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3,354,059

ELECTRODEPOSITION OF NICKEL-IRON MAGNETIC ALLOY FILMS

Herman Koretzky, Poughkeepsie, N.Y., assignor to International Business Machines Corporation, Armonk, N.Y., a corporation of New York

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ABSTRACT OF THE DISCLOSURE

Isoascorbic acid and ascorbic acid are used as additives to a standard Watts' electrolyte to obtain stress-free nickel alloy films and as additives to electrolytes that deposit nickel films so as to obtain corrosion-resistant bright nickel films. The additives act as antioxidants and keep iron ions in the ferrous state rather than in the ferric state.

This application is a continuation-in-part of application Ser. No. 389,204, now abandoned, the latter being assigned to the assignee of the present invention.

The invention disclosed in the parent application 389,204 was conceived in terms of improving the electrodeposition of permalloy type films. Ascorbic acid or isoascorbic acid was employed as an additive in a bath used for electrodepositing magnetic films consisting of alloys of nickel, such as nickel-iron, nickel-iron with cobalt and/or with phosphorus and/or with copper. In such prior application, the emphasis was on obtaining a stress-free permalloy type film so that magnetic films, such as those that can be used in computer applications, would not exfoliate or peel from the metal surfaces on which they were deposited. However, it has been discovered that isoascorbic acid or ascorbic acid can be employed with electrolytic solutions that deposit only nickel. The addition of ascorbic acid or isoascorbic acid into an electrolyte designed to deposit only nickel produces a bright nickel deposit. Consequently, the initial disclosure was unnecessarily limited in scope. Ascorbic or isoascorbic acid is now employed as an additive to aqueous acidic solutions which contain nickel ions. Therefore, isoascorbic (erythorbic) or ascorbic acid can be employed with electrolytic baths containing nickel ions wherein the presence of the ascorbic or isoascorbic acid in an electrolyte that produces a nickel alloy serves to diminish the residual stress of the nickel alloy film, and the presence of such additive in an electrolyte composed of a solution that will deposit only nickel also produces a corrosion-resistant bright nickel deposit. Although biologically, isoascorbic acid has only about $\frac{1}{20}$ of the vitamin C activity of L-ascorbic acid, an optical isomer of ascorbic acid, the two acids are equivalent for the purposes of carrying out the principles of the present invention. Description of the structure and method of preparation of ascorbic and isoascorbic acids appear in Merck Index, Seventh Edition, pages 106 and 571, respectively, published in 1960 by Merck & Company.

Heretofore, in the manufacture of nickel-iron alloy films, or alloys of nickel-iron with Co and/or P and/or Cu on flat substrates, it has not been possible to reproducibly prepare films which do not exfoliate, crack or peel spontaneously due to the stresses built up in said film by the electrodeposition process, thus leading to a lack of adhesion by the film to the substrate. When attempting to electrodeposit a permalloy type alloy film, for example Ni-Fe-P, onto a flat glass substrate made conductive by vacuum depositing upon its surface a thin film of chromium followed by approximately 300 Å. of Au, the magnetic film is prone to peel, crack or exfoliate spon-

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taneously due to the internal stresses set up in the film by the electrodeposition process when these stresses exceed the cohesive forces binding the gold to the glass substrate. Electrolytes for depositing permalloy type alloy films are compounded from salts containing Ni^{++} and Fe^{++} as sources for the metallic ions. Air oxidation or oxygen dissolved in the water used to prepare these electrolytes readily oxidize Fe^{++} to Fe^{+++} . It is well known in the art that the presence of Fe^{+++} ion in Ni electroplating baths leads to highly stressed deposits. See U.S. Patent 3,027,309, Method of Depositing Nickel-Iron Films, J. H. Stephens, Col. 1, lines 34-37, (March 27, 1962); "Stress in Electrodeposited Nickel" by W. M. Phillips and F. L. Clifton, 34th Annual Proceedings A.E.S., page 110, (1947).

This effect is seen intermittently and occasionally it is possible to electroplate sound permalloy type alloy deposits from electrolytes containing small quantities of Fe^{+++} . This intermittency is highly undesirable from an economical standpoint, however, due to the expense of preparing suitable substrates and the difficulties encountered in scheduling the manufacture of film devices.

Electrolytic baths used to electrodeposit permalloy type alloy films are highly unstable due to ferric ion build up with time and thus must be discarded within a relatively short time after compounding. The length of useful life is dependent upon the weight of alloy deposited which also decreases its already short shelf life by increasing the ferric ion concentration.

The process of the invention greatly improves the electrodeposition reproducibility in preparing permalloy type films by retarding and reversing the oxidation of ferrous ion. The addition of an antioxidant such as ascorbic acid or isoascorbic acid has been found to achieve the desired results without any concomitant degradation of the desirable properties of the film. By employing the ascorbic acid or isoascorbic acid in the electrolyte, the degradation of the bath due to the formation of ferric ion is not observed.

Additionally, it has been found that isoascorbic and ascorbic acids can be employed to obtain bright nickel deposits. Traditionally, nickel is electrodeposited from a solution of nickel sulfate, nickel chloride and boric acid, which solution also usually contains a wetting agent to reduce the interfacial tension between the electrodes and electrolytic solution, a primary addition agent to reduce the residual stress of the nickel deposit and a secondary addition agent to promote leveling. The primary addition agent has always contained sulfur in a form which is reducible under the conditions of electrolysis so that a significant quantity of sulfur is codeposited with the nickel. The secondary addition agent promotes leveling but also markedly increases the residual stress of the deposited nickel. By correctly balancing the quantities of each ingredient of the bath and by determining the optimum values of pH temperature, current density and time, it is possible to electrodeposit a brilliant, leveling, ductile and uniform nickel film, but the benefit of codeposited sulfur, which is reduced residual stress, is offset by the fact that the nickel deposited is very prone to corrosive attack.

The use of ascorbic or isoascorbic acid as a sulfur-free primary addition agent functions as most primary addition agents function in electrolytic baths, but the absence of sulfur diminishes subsequent corrosive attack of such deposited nickel films. Certain secondary brighteners act synergistically with the isoascorbic or ascorbic acid employed. Suggested secondary brighteners that work synergistically with ascorbic acid or isoascorbic acid are the general class of acetylenic alcohols, or coumarins.

In conventional electroplating of nickel, the latter is electrodeposited from a solution of nickel sulfate, nickel

chloride, boric acid, and a wetting agent to reduce the interfacial tension between the electrodes and the solution. A representative solution is known as Watts' electrolyte. However, most electroplated nickel deposits derived from electrolytes similar to that introduced by Watts are usually dull, large grained, columnar, have a residual tensile stress of less than 10,000 p.s.i., are non-leveling but highly corrosion-resistant. In order for such nickel deposit to be useful as a decorative finish, or as a substrate for a subsequent metallic deposition such as chromium or the like, the deposited nickel must be buffed to a high luster. Such buffing step is expensive, time consuming and risks the chance of buffing through to the base metal. In order to obviate these difficulties, depositions two and three times desired thickness are made. Obviously, on highly convoluted or intricately-shaped substrates, such buffing is precluded on all surfaces.

Other techniques for obtaining electrodeposits meeting the requirements for ductility, brightness, fine grained laminar structure, low stress, leveling ability and corrosion-resistance rely on the use of a double or triple nickel system. The initial undercoat is semi-bright and is obtained from an electrolyte containing a secondary brightener and the upper coat is fully bright and is obtained from an electrolyte containing the primary and secondary brighteners. The duplex system is relied upon because all available fully bright nickel electrodeposits contain varying amounts of sulfur; such sulfur coming from the primary brightener diminishes corrosion-resistance of the deposited nickel. The semi-bright deposits do not contain sulfur and approximate the corrosion-resistance of the normally dull Watts' deposits.

All presently known primary brighteners contain sulfur and are usually aromatic or aliphatic sulfonates, sulfonamides or sulfonimides, thiocyanates, thioethers, thiocarbonyls, thioalcohols or sulfides. A more comprehensive listing of primary brighteners is found in U.S. Patent 3,002,902 (Table III) which issued on Oct. 3, 1961. Generally such additives to electrolytes, although they tend to result in bright electrodeposits that have desirable characteristics as to grain structure, ductility and low stress, such electrodeposits nevertheless are prone to corrosive attack. The secondary brightener employed is generally a reactive, unsaturated, organic material that usually contains oxygen. Typical secondary brighteners are acetylenic or ethylenic alcohols, coumarins, aldehydes and hydrates, and leuco bases of triane type dyes. The proper selection of a secondary brightener with a primary brightener for use in a normal Watts' electrolyte will produce many of the desirable properties of a bright nickel deposit. However due to the codeposited sulfur, such sulfur coming from all known primary brighteners, the corrosion-resistance of the nickel deposited is poor.

If the normal primary brightener presently employed in electroplating baths for nickel deposition is replaced with isoascorbic acid or ascorbic acid, all of the desirable properties of the known primary brighteners are retained, but the absence of sulfur from isoascorbic or ascorbic acid leads to a highly corrosion-resistant deposit. There appears to be no critical upper limit of these sulfur-free addition agents save solubility, but there is generally no advantage in employing more than 50 gm./l. and, in most plating baths, substantially the full benefit of their presence is achieved with 5 gm./l., or even less. Moreover it is also desirable to employ secondary brighteners (for their leveling effects) that act synergistically with the isoascorbic or ascorbic acid in the Watts' electrolyte or with other common electrolytes such as high chloride, fluoborate and sulfamate. Suggested secondary brighteners that work synergistically with isoascorbic or ascorbic acid would be 2-butyne-1,4-diol, the general class of acetylenic alcohols, or coumarins.

It is an object of the invention to reproducibly electrodeposit permalloy type alloy films.

Another object of the invention is to reproducibly pro-

duce permalloy type alloy films from electrolytes containing zero or minimal quantities of ferric ion thus extending the useful life of the electrolyte.

Another further object of the invention is to produce thick permalloy type alloy films that will be continuous and self-supporting when removed from a strippable substrate.

Still another object of the invention is to reproducibly produce permalloy type alloy films from electrolytes containing an antioxidant.

A further object of the invention is to produce permalloy type films by electrodeposition that do not peel, crack or exfoliate spontaneously by adding to the electrolyte an antioxidant selected from the group consisting of ascorbic acid and isoascorbic acid.

Still another object of the invention is to produce permalloy type alloy films by electrodeposition from an electrolyte comprising nickel ions, iron ions and ascorbic acid.

Further another object of the invention is to produce permalloy type alloy films by electrodeposition from an electrolyte comprising nickel ions, iron ions and isoascorbic acid.

Another object is to employ ascorbic or isoascorbic acid as a primary brightener to the standard Watts' electrolyte or equivalent electrolyte.

Yet another object is to employ a novel sulfur-free primary additive to such standard Watts' electrolyte or its equivalent.

Still another object is to employ ascorbic or isoascorbic acid as a primary brightener additive coupled with a secondary brightener that cooperates synergistically with said ascorbic or isoascorbic acid.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention.

In order to practice the process of the invention and improve the electrodeposited reproducibility of the permalloy type alloy films an antioxidant such as ascorbic acid or isoascorbic acid is added to the electrolyte to retard and reverse the oxidation of the ferrous ion to ferric ion and increase the useful life of the electrolyte.

It has been found that the desired improvements are obtained with no degradation of the other properties when the concentration of the added antioxidant varies from about one gram per liter of solution to saturation, but that concentrations above 5 grams per liter of solution do not materially increase the effectiveness of the additive.

Typical permalloy type electrolytes found to benefit by inclusion of these antioxidants include solutions that deposit the following alloys:

nickel-iron
nickel-iron-phosphorus
nickel-iron-cobalt
nickel-iron-copper
nickel-iron-cobalt-phosphorus
nickel-iron-copper-phosphorus
nickel-iron-copper-cobalt, and
nickel-iron-copper-cobalt-phosphorus.

Generally the anion has no effect and baths can be compounded from chlorides, sulfates, sulfamates or mixtures thereof without adversely affecting the action of the ascorbic or isoascorbic acid. Normally a buffer such as boric acid is added to stabilize the pH of the electrolyte during the electrodeposition. In addition a primary brightener such as saccharin and an antipitting agent such as sodium lauryl sulfate are also employed in the electrolytic bath. In permalloy type alloy baths, the use of an additional sulfur-containing primary brightener, such as saccharin, is permissible because these films are used in an environment in which the possibilities of corrosive attack are minimal. In addition, the codeposition of the

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necessary iron to arrive at a film with the desired magnetic properties already results in a material exhibiting extremely poor corrosion resistance.

The operable range of pH of the subject permalloy type alloy electrolytic bath is 1-5 with a pH of 2.5 being preferred. The current density used may be from 5 to 30 ma./cm.² with a current density of 20 ma./cm.² being preferred. The bath temperature may vary from 15° C. to 95° C. with 25° C. being the preferred temperature. Although it is possible to use insoluble anodes such as Pt, or alloy anodes of the same composition as the deposit, it is preferred in the practice of this invention to use nickel anodes and replenish the iron content of the electrolyte by the addition of appropriate iron containing compounds.

Suitable substrates include conductors such as copper or copper bearing alloys, gold, silver, platinum, and stainless steel or other metals; or nonconductors such as glass, ceramic, plastics, etc., made conductive by depositing thereon a conductive coating such as copper, gold, etc., by techniques such as vacuum deposition, electroless deposition, sputtering, thermal decomposition, etc.

The permalloy type films prepared according to the process of the invention are used as logic elements or memory devices in computer mechanisms.

The following specific examples will illustrate in detail the practice of the process of the invention:

EXAMPLE 1

A Pyrex glass cover slip rendered conductive by sputtering onto its surface a thin layer of Cr followed by approximately 300 Å. of gold is degreased by spraying with acetone, followed by water rinsing, and is made the cathode in the following electrolytic nickel-iron bath containing water as the solvent:

NiCl ₂ ·6H ₂ O	-----gm./l. of solution---	200
FeCl ₂ ·4H ₂ O	-----do-----	3
H ₃ BO ₃	-----do-----	25
Sodium saccharin	-----do-----	0.8
Sodium lauryl sulfate	-----do-----	0.4
NaH ₂ PO ₂ ·H ₂ O	-----do-----	0.5
pH	-----	2.5
Temperature	-----° C---	25
Time of plating	-----minutes---	10
Anode	-----	Nickel sheet
Current density	-----ma./cm. ² ---	20
Aligning field (approx.)	-----oersteds---	35

The Ni-Fe-P film deposited (in the 35 oersted aligning field) was extensively cracked and did not adhere to the substrate. Because of the condition of the film, it was not possible to measure the magnetic parameters.

EXAMPLE 2

The process of Example 1 is repeated except that 5.0 gm./l. of isoascorbic acid is added. The Ni-Fe-P film produced is about 20,000 Å. thick and is bright, strongly adherent, and continuous. The magnetic properties were measured in a 60 cycle B-H loop tracer. The coercive force (H_c) equals 0.8 oersted, anisotropy field (H_k) equals 2.5 oersteds, and the squareness ratio (B_r/B_s) in the easy direction equals about 1.0.

EXAMPLE 3

A stainless steel panel (1 in. x 3 in.) is anodically cleaned in a solution of 60 gm./l. Na₃PO₄ and 30 gm./l. of NaOH. It is next rinsed in running water and acid dipped in a 10% by volume H₂SO₄ solution. It is again water rinsed and examined for surface cleanliness by looking for water breaks. The panel is then made the

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cathode in the following solution under the conditions set forth:

NiSO ₄ ·6H ₂ O	-----gm./l. of solution---	218
FeSO ₄ ·7H ₂ O	-----do-----	4.8
H ₃ BO ₃	-----do-----	25
Sodium saccharin	-----do-----	0.8
Sodium lauryl sulfate	-----do-----	0.4
NaH ₂ PO ₂ ·H ₂ O	-----do-----	0.5
pH	-----	2.5
Temperature	-----° C---	25
Time of plating	-----minutes---	10
Current density	-----ma./cm. ² ---	20
Aligning field	-----oersteds---	35
Anode	-----	Nickel sheet

The Ni-Fe-P film deposited showed evidence of stress cracking and when an attempt was made to remove the film from the stainless steel backing the film crumbled and could not be recovered intact.

EXAMPLE 4

The process of Example 3 is repeated except that 5.0 gm./l. of ascorbic acid is added to the electrolyte. A Ni-Fe-P film having a thickness of 20,000 Å. is produced. The film is bright, crack free and remains intact when removed from the stainless steel backing. The magnetic properties of the film were measured in a 60 cycle B-H loop tracer. The coercive force (H_c) equals 1.0 oersted, the anisotropy field (H_k) equals 2.5 oersteds and squareness ratio (B_r/B_s) in the easy direction is approximately 1.0.

EXAMPLE 5

A copper sheet (1 in. x 3 in.) is cathodically cleaned in a solution of 60 gm./l. trisodium phosphate and 30 gm./l. of sodium hydroxide. It is now rinsed in running water and acid dipped in a 10% by volume H₂SO₄ solution. It is again water rinsed and examined for surface cleanliness by looking for water breaks. The copper sheet is then made the cathode in the following solution under the conditions set forth:

Ni ⁺⁺ (as sulfamate)	-----gm./l---	113
Fe ⁺⁺ (as sulfamate)	-----gm./l---	2.82
H ₃ BO ₃	-----gm./l---	30
Sodium lauryl sulfate	-----gm./l---	0.4
NaH ₂ PO ₂ ·H ₂ O	-----gm./l---	0.5
pH	-----	2.5
Temperature	-----° C---	20
Current density	-----ma./cm. ² ---	15
Time of plating	-----minutes---	15
Aligning field	-----oersteds---	35
Anode	-----	Nickel sheet

The Ni-Fe-P film deposited exhibited many cracks and was highly stressed.

EXAMPLE 6

The process of Example 5 is repeated except that 3.0 gm./l. of isoascorbic acid is added to the electrolyte. A Ni-Fe-P film having a thickness of approximately 20,000 Å. is produced. The deposited film is bright, crack free, and strongly adherent. The magnetic properties of the film when measured in a 60 cycle B-H loop tracer were as follows:

Coercive force (H_c)=1.8 oersteds.
Anisotropy field (H_k)=3.1 oersteds.
Squareness ratio (B_r/B_s)=approximately 1.0 (in easy direction).

In Examples 1-6, the ratio of Ni to Fe in the deposit is nominally 80 to 20 (or 4:1) and the phosphorus content is approximately 1% by weight of the total film.

Ex. No.	Ni ⁺⁺ , gm./l.	Fe ⁺⁺ , gm./l.	Co ⁺⁺ , gm./l.	Cu ⁺⁺ , gm./l.	NaH ₂ PO ₄ ·H ₂ O, gm./l.	Antioxidant, gm./l.	Time, min.	pH	C.D.	H ₃ BO ₃ , gm./l.	Sodium saccharin, gm./l.	Sodium lauryl sulfate, gm./l.	Results
7	48	1.44					10	2.5	20	25	0.8	0.4	Slight cracking, adherent.
8	48	1.44			0.5		10	2.3	20	25	0.8	0.4	C-NA.
9	48	1.44	3				10	2.5	20	25	0.8	0.4	Slight cracking, adherent.
10	48	1.44	3		0.5		10	2.5	20	25	0.8	0.4	C-NA.
11	60	1.7		0.5			10	2.0	20	30	0.8	0.4	Slight cracking, adherent.
12	60	1.7		0.5	0.5		10	2.0	20	30	0.8	0.4	C-NA.
13	113	2.82	3	0.5			15	2.8	15	30		0.4	NC-A.
14	113	2.82	3	0.5	0.5		15	2.8	15	30		0.4	C-NA.
15	48	1.44				5 (E)	10	2.5	20	25	0.8	0.4	NC-SA.
16	48	1.44			0.5	5 (E)	10	2.3	20	25	0.8	0.4	NC-SA.
17	48	1.44	3			3 (A)	10	2.5	20	25	0.8	0.4	NC-SA.
18	48	1.44	3		0.5	3 (A)	10	2.5	20	25	0.8	0.4	NC-SA.
19	60	1.7		0.5		3 (E)	10	2.0	20	30	0.8	0.4	NC-SA.
20	60	1.7		0.5	0.5	3 (E)	10	2.0	20	30	0.8	0.4	NC-SA.
21	113	2.82	3	0.5		5 (A)	15	2.8	15	30		0.4	NC-SA.
22	113	2.82	3	0.5	0.5	5 (A)	15	2.8	15	30		0.4	NC-SA.

C-NA (cracked, not adherent); NC-A (not cracked, adherent); NC-SA (not cracked, strongly adherent); (E)=isoascorbic; (A)=ascorbic.

In summary, it is seen that in the practice of this invention, the nickel ion concentration can vary from 48 to 113 gm./l., the iron ion concentration can vary from 1.44 to 2.82 gm./l., and the cobalt ion concentration can vary from 0 to 3 gm./l. Other ranges in which the invention can be practiced are a pH varying from 2.0 to 2.8, H₃BO₃ varying between 25 and 30 gm./l., current density between 15–20 ma./cm.², and a time of deposition between 10–15 minutes.

In Examples 7–22, the ratio of Ni to Fe in the deposited film is nominally 80–20 (or 4:1); the phosphorus content is approximately 1% by weight of the total film, when present; the cobalt content is approximately 6% by weight of the total film, when present; and the copper content is approximately 7.5% by weight of the total film, when present.

The molar ratio of additive to nickel optionally varies from 0.003 to 0.035, but, since it is permissible to use saturation concentrations of the additive, this ratio may, in some cases, be substantially higher. One can readily calculate this molar ratio from the examples given above. Since 1 gram of isoascorbic acid equals 0.0057 mol, so 5 gms. equals 0.0285 mol; 48 gms. of Ni⁺⁺ equals 0.818 mol; and 113 gms. of Ni⁺⁺ is 1.925 mol. The range of the molar ratios of additive to nickel is obtained by dividing 1 gm. of additive by 113 gms. or

$$\frac{0.0057}{1.925} = 0.003$$

(the low value of the range). The high value of the range is obtained by dividing 5 gms. of additive by 48 gms. of Ni⁺⁺, namely, 0.0285/0.818, yielding 0.035.

Thus it has been shown that it has been difficult to reproducibly electrodeposit permalloy type alloy films that do not crack, peel or exfoliate spontaneously. By the use of the antioxidants, ascorbic acid or isoascorbic acid, it is now possible to electrodeposit these permalloy type alloy films with no degradation of properties by eliminating the stresses which caused the cracking, peeling or spontaneous exfoliation of the films. A further benefit derived from the use of the antioxidants results in a permalloy type alloy film that is strongly adherent and may be prepared in sufficient thicknesses to be self-supporting when removed from a strippable substrate.

That aspect of the invention that obtains a bright nickel deposit will now be described with respect to a Watts' bath.

A typical Watts' electrolyte would comprise the following solution:

Bath conditions

30	NiSO ₄ ·6H ₂ O	gm./l.	300
	NiCl ₂ ·6H ₂ O	gm./l.	45
	H ₃ BO ₃	gm./l.	40
	Wetting agent.		
	(Na Lauryl SO ₄)	gm./l.	0.4
35	pH		3.5
	Temperature	° C.	65
	Current density	asf.	40
	Thickness (ca. 30 minutes)	ca.	0.001"

To this bath is added 1 gm.-saturation/liter, with 5 gm./l. being preferred, of isoascorbic or ascorbic acid, the former being an isomer of vitamin C. A suitable secondary brightener was employed in conjunction with the primary brightener in the standard Watts' bath. Tests upon such samples of deposited nickel indicated a considerable diminution in the metal corrosion of such samples as compared with samples that were obtained from baths using sulfur-containing primary brighteners. It has been found that coumarin and 2-butyne-1,4-diol are leveling agents that cooperate synergistically with isoascorbic and ascorbic acids. For the selected bath noted above, a quantity of 0.1–2.5 gm./l. of 2-butyne-1,4-diol, preferably 0.35 gm./l. or 4 millimols per liter, has been found to produce a bright, corrosion-resistant nickel deposit. For coumarin, 0.1 to 4 gm./l., preferably 0.5 gm./l., is used with the bath. In general, the classes of acetylenic alcohols and coumarins are found to cooperate synergistically with isoascorbic and ascorbic acids and examples of such representative alcohol compounds are given in Table I of U.S. Patent 3,002,902 noted above. Representative coumarin compounds are coumarin, hydroxycoumarins, homocoumarins and chlorocoumarins.

To summarize the art of electrodeposition of nickel or nickel alloys has been searching for bright nickel deposits that are corrosion-resistant and relatively inexpensive to obtain, and for permalloy deposits that do not peel, exfoliate or crack spontaneously. At present, nickel deposits are corrosion-resistant when no primary brighteners are used in the bath. Since all known primary brighteners contain sulfur, the absence of the primary brighteners enhances the corrosion-resistance of the deposited nickel. However, secondary brighteners must be employed to promote leveling, but such promotion is limited because of the inherent stress-producing characteristic of the added secondary brightener. The

end product therefore is corrosion-resistant but relatively poor in leveling, usually stressed. If attempts are made to increase the leveling and brightness of these deposits, the residual stress rapidly builds up to very high levels and the deposits tend to peel, crack and exfoliate and exhibit very limited ductility. By the use of isoascorbic acid or ascorbic acid, one obtains brilliant, corrosion-resistant, leveling, stress-free nickel deposits because the isoascorbic acid or ascorbic acid, in some manner, behaves as the classical primary brighteners, but does not contain sulfur. In short, a class of primary brighteners has been discovered which behave synergistically with most secondary brighteners and gives rise to highly corrosion-resistant nickel deposits. Another desirable characteristic of this invention results from the fact that much greater leveling semi-bright nickel deposits are obtainable. The latter is obtainable because the new primary brighteners, isoascorbic and ascorbic acids, when added to conventional semi-bright baths permit the presence of higher concentrations of the secondary brightener without impairing the ductility or increasing the residual stress of the deposited nickel.

Furthermore, ascorbic and isoascorbic acids serve the role of an antioxidant in electrolytes employed in the deposition of magnetic films of a nickel-iron alloy; such acids serving to refund and reverse the oxidation of the ferrous ion to ferric ion so as to improve the type of magnetic film produced as well as to prolong the life of the electrolyte.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. An aqueous acidic bath for the electrodeposition of a crack free nickel-iron alloy containing nickel ions, iron ions and an antioxidant selected from the group consisting of ascorbic acid and isoascorbic acid in an amount sufficient to produce a crack-free electrodeposit.

2. The bath of claim 1 wherein the antioxidant is present in the bath in the range from 1 to 5 gm./l. of solution.

3. An aqueous acidic bath for the electrodeposition of a crack free nickel-iron film comprising:

48.00-113.00 gm./l. of solution of Ni^{++} ;
1.44-2.82 gm./l. of solution of Fe^{++} ;
0-0.50 gm./l. of solution of Cu^{++} ;
0-3.00 gm./l. of solution of Co^{++} ;
0-0.50 gm./l. of solution of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$; and
1.00-5.00 gm./l. of solution of an antioxidant selected from the group consisting of ascorbic acid and isoascorbic acid.

4. An aqueous acidic bath for the electrodeposition of a crack free nickel-iron alloy film comprising:

48.00-113.00 gm./l. of solution of Ni^{++} ;
1.44-2.82 gm./l. of solution of Fe^{++} ;
0-0.50 gm./l. of solution of Cu^{++} ;
0-3.00 gm./l. of solution of Co^{++} ;
0-0.50 gm./l. of solution of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$; and
1.00-5.00 gm./l. of solution of an antioxidant selected from the group consisting of ascorbic acid and isoascorbic acid.

5. The bath of claim 4 wherein the antioxidant is ascorbic acid.

6. The bath of claim 4 wherein the antioxidant is isoascorbic acid.

7. An aqueous acidic bath for the electrodeposition of a crack free nickel-iron-phosphorus alloy film comprising:

48.00-113.00 gm./l. of solution of Ni^{++} ;
1.44-2.82 gm./l. of solution of Fe^{++} ;
0.50 gm./l. of solution of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$; and
1.00-5.00 gm./l. of solution of an antioxidant selected from the group consisting of ascorbic acid and isoascorbic acid.

8. The process of electrodepositing a crack free, adherent nickel-iron alloy comprising the steps of:

(A) providing a clean, conductive substrate surface;
(B) subjecting said substrate surface to electrolytic action as the cathode in an aqueous acidic electrolyte comprising:

48.00-113.00 gm./l. of solution of Ni^{++} ;
1.44-2.82 gm./l. of solution of Fe^{++} ;
0-0.50 gm./l. of solution of Cu^{++} ;
0-3.00 gm./l. of solution of Co^{++} ;
0-0.50 gm./l. of solution of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$; and
1.00-5.00 gm./l. of solution of an antioxidant selected from the group consisting of ascorbic acid and isoascorbic acid to electrodeposit said nickel-iron alloy.

9. The process of electrodepositing a crack free, adherent nickel-iron-phosphorus alloy film comprising:

(A) providing a clean, conductive substrate surface;
(B) subjecting said substrate surface of electrolyte action as the cathode in an aqueous acidic electrolyte comprising:

48.00-113.00 gm./l. of solution of Ni^{++} ;
1.44-2.82 gm./l. of solution of Fe^{++} ;
0.50 gm./l. of solution of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$; and
1.00-5.00 gm./l. of solution of an antioxidant selected from the group consisting of ascorbic acid and isoascorbic acid to electrodeposit said nickel-iron-phosphorus film.

10. The process of preparing a continuous self-supporting nickel-iron alloy film comprising the steps of:

(A) providing a clean, conducting strippable substrate surface;
(B) subjecting said substrate surface to electrolytic action as the cathode in an aqueous acidic electrolyte comprising:

48.00-113.00 gm./l. of solution of Ni^{++} ;
1.44-2.82 gm./l. of solution of Fe^{++} ;
0-0.50 gm./l. of solution of Cu^{++} ;
0-3.00 gm./l. of solution of Co^{++} ;
0-0.50 gm./l. of solution of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$; and
1.00-5.00 gm./l. of solution of an antioxidant selected from the group consisting of ascorbic acid and isoascorbic acid to electrodeposit a continuous self-supporting nickel-iron alloy film;

(C) rinsing and drying said plated alloy film; and
(D) stripping said continuous and self-supporting alloy film from said substrate.

11. The process of electrodepositing a crack free adherent nickel-iron-phosphorus alloy film comprising:

(A) providing a clean, conductive substrate surface;
(B) subjecting said substrate surface to electrolytic action as the cathode in an aqueous acidic electrolyte comprising:

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	-----gm./l. of solution--	200.0
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	-----do-----	3.0
H_3BO_3	-----do-----	25.0
Sodium saccharin	-----do-----	0.8
Sodium lauryl sulfate	-----do-----	0.4
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	-----do-----	0.5
Isoascorbic acid	-----do-----	5.0
pH	-----do-----	2.5

(C) providing an anode of a sheet of nickel, a bath temperature of 25°C ., and a current density of 20 ma./cm.² between said cathode and said anode; and
(D) plating said cathode in the presence of a magnetic field of 35 oersteds for a period of approximately 10 minutes so as to electrodeposit said nickel-iron-phosphorus alloy film.

12. The process of electrodepositing a crack free adherent nickel-iron-phosphorus alloy film comprising:

(A) providing a clean, conductive substrate surface;
(B) subjecting said substrate surface to electrolytic ac-

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tion as the cathode in an aqueous acidic electrolyte comprising:

	Gm./l. of solution
NiCl ₂ ·6H ₂ O	200.0
FeCl ₂ ·4H ₂ O	3.0
H ₃ BO ₃	25.0
Sodium saccharin	0.8
Sodium lauryl sulfate	0.4
NaH ₂ PO ₄ ·H ₂ O	0.5
Ascorbic acid	5.0

- (C) providing an anode of a sheet of nickel, a bath temperature of 25° C., and a current density of 20 ma./cm.² between said cathode and said anode; and
 (D) plating said cathode in the presence of a magnetic field of 35 oersteds for a period of approximately 10 minutes so as to electroplate said nickel-iron-phosphorus alloy film.

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ROBERT K. MIHALEK, *Primary Examiner.*

JOHN H. MACK, *Examiner.*

¹⁵ G. KAPLAN, *Assistant Examiner.*