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AUTOCATALYTIC DEPOSITION OF NICKEL, COBALT AND ALLOYS THEREOF

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This specification relates to an invention whereby nickel and cobalt coatings, and their alloys, are deposited upon metallic and non-metallic surfaces by an autocatalytic chemical action involving the means to a uniquely-controlled metallic reduction.

The general object of this invention is to provide novel solutions and methods of producing nickel, cobalt and alloy deposits which are satin to bright in appearance and which possess the qualities of ductility, adhesion, excellent corrosion resistance, low-to-zero internal tensile stresses and a high degree of hardenability under ordinary precipitation hardening treatments.

A further object of this invention is to introduce sulfamic acid, in its own form and in the forms of any of its derivatives, i.e. nickel sulfamate, cobalt sulfamate, etc., into the metallic plating solutions of the invention, thereby enabling a combined and emission type buffering action to take place in the intermediate film from which the autocatalytic reduction of the various metals and alloys proceeds.

Yet another object of this invention is to provide metallic coatings of such ductility and potential adherence that they may be applied directly to sensitized, non-metallic surfaces such as glass, rubber, fiberglass laminate, polyester plastics, epoxies, acrylics, vinyls, polypropylenes and many other inert materials without acquiring the inherent tensile stresses often contained in the as-formed structure of the thermosetting or thermoplastic non-metallic surfaces upon which they are deposited.

Another object of this invention is to provide a number of plating solutions which will deposit autocatalytic metal coatings upon metallic and non-metallic surfaces at a rate within the range of .0001 inch and .0009 inch per hour, depending upon temperature, pH and relative volumes or weights of constituents in the solution, such metallic coatings having a Rockwell C hardness in the range of 35 to 50 as plated, depending upon the finish and grain structure of the receiving surface and the metallic coating itself, and capable of being hardened to a Rockwell C hardness in the range of 55 to 70 by ordinary precipitation-hardening methods, i.e. heating in an air or other heat treating oven to a temperature range within 400° to 800° F., allowing to dwell at this temperature for at least two hours and then cooling in air to room or ambient temperature.

A further object of this invention is to provide metallic coatings possessing certain magnetic properties as demanded by the usage for which the plated parts or surface is intended. The plated nickel-cobalt ratio and percentage is varied to whatever extent is required for the specified magnetic, physical and corrosion resistant qualities desired in the deposit.

Another object of this invention is to provide a means of continuous plating operation and consequent production of plated parts by constantly or intermittently introducing the metal-producing additives, the buffers and the reducing agents to the various solutions of the invention in liquid form, thus obviating any roughness and/or pitting which might result from additions in the form of dry salts.

The foregoing and other objects and advantages of the invention will be made more apparent as the specification proceeds.

Generally speaking, the present invention relates to a novel and improved bath for use in autocatalytic plating of nickel, cobalt or nickel-cobalt alloys and this bath comprises between about 0.1 and 35.0 oz./gallon of nickel or cobalt sulfamate, conventional quantities of buffering materials including citrates and acetates and conventional quantities of sodium or potassium hypophosphite, and with the concentrations of the materials being varied substantially proportionally within the limits stated. The present invention also relates to the method of depositing these materials by autocatalytic deposition and wherein the bath is maintained at a pH of between about 2.5 and 12.5 and at a temperature between about 170° and 210° F.

Nickel ammonium sulfate, a salt containing the ammonium ion, has been mentioned in U.S. Patent No. 3,060,059 as a source of enhanced buffering action in a nickel-phosphorous alloy solution. However, in the nickel-ammonium salt, the ammonium ion escapes rather readily in its gaseous form from the host crystal of nickel sulfate under the attrition of continuous autocatalytic reducing action within the pH and temperature ranges necessary to deposit the nickel plating. In the sulfamic acid-bearing solutions of my invention, the ammonium ion is more nearly chelated, since it is more intimately contained within the lattice structure of the sulfamic acid crystal, and hence more resistant to rapid removal by the attrition of reducing agents, temperature and pH. Therefore, by the use of sulfamic acid and/or its derivatives, I am able to provide a steady, emission type buffering action which does not dissipate suddenly, which aids in brightening and grain refining the metallic deposit and which, in combination with other buffering agents, successfully retards the rapid and random deposition which could result in micro-roughness and porosity of the coating.

This emission type buffering action takes place when ammonia (NH_3) is slowly released from the sulfamic acid (NH_2SO_3H) and/or amidosulfuric acid, or aminosulfonic acid present in the plating solutions. Since sulfuric acid (H_2SO_4), and hydrochloric acid (HCL) present in the nickel sulfate, and nickel chloride do not contain nor emit such a buffering agent, this emissive chemical action becomes a unique and stabilizing characteristic of the solution of the invention into which the sulfamic acid ion is introduced.

This buffering action of the sulfamates, which is correlated with that of a citrate, is possible because of the unique structure of the sulfamic acid crystal and its containment of NH_3, the release of which, in the thin cationic film from which the metallic coatings are deposited, aids in achieving the very efficient buffering characteristics of the various plating solutions of the invention and retards their otherwise inherent tendency toward random reduction of metallic ions. Another unique benefit derived from the addition of sulfamic acid and/or its derivatives into the plating solutions of the invention is its combination in the cationic film with a chloride, such combination providing a continuous activating effect upon the metallic or sensitized surface being plated and upon the coating itself during the entire build-up and throughout the total thickness of the metallic deposit, further providing a coating of metal which is ductile, adherent, compressive, and free of cracks, blisters, pits, voids and inclusions.

Although the vast number of chemical combinations made possible by the use of the aforementioned constituents in singly, doubly or triply combined form makes a complete listing of various plating baths virtually prohibitive, a few typical and operational plating baths made up from the foundation materials and/or their derivatives are as follows:

The Sulfamate Bath (Nickel)

Constituents	Range	Preferred
Nickel Sulfamate	0.1 to 35.0 oz./gallon	5-15
Sodium Citrate	0.5 to 3.0 oz./gallon	1 to 2
Sodium Acetate	do	1 to 2
Sodium Hypophosphite	0.2 to 3.0 oz./gallon	1 to 2
The Sulfamate-Chloride Bath (Nickel)		
Nickel Sulfamate+Nickel Chloride.	0.1 to 35 oz./gallon (any ratio).	5-15
Sodium Citrate	0.5 to 3.0 oz./gallon	1 to 2
Sodium Acetate	do	1 to 2
Sodium Hypophosphite	0.2 to 3.0 oz./gallon	1 to 2
The Sulfamate Bath (Cobalt)		
Cobalt Sulfamate	0.1 to 35 oz./gallon	5-15
Sodium Citrate	0.5 to 3.0 oz./gallon	1 to 2
Sodium Acetate	do	1 to 2
Sodium Hypophosphite	0.2 to 3.0 oz./gallon	1 to 2
The Sulfamate-Chloride Bath (Cobalt)		
Cobalt Sulfamate+Cobalt Chloride.	0.1 to 35 oz./gallon (any ratio).	5-15
Sodium Citrate	0.5 to 3.0 oz./gallon	1 to 2
Sodium Acetate	do	1 to 2
Sodium Hypophosphite	0.2 to 3.0 oz./gallon	1 to 2
The Sulfamate Bath (Nickel-Cobalt Alloy)		
Nickel Sulfamate+Cobalt Sulfamate.	0.1 to 35 oz./gallon (any ratio).	5-15
Plus Sodium salts of Citrate, Acetate and Hypophosphite in same ratios as above.		
The Sulfamate-Chloride Bath (Nickel-Cobalt Alloy)		
Nickel Sulfamate+Cobalt Chloride.	0.1 to 35 oz./gallon (any ratio).	5-15
Plus sodium salts of citrate, acetate and hypophosphite as above.		
The Sulfamate-Sulfate Bath (Nickel)		
Nickel Sulfamate+Nickel Sulfate.	0.1 to 35 oz./gallon (any ratio).	5-15
Plus salts of citrate, acetate and hypophosphite as above.		
The Sulfamate-Sulfate Bath (Cobalt)		
Cobalt Sulfamate+Cobalt Sulfate.	0.1 to 35 oz./gallon (any ratio).	5-15
Plus salts of citrate, acetate and hypophosphite as above.		
The Sulfamate-Sulfate Bath (Nickel-Cobalt Alloy)		
Nickel Sulfamate+Cobalt Sulfate.	0.1 to 35 oz./gallon any ratio).	5-15
Plus salts of citrate, acetate and hypophosphite as above.		

NOTES.—Preferred range for metal concentation in all of the above is 2 to 5 oz./gallon as metal.

The acid form may be substituted for the salt form in any of the above formulations.

Potassium or ammonium salts may be substituted for the sodium salt in any or all of the above formulations.

As may be seen from the above few samples, a countless number of autocatalytic plating solutions may be formulated by combining the various salts of nickel and cobalt.

A further feature of this invention is the provision of a high pH autocatalytic version of any or all of the aforementioned baths for use in plating nickel, cobalt or the alloys of each on acid-volatile materials such as zinc, zinc coatings or the alloys thereof by complexing the nickel and/or cobalt and raising the pH to a range above that which corrodes these materials (example 6.0 to 12.0 pH range). The usage of ammonium hydroxide and/or an ammoniacal salt to accomplish a complex and pH adjustment are not necessarily unique with this invention; however, the usage of ammonium hydroxide and/or its salts to complex and adjust solutions containing sulfamic acid, or its derivatives is unique and hitherto unknown in the autocatalytic (electroless) plating of nickel, cobalt and nickel-cobalt alloys.

The invention and novel plating baths are quite useful in plating upon non-metallic materials. For example, certain of the formulations of the invention may be used to deposit plating upon sensitized acrylic surfaces without acquiring the stresses inherited by the acrylic substrate under the physical duress of casting and forming operations. The deposits may be varied in ductility, hardness, compressive strength, grain refinement and brightness by additions to the solutions of the invention of controlled buffering and brightening agents.

The unique and valuable features of this invention are the satin-to-bright, leveled, ductile, adherent and void-free coatings produced from the solutions of the invention. These metallic coatings are possible because of a unique buffering and brightening system induced by the additions, in varying amounts, to provide balanced concentrations, of sulfamic acid and its derivatives, citrate salts, and acetate salts. The primary and secondary buffering action made possible by the inclusion of the sulfamate ions is unique in autocatalytic plating of nickel, cobalt and/or their alloys. Also unique is the grain refining and brightening effects induced by their containment within the autocatalytic films of the plating solutions.

From the foregoing, it will be seen that the invention relates, in general, to the use in autocatalytic plating baths of the sulfamates, chlorides, sulfates, or combinations thereof of nickel and/or cobalt. A metallic sulfamate is used in all of the baths.

It must be realized that the illustrative details and general requirements of this invention may be altered or modified without departing from the spirit or scope of the invention, as defined in the appended claims.

While one complete embodiment of the invention has been disclosed herein, it will be appreciated that modification of this particular embodiment of the invention may be resorted to without departing from the scope of the invention as defined in the appended claims.

What is claimed is:

1. A bath for use in autocatalytic nickel, cobalt or nickel-cobalt alloy plating and comprising between a total of about 0.1 and 35.0 oz./gallon of at least one material from the group consisting of nickel sulfamate, and cobalt sulfamate, and at least one material from the group consisting of nickel chloride, and cobalt chloride; at least about 0.5 oz./gallon of a citrate; at least about 0.5 oz./gallon of an acetate; and at least about 0.2 oz./gallon of a hypophosphite.

2. A bath for use in autocatalytic nickel or cobalt plating and comprising a total between about 5 to 15 oz./gallon of one or more materials from the group consisting of cobalt sulfamate and nickel sulfamate; about 0.5 to 3.0 oz./gallon of a citrate; about 0.5 to 3.0 oz./gallon of an acetate; and about 0.2 to 3.0 oz./gallon of a hypophosphite.

3. A solution for use in autocatalytic nickel plating and comprising between 0.1 and 35.0 oz./gallon of materials from the group consisting of nickel sulfamate, nickel sulfate and nickel chloride, at least 0.1 oz./gallon of nickel sulfamate always being present, between 0.5 and 3.0 oz./gallon of a citrate, between 0.5 and 3.0 oz./gallon of an acetate and between 0.2 and 3.0 oz./gallon of a hypophosphite.

4. A solution for use in autocatalytic cobalt plating and comprising between 0.1 and 35.0 oz./gallon of materials from the group consisting of cobalt sulfamate, cobalt sulfate and cobalt chloride, between 0.5 and 3.0 oz./gallon of a material from the group consisting of a citrate and an acetate, and between 0.2 and 3.0 oz./gallon of a hypophosphite, at least 0.1 oz./gallon of cobalt sulfamate always being present.

5. A solution for use in autocatalytic nickel-cobalt alloy plating and comprising between 0.1 and 35.0 oz./gallon of material from the group consisting of nickel sulfamate and cobalt chloride with at least 0.5 oz./gallon of each material being present, between 0.5 and 3.0 oz./gallon of citrate, between 0.5 and 3.0 oz./gallon of an acetate, and between 0.2 and 3.0 oz./gallon of hypophos-

phite, the nickel and cobalt combining to deposit in alloy form.

6. A solution for use in autocatalytic nickel-cobalt alloy plating and comprising between 0.1 and 35.0 oz./gallon of material from the group consisting of cobalt sulfamate and nickel chloride with at least 0.5 oz./gallon of each material being present, between 0.5 and 3.0 oz./gallon of citrate, between 0.5 and 3.0 oz./gallon of an acetate, and between 0.2 and 3.0 oz./gallon of hypophosphite, the nickel and cobalt combining to deposit in alloy form.

7. A method of nickel, cobalt or nickel-cobalt alloy plating comprising the steps of forming a bath from about 0.05 to 17.5 oz./gallon of material from the group consisting of nickel sulfamate and cobalt sulfamate, adding to the bath material from the group consisting of nickel chloride, nickel sulfate, cobalt sulfate and cobalt chloride in amounts from about 0.05 to 17.5 oz./gallon; at least one buffer from the group consisting of acetates and citrates in quantity of more than 0.5 oz./gallon, and a hypophosphite reducing agent in the amount of about 0.2 to 3.0 oz./gallon, and immersing into the bath an article for autocatalytic plating thereon.

8. A method as in claim **7** where the bath is maintained at a pH of 2.5 to 12.5, a temperature of between about 70° to 210° F. and the bath is replenished with new quantities of its ingredients to maintain the bath with the compositions stated.

9. A method of nickel, cobalt or nickel-cobalt alloy plating comprising the steps of forming a bath containing from about 0.1 to 17.5 oz./gallon of material taken from the group consisting of nickel sulfamate and cobalt sulfamate, the bath also containing a material from the group consisting of nickel sulfate, nickel chloride, cobalt sulfate, and cobalt chloride in amounts from about 0.1 to 17.5 oz./gallon, at least one buffer from the group of materials consisting of acetates and citrates in the range of more than about 0.5 oz./gallon and a hypophosphite reducing agent in the amount of about 0.2 to 3.0 oz./gallon, into which bath is immersed an article for autocatalytic plating thereon, and maintaining the bath at a pH of between 2.5 to 12.5, a temperature of 70° to 210° F., and intermittently replenishing the bath with new ingredients to maintain it at the levels stated.

10. A bath for use in autocatalytic nickel, cobalt or nickel-cobalt alloy plating and comprising between a total of about 0.1 and 35.0 oz./gallon of at least one material from the group consisting of nickel sulfamate, and cobalt sulfamate, and at least one material from the group consisting of nickel chloride, and cobalt chloride; at least about 0.5 oz./gallon of at least one material from the group consisting of citrates and acetates, and at least about 0.2 oz./gallon of a hypophosphite.

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