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## COATING OF ALUMINUM SUBSTRATES WITH A MAGNETIC MATERIAL

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The present invention relates to pre-plating processes for use in the production of electroless or electrodeposited coatings on aluminum bearing surfaces and, more particularly, to methods for preparing aluminum surfaces for electroless or electrodeposition with magnetic materials.

The electroless or electrodeposition of magnetic materials such as the ferromagnetic elements and alloys, and in particular, such as cobalt, nickel, iron, cobalt-nickel, cobalt-iron, nickel-iron, cobalt-phosphorus, nickel-phosphorus, iron-phosphorus, cobalt-nickel-phosphorus, cobalt-iron-phosphorus, nickel-iron-phosphorus, Alnico, Cunife, Permalloy, cobalt-platinum, iron-platinum, nickel-platinum or the like, find particular utility in the data processing art as a means for fabricating memory units in the form of recording drums, discs, tapes, planes, spots, rods, wires and the like. In general, there are a number of substrate materials available in the industry suitable for coating with magnetic material. For a number of reasons, including low mass and easy workability, aluminum bearing substrates have become popular.

However, in several aspects an aluminum bearing substrate has difficulties associated with the electroless or electrodeposition of a magnetic material thereto, such as those enumerated above. One reason for this is that aluminum is an active metal and is usually found with a passive oxide film on its surface. In order to deposit coatings on aluminum substrates with a high degree of adhesion, this oxide film must first be removed. If such is done in an atmosphere where the bare aluminum is not in any way protected from further oxidation, this oxide film persistently forms and reforms. Hence, in order to electroplate onto an aluminum or aluminum alloy surface it is conventional in the prior art to remove or replace the oxide by a dipping in a zincating solution. This serves to replace the oxide present with a protective immersion-deposit of zinc. The thin zinc coating can be plated with a thick copper overlayer and thereafter magnetic materials or some other conventional deposit can be electrolessly (after suitable sensitization and activation) or electrodeposited thereover. It is not practicably possible to electrolessly or electrodeposit directly onto the zinc coated substrate without this copper-type overlayer. This zincating process suffers from some other inherent disadvantages, besides being difficult to overplate and requiring a heavy copper overcoating. Under certain conditions this zinc coating tends to migrate, thus eventually giving rise to void areas under the copper and the appearance of blisters. If sufficient zinc diffuses into the copper overlayer, metastable compounds may form thus giving rise to poor adhesion of the entire deposited film to the aluminum substrate. In addition, zincate baths require a very careful substituent balance and parameter, such as pH, temperature, time, control for successful operation. The prior art is replete with various zincate formulations which have been tried, but do not solve these problems. The present invention does solve them, however, by replacing the zincating process with a process for immersion-depositing a coating of copper containing from 0.1% to 10% tin from a cyanide-stannate bath.

A major disadvantage of this conventional zincate coating is the poor and non-uniform adhesion to the aluminum substrate, which is the reason for the blistering or lifting

of zincated coatings commonly observed. Part of the reason is the above mentioned difficulty of deposition onto a zincate coating; but this difficulty is intensified by the high residual stresses characteristic in the magnetic materials commonly electrolessly or electrodeposited for data processing applications. These materials commonly develop surface stresses during the deposition operation or thereafter. Such stressing may take the form of a tensile stress, such as most cobalt-nickel alloys exhibit and which produces a concave lifting of the deposited magnetic coating, or may result in a compressive stress, such as certain types of nickel coatings exhibit, producing a convex lifting. The only remedy for such blistering is to achieve extremely good adhesion over the entire interface between the deposited coating and the substrate by means of the preplating process. Zincate coatings cannot achieve this consistently. However, the excellent adhesion achieved by the copper-tin coating of my invention has been sufficient to remedy this blistering problem.

A second cause of blistering of the prior art zincated substrates is the self-diffusion, or transmigration, properties inherent in zinc and zinc alloys. This means that the zinc in such alloys will commonly migrate during life into a copper overlayer and form a metastable alloy at the interface between the undercoating and the deposited magnetic coating. This results in blistering, lifting and poor adhesion at this interface. Replacement of the prior art zincate undercoatings with the copper-tin coating of my invention remedies this problem also, as no transmigration or diffusion results and no blistering is observed.

A further advantage in using my inventive technique is that the copper-tin coating is easier to deposit than the zincate coating because the constituent balance can vary within wide limits (as can the deposition parameters of time, pH, temperature and substrate) without adversely affecting the composition and characteristics of the resultant coating. While the copper-tin coating is a hospitable substrate for subsequent electroless (after suitable sensitization) or electrodeposition of magnetic material, it is also a hospitable substrate for further heavy electrodeposits of copper. In this latter regard, the copper-tin coating is also more readily electroplated than the zincate coatings now available in the art. It may be noted that the presence of some tin is significant. While we find it possible to deposit copper coatings containing no tin, it has also been found that the adhesion of subsequent electroless or electrodeposits to the aluminum bearing substrate is definitely inferior to the adhesion value found when as little as 0.1% tin is present in the copper coating. This adhesion value reaches a maximum when the tin content is about 0.7% and remains constant up to the maximum tin deposited by this procedure which is about 10%.

Hence, the substitution of the copper-tin undercoating of my invention for the conventional zincate coating as an intermediary between an electroless or electrodeposited magnetic coating and an aluminum-bearing substrate is of patentable and inventive significance because: it is easier to deposit on the substrate, it is easier to electrolessly or electrodeposit upon and does not require an overcoating to which electroless or electrodeposition is feasible, such as the bulky copper coating conventionally deposited over zincate undercoatings and does not exhibit the adhesion inadequacies of the zincates, nor the blistering due to a transmigration of zinc—problems which are intensified by the high residual stresses inherent in deposited magnetic materials. Hence, my precoating method is not only unique in the art, but solves many problems.

In connection with solving the above problems by substituting my copper-tin coating for zincate coatings on an aluminum-bearing substrate, I have found that, although all aluminum-bearing alloys are suitable for this process,

some are more suitable than others and for optimum results relatively pure aluminum substrate is required.

Besides solving the problem of finding a more suitable undercoating than the conventional zincates, my inventive process also involves a means for solving another bothersome problem associated with processing aluminum and aluminum alloy objects in alkaline processing solutions, namely removing hydrated alumina. The alumina precipitate usually assumes the form of a hard refractory scale which is troublesome because it adheres to the processing vessels and other equipment, as well as to the substrate in some cases. Formation of the hydrated alumina scale on the substrate and processing vessels is a vexing problem in this art and seems to be inherent in the use of any alkaline bath. This hydrated alumina arises from the reaction between metallic aluminum and hydroxyl ion. The scale formed is rough and tough and obviously will mar the surface of the substrate permanently as well as permanently coat the surface of the vessel used for processing. This scale is virtually impossible to remove. My inventive process provides the answer to this problem by the addition of a polyhydric alcohol to the bath whereby the precipitation of this alumina scale is somewhat retarded and when this alumina does precipitate, it does so as a soft, bulky and easily filtered precipitate readily removed by filtration. The addition of this polyhydric alcohol to the processing bath in no way changes the rate of deposition or the composition of the copper-tin coating, all other conditions being equal. All polyhydric alcohols stable and sufficiently soluble in the processing solution so far examined have been effective, but the preferred polyhydric alcohols are chosen from the group consisting of sorbitol, mannitol, pentaerythritol, hexoses, pentoses, saccharides, polysaccharides, ketoses and polyethylene and polypropylene glycols and mixtures thereof.

Hence, my invention constitutes a step forward in the art by solving some imposing plating problems and by yielding the above noted improvement over conventional methods. More particularly, my inventive process is an improvement in methods for preparing aluminum-bearing substrates for electroless and electrodeposition, which has special advantages for deposit-materials having high residual stresses, such as the magnetic materials commonly deposited for data processing applications. These improvements involve the immersion of the substrate in a copper-tin bath so as to yield a replacement coating which will prevent the reformation of aluminum oxides and also be easily electrolessly or electrodeposited upon. The immersion coating bath comprises generally: sodium cyanide, sodium hydroxide, copper cyanide and sodium stannate. Further a small amount of polyhydric alcohol is added to the bath to inhibit the formation of hydrated alumina scale and to facilitate the filtration of the alumina precipitate.

Therefore, it is an object of the present invention to provide an improved preplating coating for aluminum-bearing substrates.

A further object of the invention is to provide a copper coating containing up to 10% tin as a substitute for conventional zincate undercoatings on aluminum-bearing substrates to eliminate the problems attendant therewith.

Yet another object is to provide a copper-tin dip for aluminum-bearing substances to be electrolessly or electrodeposited upon.

Another object is to deposit magnetic materials upon aluminum substrates with convenience and high adhesion.

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

In accordance with the present invention, an immersion bath is provided for depositing electrolessly, or by immersion, a copper undercoating containing up to 10%

tin on an aluminum-bearing substrate. The ranges of electrolyte constituents and the bath parameters are summarized in Table I and in the accompanying description thereof.

TABLE I

	Maximum	Minimum	Preferred	Optimum
Cu <sup>+</sup> (gm./l.)	150	1.6	13-35	16.5
CN <sup>-</sup> (gm./l.)	175	3.0	15-50	21.9
Cu/Sn	(1)	0.2	0.5-10	0.91
SnO <sub>2</sub> (gm./l.)	100	0	15-50	23.2
Polyhydric ale. (gm./l.)	100	0	0.1-25	0.75
OH <sup>-</sup> (gm./l.)	100	1.0	2.0-15	2.13
pH at 25° C.	13.5	7.0	11-12	11.4
Temp. ° C.	95	20.0	60-90	75.0
Imm. Time (sec.)	180	5.0	25-60	30.0

<sup>1</sup> ∞ (No Sn).

The copper and tin ions may be conveniently supplied by cuprous cyanide and sodium stannate, respectively, although any salt yielding the correct specific active ions may be used. The range of aluminum-bearing substrates which are suitable for this process is wide and includes such aluminum alloys as EC: 1100, 3003, 5050, 5557, 6061 and 7075, as well as other equivalents thereof which will be known to those skilled in the art.

This electrolyte bath, which is typical of the present invention, was prepared as follows: 5.0 grams of sodium hydroxide and 28.6 grams of sodium cyanide were dissolved in about 500 milliliters of water. After solution was effected, 23.2 grams of cuprous cyanide were added and dissolved. This was followed by the addition of 41 grams of sodium stannate (trihydrated) and 0.75 gram of pentaerythritol. Water was added to bring the volume to one liter and the pH at 25° C. was 11.4.

In order to aid those skilled in the art in the use of electrolytic immersion baths like that of the present invention to prepare aluminum-bearing substrates for electroless or electrodeposition, the following details of the substrate preparation and immersion steps, together with the electroless or electrodeposition procedures, will now be described.

#### Example 1

A copper-tin immersion bath was prepared exactly as described above and a rectangular sample of 1100 aluminum was cleaned by dipping in methylethyl ketone followed by a running, cold water rinse. The sample was 1 inch wide by 4 inches long by  $\frac{1}{16}$  inch thick. It was then immersed in the copper-tin bath for 30 seconds at a temperature of 75° C. Much gassing was evident at the outset of the test, but it was considerably reduced after the 30 seconds immersion time. The sample piece was next rinsed in a running, cold water rinse and was found to have a bright, adherent, blister-free protective film containing 94% copper and 6% tin. A magnetic cobalt-phosphorus alloy was then electrodeposited to a thickness of one micron, as described in a co-pending application of the same inventor, Serial No. 50,568, filed Aug. 19, 1960, now U.S. Patent 3,202,590. Again, the coating was found to be bright, uniform and blister free. A 180° "pull-back" adhesion test gave an adhesion value in excess of 5000 grams/inch of width.

#### Example 2

The test described in Example 1 was repeated except that the pentaerythritol was not included in the immersion processing bath all other conditions being constant. X-ray fluorescent analysis of the immersion deposit determined that the composition was 96.2% copper and 5.8% tin. After electrodeposition of the magnetic cobalt-phosphorus alloy as described in Example 1, an adhesion value in excess of 5000 grams/inch of width was found in this case also.

## Example 3

The test described in Example 1 was repeated except that the sodium stannate was not included in the immersion processing bath, all other conditions being constant. The deposit again was bright, adherent and blister-free. After electrodeposition of the magnetic cobalt-phosphorus alloy described in Example 1, an adhesion value of only 2300 grams/inch of width was found, as opposed to the 5000 plus grams/inch of width adhesion found with the stannate baths above.

## Example 4

The test described in Example 1 was repeated using the immersion processing bath as described, as well as the same conditions for preparation. The copper-tin film was bright, adherent, and blister-free after rinsing. The surface of the film was activated by dipping for 30 seconds in a solution containing 0.1 gm./l. palladous chloride and 10 m./l. of concentrated hydrochloric acid at 25° C. This activated surface had electrolessly deposited thereon, to a thickness of 1 micron, a magnetic cobalt-nickel-phosphorus alloy, as described in a co-pending application of the same inventor and Bernard Leland, Ser. No. 197,618, filed May 25, 1962, now U.S. Patent 3,238,061. The adhesion value found by the described test was 4800 gms./inch of width.

Further examples will be found in Table II:

TABLE II

Example No.	5	6	7	8	9	10
Cu <sup>+</sup> (gm./l.)	16.5	13	35	1.6	75	16.5
CN <sup>-</sup> (gm./l.)	21.9	15	50	3.0	175	21.9
Cu/Sn	0.91	0.52	10	0.9	15	0.91
Polyhydric Alc. (gm./l.)	0.75 PE	15 PE	15 Sorb	*100	1.5 PE	0.75 PE
OH <sup>-</sup> (gm./l.)	2.13	2	15	1	100	2.13
pH at 25° C	11.4	11.1	12.7	8.1	13.5	11.4
Temp., ° C	75	60	90	20	75	75
Imm. Time (Seconds)	30	25	90	180	30	30
Overcoating	CoP EP	CoP EP	CoNi EP	CoNi EP	NiFe EP	CoPt EL
Adhesion (gm./inch)	>5,000	4,900	>5,000	>5,000	>5,000	>5,000
Aluminum Alloy	7,075	EC	3,003	3,003	5,050	5,557
Percent Cu	95.1	94.2	98.4	94.1	98.3	94.7

  

Example No.	11	12	13	14	15
Cu <sup>+</sup> (gm./l.)	16.5	16.5	16.5	16.5	16.5
CN <sup>-</sup> (gm./l.)	21.9	21.9	21.9	21.9	21.9
Cu/Sn	0.91	0.2	0.91	0.91	0.91
Polyhydric Alc. (gm./l.)	10 Mann	7.5 Glu	22.5 Suc	0.05 SS	5 PE
OH <sup>-</sup> (gm./l.)	2.13	2.13	2.13	2.13	2.13
pH at 25° C	11.6	11.0	11.2	11.4	11.7
Temp., ° C	75	75	75	75	75
Imm. Time (Seconds)	30	30	30	30	30
Overcoating	Co EP	Ni EP	NiFe EP	Fe EP	Co EL
Adhesion (gm./inch)	>5,000	4,500	>5,000	>5,000	>5,000
Aluminum Alloy	6,061	7,075	7,075	7,075	7,075
Percent Cu	99.3	99.9	94.3	94.0	94.4

Abbreviation For Table II.—CoP, Cobalt-Phosphorus; CoNi, Cobalt-Nickel; EL, Electroless Plated; EP, Electroplated; Glu, Glucose; Mann, Mannitol; PE, Pentaerythritol; \*PEG300, Polyethylene Glycol 300 (a product of UCC); Sorb, Sorbitol; SS, Soluble Starch; Suc, Sucrose.

In the above tests, it was always found that it was easy to electrolessly or electrodeposit to the copper-tin coating and that the resulting adherence was high. No blistering or lifting due to residual stresses of the electrolessly or electrodeposited magnetic material was observed.

A distinct phenomenon was noted while the immersion dip was taking place. The presence of the polyhydric alcohol caused a light, fluffy precipitate of alumina, rather than the conventional alumina hydrate scale. This precipitate is desirable since it may be easily filtered out, using conventional techniques for the removal of such precipitates from solution. Filter aids such as are commonly used for the filtration of cyanide solutions may be used in this regard with no deleterious effects. Suitable alcohols, equivalent to the polyhydric alcohol, for inducing a fluffy precipitate to form would be mannitol, sorbitol, pentaerythritol, polyethylene glycol, polypropylene

glycols, hexoses, pentoses, saccharides, polysaccharides and others generally known to those skilled in the art.

Other instances will suggest themselves to those skilled in the art wherein the instant improved method for facilitating and improving electroless and electrodeposition onto an aluminum-bearing substrate may be advantageously employed. One such instance would be in the coating of an aluminum-bearing tape substrate for application as a memory device in data processing equipment. The improved depositability and better adhesion, as well as the elimination of blistering and the need for the weighty copper overcoating, necessary when zincates are used, are significant advantages here, especially since metal tapes are becoming of increasing interest due to their higher mechanical strength and depositability as opposed to plastic tapes. Another apt use for the invention would be for coating an aluminum alloy drum with a magnetic material, again for use in data processing equipment. Other applications obvious to those skilled in the art will be apparent and the invention should not be considered as confined to the few embodiments described above.

While the invention has been particularly shown and described with reference to the preferred embodiment thereof, it will be understood by those skilled in the art that various changes in form, details, and constituents, and in steps in concentrations and ranges may be made

without departing from the spirit and scope of the invention.

What I claim is:

A method of coating an aluminum bearing substrate with a magnetic material incompatible with an aluminum oxide formed on the surface of said aluminum bearing substrate, said method comprising the steps of:

immersing said substrate in a copper-tin bath containing about 13 gm./l. to about 35 gm./l. Cu<sup>+</sup> and having a Cu/Sn ratio of about 0.5 to about 10 so as to protectively coat the substrate by displacement with a compatible, highly adherent, non-blistering layer consisting essentially of between 90% and 99.9% copper and between 10% and 0.1% tin, said bath also containing a polyhydric type alcohol so as to cause the precipitation of an easily filterable alumina from the bath and prevent the formation of alumina scale, and wherein said immersion step includes the step

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of filtering said bath so as to remove said alumina from the bath; and thereafter plating a magnetic material on said layer.

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