polysulfonates. The partially hydrogenated biphenyl high-boilers are mixtures comprising mainly isomeric mono- and di-cyclohexylbenzenes, the proportion of these cyclohexylbenzenes depending upon the extent of hydrogenation.

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As illustrative of the process for the preparation of the compounds of the present invention, biphenyl high-boiler which was 40% hydrogenated, is converted into polysulfonic acids and thence into the nickel polysulfonates by the following procedure:

Approximately 75 g. of the 40% hydrogenated biphenyl high-boiler and 150 g. of carbon tetrachloride are placed in a sulfonation flask, cooled by an ice bath, and sulfur trioxide (prepared by heating 65% oleum in a sulfur trioxide generator) is passed in until the weight gain is about 77 g. and loss in weight of the oleum flask is 100.5 g. The sulfur trioxide generator is then uncoupled and dry air is blown through the sulfonator charge until all absorbed sulfur trioxide is removed. Throughout the sulfonation and blowing operations a temperature of approximately 70° C. to 80° C. is maintained. The solvent is then removed, and the product is converted to the nickel salt as by neutralization with nickel carbonate. The product was thereafter drum-dried.

The sulfonates produced by the above process are believed to be polysulfonates, that is di-, tri-, and tetra-sulfonates are present in the product. When polysulfonating a hydrocarbon mixture such as that herein treated, I prefer to carry the sulfonation to the point where the mixture contains on the average, sulfonation products equivalent to the trisulfonate. Where sulfonation is conducted as described the product while containing largely trisulfonated hydrocarbons will also contain some proportion of the di- and the terasulfonated product.

The nickel polysulfonate, largely trisulfonate of 40% hydrogenated biphenyl high-boiler, thus obtained was evaluated as an adjuvant in the electrodeposition of nickel. For this purpose there was used a representative nickel bath, known as Watt's solution, and comprising the following constituents:

	Per cent
Nickel sulfate	24.0
Nickel chloride	7.5
Boric acid	3.75
Water	64.75

To two liters of the above solution there was added 70 g. (3.5% by weight based upon volume of Watt's solution) of the nickel polysulfonate of this invention, and electrodeposition of nickel was effected under the following conditions:

Cleaning cycle before plating	4% trisodium phosphate solution, boil 10 minutes and rinse; 3% KCN solution at 100° F. for 5 minutes, and rinse; 10% sulfuric acid at 160° F. to 180° F. for 5 minutes and rinse.
Current density	20–30 amps/sq. ft.
Source of current	D. C. generator
Temp. of bath	160° F.–175° F.
Plating time	30 minutes
Anodes	Nickel, bagged in desized cotton
Metal	Brass strip
Area of strip	11.5 sq. in.

Nickel plate obtained by the process of this invention is an adherent and ductile plate characterized by high luster, density and uniformity.

Nickel polysulfonates of other hydrogenated biphenyl high-boiler, e. g., 60% hydrogenated biphenyl high-boiler, or of biphenyl high-boiler, itself, may also be used for the purposes of this invention. Instead of the nickel salts herein described there may likewise be used alkali metal salts of polysulfonates of biphenyl high-boiler or of a partially hydrogenated biphenyl high-boiler. The individual constituents of biphenyl high-boiler, e. g., o-, m-, or p-diphenylbenzene or synthetic mixtures of the same may be converted into nickel or alkali metal polysulfonates and added to nickel plating baths for the production of adherent and ductile nickel plate which is characterized by high luster, density and uniformity. Likewise, the individual constituents of partially hydrogenated biphenyl high-boiler, e. g., o-, m-, or p-monocycloalkyl biphenyl or o-, m-, or p-dicycloalkyl benzene or synthetic mixtures of the same may be converted into nickel or alkali metal polysulfonates and added to nickel plating baths for the production of nickel deposits having the above-mentioned desirable properties. Obviously, for economic reasons, the use of the biphenyl high-boiler or of the hydrogenated biphenyl high-boiler mixture is to be preferred.

It will be realized by those skilled in the art that changes may be made in the process of electroplating and in the composition of the electrolytes without departing from the invention. The compounds of the present invention may be used in the known acid nickel plating baths, with or without the use of other additives, e. g., anti-pitting and/or surface tension reducing agents, for the formation of adherent and ductile deposits of nickel which are characterized by high luster, density and uniformity.

It will also be realized by those skilled in the art that changes may be made in the preparation of the nickel or alkali metal polysulfonates of this invention. Thus, the sulfonation need not be effected with sulfur trioxide; any of the well-known sulfonating agents, e. g., oleum, chlorosulfonic acid, etc., may be used for this purpose under such conditions as are best suited for sulfonating with the particular sulfonating agent employed. Neutralization may be effected with other basic compounds of nickel or by metathesis employing an alkali metal or ammonium salt with a soluble nickel salt.

What I claim is:

1. A nickel plating bath comprising essentially a water solution of nickel sulfate, nickel chloride and boric acid, containing as an organic brightening agent a mixture of polysulfonates of isomeric biphenyl benzenes, said agent being present in amount up to 3.5% by weight of said solution.

2. A nickel plating bath comprising essentially a water solution of nickel sulfate, nickel chloride and boric acid, containing as an organic brightening agent a trisulfonate of biphenyl benzene, said agent being present in amount up to 3.5% by weight of said solution.

3. A nickel plating bath comprising essentially a water solution of nickel sulfate, nickel chloride and boric acid, containing as an organic brightening agent a mixture of polysulfonates of hydrogenated isomeric biphenyl benzenes, said agent being present in amount up to 3.5% by weight of said solution.

4. A process of nickel plating comprising electro-depositing nickel from an essentially water solution of nickel sulfate, nickel chloride and boric acid, said solution containing as an organic brightening agent a mixture of polysulfonates of isomeric biphenyl benzenes, said agent being present in said solution in amount up to 3.5% by weight.

5. A process of nickel plating comprising electro-depositing nickel from an essentially water solution of nickel sulfate, nickel chloride and boric acid, said solution containing as an organic brightening agent, a mixture of trisulfonates of hydrogenated hydrocarbons, said hydrocarbons consisting of isomeric biphenyl benzenes boiling above 369° C., said agent being present in amount up to 3.5% by weight of said solution.

MILTON KOSMIN.