Come /liter

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2,993,810 BATH AND PROCESS FOR CHEMICALLY NICKEL

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This invention deals with the problem of nickel plating 10 magnesium containing articles chemically, or "electro-lessly."

It is a fact that prior proposals for dealing with this problem have invariably met with failure, for one reason, because all known chemical nickel-plating baths have 15 effected destructive or unacceptable corrosion of the magnesium being plated. These baths all contain, or are made up with, water and at even the minimum operating temperatures feasible, for example, $90^{\circ}-95^{\circ}$ C., even the water detrimentally reacts with the magnesium. The 20 presence of the "free" ions in this heated water bath materially augments corrosion, particularly if these ions are the conventional chloride ions derived from NiCl₂.

Further, the products of corrosion react back on the bath and disassociate its components, breaking the bath 25 down into an ineffective mixture of separate components.

We have discovered that a bath which, among other advances, (1) totally obviates chloride ions; (2) employs fluorine ions which prevent attack on the magnesium while plating it; (3) operating the bath at a critical pH range of 9–12, inc., while (4) concurrently employing a reagent which buffers the reaction and maintaining the pH constant, and also prevents precipitation of nickel ions due to this alkalinity of the bath; and (5) operating the bath at a critical temperature range of 90°–95° C., magnesium articles can, for the first time in this art, be satisfactorily nickel plated without possibility of corrosion or other deleterious action.

Several examples of bath-formulation according to the present invention are set forth hereinbelow but only by 40 way of exemplification of the inventive concepts.

One of the now-preferred formulations of the present bath which has, over a satisfactory period of usage, been found to eliminate the aforestated, and other, defects is as follows:

	Gms./li	ter	
NiSO ₄ .6H ₂ O	_ 10 to	20	
NaH ₂ PO ₂ H ₂ O			
NH2CH2COOH	. 20 to	30	
NaF			ł

Water sufficient to make up 1 liter is added.

Further, in order to establish the essential alkalinity, a 10% solution of NaOH or other caustic or base, is added to the foregoing in an amount sufficient to raise the pH to a range of 9–12, inc. This pH is maintained stable by the buffer aforementioned, while the NaF protects the magnesium chemically while it is plated by the reduction of the chloride-free nickel salt via the hypophosphite.

It is also preferable that a bath-temperature be maintained that is in the range of 90° C. -95° C.

This particular bath has been found to deposit nickel on the magnesium article at the rate of substantially 1 mil per hour.

It will be observed that nothing in the nature of the usual preliminary coating of the magnesium is employed herein.

The nickel plating herein is rather bright, although no discrete brightener is employed. The plating is hard, homogeneous, and dense, lacking any appearance of sponginess. It is quite adherent and does not blister or peel despite exposure to salt air, etc. 2

In the aircraft industry, for example, present bath and process are eminently well adapted for nickel plating magnesium wave guides and the vital airframe parts of guided, and ballistic, missiles.

In the electronics industry, the invention is sharply advantageous in enabling magnesium parts to be so plated that they can be soldered to other parts.

A second desirable formulation of the bath for electrolessly nickel-plating magnesium containing articles is as follows:

(1) NiSO₄.6H₂O, 10 to 20 gms./liter;

(2) NaH₂PO₂.H₂O, 10 to 30 gms./liter;

(3) NaF, 2–10 gms./liter;

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(4) Water to make up 1 liter;

(5) An alkalinizing, complexing and buffering agent like NH_4OH , in an amount sufficient to raise pH to 9–12 is added and the bath is maintained at 90°–95° C.

The NH_4OH serves, here, a triple function, acting as (1) a buffering agent, (2) a nickel-complexing agent, and

20 (3) as a replacement for caustics as an alkalinizing agent.

A third formulation which has satisfactorily achieved the present objectives is composed as follows:

		ums./ II	
<	NiCO ₃ H ₃ PO ₂	10 to	20
,	H_3PO_2	10 to	30
	HF		
	NH ₂ CH ₂ COOH	20-	-30

Water to make up 1 liter is also employed, while NaOH, or other base or caustic is added in an amount sufficient to raise the pH to a value of 9-12, inclusive.

Although certain quantities, ratios, volumes and other parameters have been set forth hereinabove for the sake of concreteness, it is to be understood that the invention is limited, both in fact and at law, only as required by the scope of the subjoined claims.

We claim:

A process for nickel plating a body that incorporates magnesium, comprising: contacting a magnesium-contain-40 ing body with a chloride ion-free aqueous solution, at 90-95° C., of (1) 10-20 grams per liter of a nickel salt that is free of the chloride-ion; (2) 10-30 grams per liter of a hypophosphite-ion-containing reducing compound that is free of the chloride-ion; (3) 2-10 grams per liter of an inorganic compound that is free of chloride ions and incorporates the radical of hydrofluoric acid as its active factor and establishes fluoride ions in aqueous solution; and adding, in an amount per liter of the aqueous solution adequate to complex the nickel ions in the solution, buffer the body against free hydrogen ions and alkalinize the solution to pH=9-12, a chemical system that is free of the

chloride ion and that contain ions which contain the amino group and hydroxyl ions.2. A process according to claim 1, in which the nickel

⁵⁵ salt is nickel sulphate.

3. A process according to claim 1, in which the nickel salt is nickel carbonate.

4. A process according to claim 1, in which the reducing compound is sodium hypophosphite.
 5. A process according to claim 1 in which the reduc-

5. A process according to claim 1, in which the reducing compound is hypophosphorous acid.

6. A process according to claim 1, in which the compound that incorporates the radical of hydrofluoric acid is sodium fluoride.

7. A process according to claim 1, in which the compound that incorporates the radical of hydrofluoric acid is hydrofluoric acid.

8. A process according to claim 1, in which the chemical system that contains amino-ions and hydroxy-ions is
70 amino-acetic acid, 20-30 grams/liter, and a 10% NaOH aqueous solution in an amount sufficient to raise the pH to 9-12,

9. A process according to claim 1, in which the chemical system that incorporates amino, including ions and also hydroxy ions, is ammonium hydroxide.

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10. A bath for nickel-plating articles incorporating magnesium, comprising: nickel sulphate, 10–20 grams/ 5 liter; sodium hypophosphite, 10–30 gms./liter; amino-acetic acid, 20–30 gms./liter; sodium fluoride, 2–10 gms./ liter; water sufficient to make up one liter of bath; and sodium hydroxide sufficient to establish a pH of 9–12, inclusive.

11. As a new composition of matter for nickel plating magnesium articles: an aqueous solution, free of chlorine ions, of a nickel salt that is free of the chlorine-ion and is present as 10–20 gms./liter; 10–30 grams/liter of a hypophosphite-ion containing reducing compound that is free of the chloride ion; an inorganic compound that is free of the chlorine ion, and incorporates the radical of hydrofluoric acid and is present as 2–10 gms./liter; and a chemical system consisting of amino-ions and hydroxy ions, said system being free of chlorine ions and present in an amount per liter, based on the amount of

nickel ions, hypophosphite ions and fluorine ions present per liter, that is adequate to effectuate complexing of the nickel ions, buffering of the magnesium article against free hydrogen ions and alkalinizing of the solution to a pH=9-12, inclusive.

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12. A composition according to claim 11, in which the complexing, buffering and alkalinizing system consists of an aqueous solution of H_2 .NH₂.OH in an amount sufficient to raise the pH of the composition to 9–12, inclusive.

13. A composition according to claim 11, in which the chlorine-free nickel salt consists of 10-20 gms. liter of NiCO₃.

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