ELECTROPLATING A BLACK NICKEL-ZINC ALLOY DEPOSIT

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ABSTRACT OF THE DISCLOSURE

Black electroplates are obtained from an alkaline solution of nickel, zinc, and polyethyleneimine.

BACKGROUND OF THE INVENTION

Articles having lustrous black finishes are desirable and suitable for numerous applications and uses, particularly for decorative purposes and/or to promote absorption or radiation of heat. Matte black finishes are also important in providing non-reflecting surfaces in industrial and military instruments of various types such as the propellor and the naval anemometer. However, black deposits produced heretofore have been found unsatisfactory because of poor abrasion resistance and/or poor adherence of the nickel deposit to the substrate surfaces and/or poor ductility characteristics.

The prior art black nickel plating processes, in addition to yielding films characterized by unsatisfactory physical properties, have been found difficult to control so as to produce a uniform black coating. It has been recognized that factors contributing to difficulties encountered in the controllability of known black plating processes often stem from the comparatively rigid and restrictive operating conditions imposed by those processes, particularly the pH control, range of concentration of the constituents of the plating baths, current density limits, plating times, and the like. For example, the prior art solutions are operated under acid conditions and the normal operating range for the pH of the well known black nickel sulfate type plating baths generally falls within the relatively narrow range of 5 to 6. The permissible current densities employed in many of these sulfate type plating baths are often of a narrow and restrictive scope, e.g., about 0.5 to about 1.5 amperes per square foot. By using a plating bath containing nickel chloride hexahydrate, ammonium chloride, sodium thiocyanate and zinc chloride, it has been possible to expand the permissible pH to 2.3 to 5.5, and to employ current densities of 1.6 to 6 amperes per square foot. See, e.g., United States Patent 2,844,530. However, this special system is still operated under acid conditions requiring special equipment to prevent corrosive acid action and also requires plating times that range from 7½ to 30 minutes to obtain an acceptable black finish.

It has previously been known to add polyethyleneimine to an acid solution of a cell feed composition for the electrowinning of copper or zinc (United States Patent 2,855,444). It is also known to employ a combination of an amine oxide and polyethyleneimine in a zinc cyanide electropolating bath as a brightening agent (United States Patent 3,296,105). Surprisingly, it has now been found that the polyethyleneimine can be employed in an alkaline plating solution of nickel and zinc to produce a black deposit. A much broader range of current densities than employed in the prior art can be used and a uniform deposit will be produced in one to three minutes. Moreover, because an alkaline system is employed, the corrosive acid conditions of the prior art do not have to be considered in the equipment requirements. Additionally, the toxic arsenic and cyanide compounds employed in many prior art black nickel formulations are not necessary in the present plating solution.

It is the object of this invention to provide a novel alkaline plating bath from which a durable, uniform, black electroplate can be obtained in a short period of time using a broad range of current densities. This and other objects will become apparent to those skilled in the art from the following detailed description.

SUMMARY OF THE INVENTION

This invention relates to a novel bath composition and process for producing decorative surfaces on conductive substrates and more particularly, to a novel electroplating bath solution and process for the electrodeposition of black finishes on conductive surfaces and to the production of articles having black finishes and/or "antique" finishes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, black electroplates are obtained from an aqueous, alkaline solution of nickel, zinc, and polyethyleneimine. In preparing the plating bath, the nickel and zinc can be obtained from any suitable metal containing salt such as the sulfates, chlorides, acetates, carbonates, hydroxides, and the like. Typical metal salts which can be employed include nickel sulfate, nickel chloride, nickel acetate, nickel carbonate, nickel hydroxide, zinc sulfate, zinc chloride, zinc acetate, zinc carbonate, zinc hydroxide, and the like salts. Nickel is the major metal ion constituent of the plating solution.

Generally, the concentration of the nickel ion can be about 2.5 to 50 grams per liter, preferably about 5 to 10 grams per liter. The zinc ions generally constitute about 0.25 to 5 grams per liter and preferably are about 0.5 to 1.0 gram per liter.

The plating solution can be made alkaline by employing a suitable hydroxide in an amount sufficient to provide a pH of about 8 to 14 and preferably about 10 to 13. The alkali metal hydroxides such as sodium hydroxide and potassium hydroxide are preferred.

Aqueous solutions containing nickel and zinc ions which are made alkaline with caustic or potassium hydroxide precipitate insoluble nickel hydroxide and zinc hydroxide. By adding polyethyleneimine to these solutions, the precipitated hydroxides are redissolved without decreasing the pH of the aqueous solutions. Without being limited to theory, it is believed that because of the metal-polyethyleneimine complexes formed, the electrodeposition potential of the metals, normally very different, are brought closer together and result in an alloy codeposit.

The water soluble polyethyleneimines are mildly alkaline, hydrophilic, highly branched polymers produced by the acid catalyzed polymerization of ethyleneimine. The polymer is composed of units which have 2 carbon atoms per nitrogen atom and these units are randomly distributed in the approximate ratios of 1 primary amino nitrogen/2 secondary amino nitrogen/1 tertiary amino nitrogen. Commercially available polyethyleneimines have molecular weights of about 600 to about 100,000 and Brookfield viscosities at 25°C of about centipoises when measured in a 5% aqueous solution. The polyethyleneimine is employed in an amount sufficient to dissolve any nickel hydroxide or zinc hydroxide which forms. Generally, the polyethyleneimine will be employed at the rate of about 15 to 250 grams per liter and preferably at about 30 to 50 grams per liter.

The electroplating solutions of the present invention are prepared by mixing the metal salts, alkaline hydroxide
and polyethyleneimine in water. The article to be plated is used as the cathode and a nickel or carbon or other inert anode is employed. Direct current is supplied at a current density of about 2 to 150 amperes per square foot, preferably about 20 to 50 amperes per square foot. The operating temperature of the bath is about 100° to about 180° F., preferably about 150° to 160° F. It has been found that when the bath is operated at the preferred operating temperatures and the preferred current densities, a uniform, black deposit will be produced in 1 to 3 minutes. The resulting electroplated article has an adherent black electroplate on the substrate which is generally about 5 to 50 millionths of an inch thick and more usually about 20 to 40 millionths of an inch thick. The alloy electroplate contains up to 50 weight percent metallic nickel, preferably about 20-30 weight percent, and up to 60 weight percent metallic zinc, preferably about 45-55 weight percent. Without being limited to theory, it is believed that the remainder of the alloy electroplating contains gaseous hydrogen, occluded polyethyleneimine and possibly water.

The following examples serve to further illustrate the invention but are not intended to limit it.

Example I

An electroplating solution was prepared by mixing 33 grams of NiSO₄·7H₂O, 15 grams NaOH, 36.5 grams of PEI 6 (a commercial polyethyleneimine having a molecular weight of 600 and a Brookfield viscosity of 2.3 at 25° C. when measured in a 5% aqueous solution), 3 grams of ZnSO₄·7H₂O, and sufficient water to make a liter of solution. The pH was 12.5. A brass panel as the cathode and a stainless steel anode were inserted into the solution which was heated to about 160° F. Direct current was applied to the electrodes at a current density of 25 amperes per square foot and after 2.5 minutes, a uniform, adherent, black electroplate was produced on the cathode.

Example II

Example I was repeated except that the electroplating solution contained 30 grams of nickel chloride hexahydrate, 15 grams of caustic soda, 32 grams of PEI 6, 1.5 grams of zinc chloride and sufficient water to make up a liter of solution. The pH of the plating bath was 12.5. An adherent, uniform, black electroplate was formed on the cathode after 2.5 minutes.

Example III

Examples I and II were repeated except that PEI 12 (a commercial polyethyleneimine having a molecular weight of 1200 and a Brookfield viscosity of 3.1 at 25° C. when measured in a 5% aqueous solution) was employed in place of PEI 6. A uniform, adherent, black electroplate was obtained.

Example IV

The electroplating solution of Example I was placed in a 267 ml. Hull cell heated to 140° F. and a polished brass cathode was plated for 4 minutes using a stainless steel anode and a current of 2 amperes on the cathode. The Hull cell is an accepted test method for evaluating plating performance and characteristics at various current densities. At 140° F., the Hull cell showed a uniform black electrodeposited throughout the current density range 16–100 amperes per square foot. In the range of 2–16 amperes per square foot, the electrodeposited was indiscernible. The temperature was raised to 150° F. and the foregoing Hull test was repeated. An adherent, uniform, black electroplate was produced throughout the range of 6 to 100 amperes per square foot current density tested. The temperature was then raised to 160° F. and the foregoing Hull test repeated to obtain a uniform black electroplate over the range of 2 to 100 amperes per square foot current density tested.

All of the foregoing was repeated except that the electroplating solution of Example II was employed and the results obtained were identical to the foregoing results.

Example V

A cleaned and weighed steel coupon was immersed in the electroplating solution of Example I at 160° F. The coupon was connected to the cathode of a DC rectifier and another steel coupon was connected to the anode of the rectifier. A current of 3.5 amperes (equivalent to a current density of 40 amperes per square foot) was passed through the circuit for 5 minutes. The plated steel cathode was then thoroughly rinsed in distilled water, dried and reweighed. The deposit was thereafter removed from the cathode by dissolution in a mixture of hydrogen peroxide and ammonia. Chemical analysis of the resulting solution showed that the deposit contained 22.5 weight percent nickel and 52.3 percent zinc. No evidence of sulfur was found. It was calculated that the thickness of the deposit had been 20 millionths of an inch.

Various changes and modifications can be made in the process and products hereof without departing from the spirit and scope of the invention. The various embodiments disclosed herein serve to further illustrate the invention but are not intended to limit it.

We claim:

1. A composition for the deposition of a black electroplate which comprises an aqueous, alkaline solution of nickel, zinc and polyethyleneimine wherein the nickel ion concentration is about 2.5 to 50 grams per liter, the zinc ion concentration is about 0.25 to 5 grams per liter, and the polyethyleneimine concentration is about 15 to 250 grams per liter.

2. The composition of claim 1 wherein the pH is about 10 to 13.

3. A process for electrodipping a black finish on an article which comprises subjecting the article to be blackened to the composition of claim 1 at a temperature of about 100° to 180° F. and applying a direct current at a current density of about 5 to 150 amperes per square foot.

4. A process for electroplating a black finish on an article which comprises subjecting the article to be blackened to the composition of claim 1 at a temperature of about 150° to 160° F. and the current density is about 20 to about 50 amperes per square foot.

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