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1

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METAL TREATMENT

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ABSTRACT OF THE DISCLOSURE

A wire substrate, typically beryllium-copper, for subsequent plating with magnetic films for information storage is prepared by electrolytically eroding the wire continuously in an acid bath to remove the outer, Bielby layer, and subsequently depositing thereon metal, typically copper, to rebuild the substrate to the desired thickness. The reducing bath preferably includes a halogen additive.

The present invention relates to wire substrates of prescribed controlled configuration and metallurgy and to methods for continuously producing such. In particular, the invention relates to a novel wire substrate for plating magnetic films which has been electrolytically reduced and subsequently rebuilt with a copper deposit and polished; and to methods for continuously producing such.

Although workers in the art have before subjected wire substrates to acid baths, the novel bath composition and associated conditions taught according to the invention are surprisingly effective in producing results never before seen in the art, namely the continuous electrolytic reduction of a relatively rough wire to a prescribed thickness, including removing a major portion of the wire, while yet maintaining it relatively smooth. This reduction or "drawing" is especially apt for preparing a wire for deposition of a thin magnetic film, especially when followed by a continuous coating with copper in a relatively thick, yet smooth layer. The concept of chemically reducing a wire by a major portion of its diameter and then rebuilding the diameter somewhat by plating a smooth thick layer of copper is new in the art, especially when performed continuously, on-line. While acid dips have been provided in the art to treat wire surfaces, such as by etching a very minor portion of the wire for surface finishing and the like, no one has heretofore electrolytically "drawn" wire by re-forming it to assume a precise controllable diameter, doing so efficiently, and eliminating surface imperfections and with high smoothness. Drawing efficiency is also optimized according to the invention, by providing a plurality of electrolytic drawing cells, each removing a portion of the desired amount, interspersed by rinsing stations.

The reducing and coppering treatments are further improved when followed by a novel electro-polishing treatment which continuously and quickly smooths the substrate. For instance, the above steps and especially the electro-polishing can accept a wire having a roughness of over 40 units (STM) and reduce this to a maximum of about 4 units. The polishing bath includes sulfamic acid and is especially advantageous when used preparatory to dipping a wire into sulfamate baths (e.g. for magnetic plating).

The above wire-conditioning treatments have filled a need in the art for providing a chemical method for quickly and continuously forming wire to a prescribed precise diameter and high smoothness and providing it with a smooth substitute finish of copper or the like. This is especially advantageous in the art of depositing thin magnetic films upon such wires wherein standard drawn wire "off the shelf" has been hopelessly inadequate; and where even expensive specially-drawn wire is relatively

2

unsatisfactory. For instance, prior art wires have been impractical for efficient, reliable DRO (destructive read-out) films, let alone the fussier NDRO (non-destructive read-out) films; whereas the invention can provide a substrate for either.

For instance, prior art wires are commonly not controllably smooth enough and, more importantly, exhibit surface and subsurface discontinuities that are obviously intolerable, upsetting reproducibility of deposit uniformity, magnetic properties and the like. By contrast, the methods of the invention can accept a rough "off the shelf" wire and nonetheless derive precise, finished wire having no such discontinuities and a controlled reproducible smoothness of up to $\frac{1}{40}$ the thickness of a typical magnetic film (from 1 RMS–400 RMS).

It is thus an object of the present invention to provide an electrolytically-drawn wire of prescribed fine smoothness and precise diameter and to methods for producing such continuously and with high efficiency.

Another object is to provide such a wire which is electrolytically reduced in diameter by about a few mils with high smoothness and efficiency to be apt for subsequent deposition of thin magnetic films.

Another object is to provide such a reduced wire efficiently and continuously by using halogenated acid baths, i.e. baths having halogen additives, and by operating at prescribed high current densities.

Yet another object is to optimize this efficiency and improve smoothness by using a plurality of such baths interrupted by rinses.

Another object is to continuously produce such a wire substrate and additionally to rebuild a substantial portion of the removed diameter by a massive, yet smooth copper plating.

Yet another object is to so provide an electrolytically reduced, copper plated wire substrate continuously and to thereafter electro-polish it with an aqueous phosphoric acid-sulfamic acid solution to polish efficiently while preventing formation of oxidation sites.

Still another object is to continuously provide such wire treatment prior to plating a magnetic film of prescribed controlled properties; especially from sulfamate type baths.

In accordance with the present invention, a copper type wire will be selected for reduction to a prescribed, carefully controlled diameter and to a smooth finely-polished finish with a minimum of surface discontinuities both mechanical and metallurgical. The wire will be subjected to the electrolytic action of an aqueous phosphoric acid, chromic acid solution, preferably halogenated, at a prescribed high current density, chosen to be optimized for the particular bath composition. The drawn wire may then be partly rebuilt with a copper layer. This layer then is electro-polished to a prescribed smoothness in a phosphoric acid, sulfamic acid bath. It will be seen that the aforementioned novel drawing process, and as well as the associated copper plating and electro-polishing processes, are especially suited for preparing moving wire substrates continuously, and particularly for preparing wires for deposition of thin magnetic films thereon.

PRELIMINARY STEPS

A standard precision-drawn wire may be selected "off the shelf" for draw-forming according to the invention, being comprised of a copper alloy type metal and selected to exhibit a minimum of surface and subsurface imperfections, discontinuities, etc. It is preferred to specify a strong wire "core metal," such as a beryllium-copper alloy having good tensile strength and the like. This is especially true for cases where an appreciable layer of "subtrate-metal" (e.g. copper) is to be plated on this core as a substrate for magnetic films since the copper

is relatively soft and weak, although more desirable for plating efficiency and for magnetic properties of the plated film. A prescribed wire diameter will also be specified. Wires of from six to ten mils (thousandths of an inch) in diameter have been satisfactorily "drawn" and resurfaced according to the invention. Maximum surface roughness may also be specified, for instance, being kept below about #40 S.T.M. roughness (i.e. 40 micro-inches, peak-to-peak) although using the inventive techniques this becomes less critical. Roughness over about #6–#8 can be intolerable for magnetic thin film substrates since it is on the order of magnitude of film thickness. Standard drawn wire has more serious drawbacks for magnetic film plating, however, even when satisfactorily smooth. For instance, such wire is characterized by an external layer of surface and subsurface discontinuities, physical (i.e. topographical) and chemical, often called the "Bielby layer." The "Bielby layer" commonly includes deposits of oil, oxides, broken grains, stressed particles and the like which cannot accept plating satisfactorily. The invention removes such imperfections as seen below.

Preferably, the wire substrate is introduced at the beginning of a continuous magnetic plating line, being wound on a spool to be continuously drawn therefrom down the line through each treating station successively. For instance, in the following described steps it may be assumed that a beryllium copper wire is being continuously advanced at about 5 inches per minute and is charged at suitable electronic potentials at various treating stations therealong.

As the wire is unspooled, it is first introduced into a cleaning, or degreasing, station to remove organic and other contaminants. The degreasing bath is a solution which will not dissolve the beryllium copper appreciably; preferably comprising a mild "Enthone-75" emulsion at room temperature. This emulsion was found preferable, for instance, to a number of common acidic cleaning solutions having a dilute sulfuric acid constituent. The degreased wire is then passed through a rinsing station adapted to flush it with continuously-renewed clean water at room temperature. Subsequent treatments will prescribe like water rinses which may be understood to be of this general nature.

DRAWING

The wire is next introduced into a novel electrolytic drawing station adapted to reduce the imperfect (for magnetic plating) "off the shelf" wire to a precise diameter, while maintaining a smooth, continuous surface; doing so in an "on-line" continuous process with high efficiency. It will be seen that the novel drawing process according to the invention is adapted to remove a major portion of the wire diameter (up to about 50%; for example, about 4 mils from an approximate 8 mil wire). This major diameter reduction also acts, advantageously, to eliminate surface and subsurface, Bielby-Type discontinuities and impurities which can badly degrade the characteristics of following magnetic deposits. For instance, although standard drawn wire is more convenient and available for use, it characteristically has large (relative to magnetic film thickness) surface protuberances thereon from the drawing-dies, as well as some surface impurities, such as accluded grit, oxidation sites and the like. These surface discontinuities, physical and metallurgical, will prevent proper magnetic film formation. The described electrolytic reduction of the wire eliminates these imperfections very efficiently and in a continuous process, while also leaving the wire satisfactorily smooth. It will be recognized by those skilled in the art that a homogeneous uniform substrate is of prime importance for subsequent plating a copper strike and a magnetic film. The instant drawing process can easily maintain smoothness within acceptable tolerances, such as within ±0.15 mil. The baths prescribed by the instant drawing process also can be specifically employed to prepare a wire substrate for subsequent

copper plating by completely removing this Bielby layer.

To provide the prescribed novel electrolytic drawing action, the wire is run through an aqueous phosphoric-chromic acid solution, preferably including halogen additives and under high current density. The basic drawing bath preferably comprises dilute ortho-phosphoric acid in a major concentration together with lesser concentrations of sulfuric acid and chromic acid, as indicated, for instance for Baths 1_A, 1_B and 1_C below. It is preferred, for increased drawing efficiency, to add a prescribed halogen additive to such basic baths, as indicated below for Baths 1_{A-1} through 1_{B-3}. These additives advantageously optimize drawing efficiency at their characteristic operating ranges without significantly roughening the wire surface. To maintain smoothness and achieve maximum efficiency, one must keep within a prescribed current density range associated with each of these different exemplary "halogenated" baths as noted below. Of course, the bath temperature, acid concentrations and immersion times may equivalently be varied to effect this, as understood by those skilled in the art. Except where otherwise stated, it will be presumed that for the exemplary baths, immersion time is about 100 seconds, the wire being advanced at about 5 inches per minute continuously through two cells about 4 inches long (50 sec. per cell), for instance. For these examples, it will also be presumed that the baths are kept at about room temperature and that the cathode in each cell comprises a hollow inert (lead) cylinder disposed and shaped to provide a uniform field coaxially around the wire.

According to a feature of the invention, a plurality of such drawing stations (cells) are employed, each being followed by a rinsing station, the number of stations depending upon the thickness (layer depth) of wire to be removed and the smoothness desired. For instance, it has been found that baths 1_A, 1_B and 1_C may be used to form uniform wire of a 4.6 mil (±.1) diameter by removing about ½ to 1 mil from a 5–8 mil diameter wire having average surface discontinuities by using two 4 inch long cells with an intermediate water rinse. Roughness will also be reduced, in this case, from about #16 #14 STM. Using a single 8 inch cell for this "drawing" treatment, on the other hand, yields a considerably rougher wire surface.

Baths 1_A, 1_B and 1_C in Table I comprise "basic" or "standard" phosphoric acid baths found somewhat adequate for the described electrolytic drawing. Substitute basic, or standard aqueous acidic baths may be used, being adapted to attack beryllium copper and preferably be compatible with the aforementioned halogen additives. It is an advantageous characteristic of these baths that a high current density may be used therewith for quick metal removal, the maxima varying somewhat according to the bath constituents. It will be noted that current density for significant drawing effects can be varied widely, according to the bath used, ranging from under 100 to about 1000 ma./cm.^{2}.

TABLE I.—STANDARD DRAWING BATHS

Example	1_A	1_B	1_C
Orthophosphoric acid, ml	300	300	400
Water, ml	100	200	100
Sulfuric acid, ml	1	4	1
Chromic acid, gm	12	20	32
Maximum operating C.D. (approx.), ma./cm.^{2}	500	1,000	1,000

Table I shows that bath 1_A has essentially a total volume of 400 milliliters, and hence the concentration of the acid ingredients are: 750 ml./l. orthophosporic acid, 2.5 ml./l. sulfuric acid, and 30 gm./l. chromic acid. Similarly, bath 1_B has a volume of essentially 500 milliliters and hence it contains 600 ml./l. orthophosphoric acid, 8 ml./l. sulfuric acid, and 40 gm./l. chromic acid. In bath 1_C, for which Table I sets forth the acid amounts for 500 milliliters, the orthophosphoric acid concentration is 800 ml./l., the sulfuric acid concentration is 2 ml./l., and the chromic acid concentration is 64 gm./l.

However, it is preferred, as aforementioned, to "halogenate" such "standard" drawing baths, i.e. to modify them with Halogen additives, especially for more efficient continuous operation. Hence, a number of more preferable electrolytic drawing baths including Halogen addition agents according to the invention are indicated in Table II. These "halogenated" baths are each a modification of a "standard" bath (1_A or 1_B) as indicated, from which the indicated sulfuric acid constituent has been eliminated. The indicated min./max. current densities (CD) are only illustrative of relative sensitivities and operating levels between baths and are not to be taken as universally and absolutely repeatable.

TABLE II.—HALOGENATED BATHS

	In standard bath—	Replace H_2SO_4 with—	Min./max. CD (approx. Ma/cm.² for acceptable roughness.)
Example:			
1_A			5/60; and 150/500
1_B			50/1,000
1_C			75/1,000
1_{A-1}	1_A	5 ml. HBr (10 N.)	150/800
1_{A-2}	1_A	5 ml. HCl (3 N.) plus 2 gm. $SnCl_2$	250/600
1_{A-3}	1_A	5 gm. ammonium acid fluoride salt	150–200/600–650
1_{B-1}	1_B	do	200–250/650–700
1_{B-2}	1_B	5 ml. HCl (3 N.) plus 10 gm. $SnCl_2$	200/600
1_{B-3}	1_B	5 ml. HBr (10 N.)	300/600

The changes in the Table I baths as set forth in Table II result in the baths having the following concentrations of halogen compounds:

Example	1 A-1	1 A-2	1 A-3	1 B-1	1 B-2	1 B-3
H Br (gm./l.)	10	--	12.5	--	--	8.1
H Cl (gm./l.)	--	1.4	--	--	1.1	--
Sn Cl_2 (gm./l.)	--	5.0	--	--	20	--
Ammonium acid fluoride salt (gm./l.)	--	--	--	10.0	--	--

Standard baths 1_B, 1_C operate satisfactorily over a broad CD range (about 75–1000 ma./cm.²) while the CD range of the halogenated baths is much narrower (200–600 ma./cm.², with some broader) and more critical, though their operation is more efficient. The CD range of bath 1_A is lower than the other standard baths and has a discontinuity (60–150 ma./cm.²).

The above-described electrolytic drawing baths have various characteristic rates of metal removal at characteristic current density ranges and also give varying degrees of smoothness at these ranges, yielding rougher surfacing outside their characteristic CD range. Table III indicates satisfactory operating ranges for these baths, also indicating characteristic drawing efficiencies (rate of metal removal) as a function of these current densities.

TABLE III.—SATISFACTORY OPERATING CURRENT DENSITIES

	Range CD, (ma./cm.²)	Draw rate (mils diam./min.)	Finish rougness (mils RMS)
Bath:			
1_A	10–50	.01–.05	Good (16 RMS).
1_A	60–150		Poor (about 40 RMS or over).
1_A	200–400	.20–.30	Excellent (1 RMS).
1_A	(500)		Satisfactory.
1_B	100–500	.30–.75	Very good (4–8 RMS).
1_B	[1] 1,000	1.20	Fair (32 RMS).
1_C	100–400–350	.30–.70–1.00	Satisfactory.
1_{A-3}	300–400	1.25–1.75	Good (12 RMS).
1_{B-1}	300–600	1.50–1.50	Good (20 RMS).
1_{B-1}	about 700		Poor (35–40 RMS).
1_{B-2}	300–500	.75–1.00	Very good (8 RMS).
1_{B-3}	400–500	1.00–1.25	Do.

[1] Maximum.

Table III indicates how the "halogenation" of a basic drawing bath (1_A, 1_B or 1_C) increases its drawing efficiency. For instance, a significant rise in (thickness) removal rate is apparent in going from bath 1_A to bath 1_{A-3}; or from bath 1_B to any of baths 1_{B-1}, 1_{B-2} or 1_{B-3}. It will further be evident from Table III how a set of baths is taught by the invention for advantageously providing a wide operating range of high-efficiency drawing rates, these rates being somewhat complementary over a broad spectrum and different for each bath at characteristic current densities. For instance, maths 1_A, 1_{B-3} and 1_B (upper CD level of 1_B) provide a set of operating current densities extending somewhat continuously from about 10 to 1000 ma./cm.²; while similarly all of the listed baths (1_A through 1_{B-3}) can provide smooth efficiently reduced wire over a broad range of drawing rates extending from about 0.20 to 2.50 mils/min., extending complementarily in the following ascending order (of increasing draw rates): 1_A; 1_B; 1_{B-2}; 1_{B-3}; 1_{A-3}; and 1_{B-1}.

It will be appreciated therefore from Table III that addition to a standard electrolytic drawing bath (e.g. bath 1_A, 1_B, or 1_C) of a halogen additive according to the invention greatly extends the range of rates at which metal can be removed with good accuracy while maintaining a satisfactory smoothness.

Table IV indicates variations in thickness reduction as a function of bath composition at "optimum" for (smoothness) characteristic current densities. It is assumed for Table IV that the conditions heretofore enumerated still obtain. For instance, it is assumed for each case that Be–Cu wire of approximately 8 mil diameter (5–8 mil for bath 1_C) is transported at 5 inches per second continuously through two drawing cells for a total 100 sec. immersion time, etc., to derive the indicated total thickness removal.

TABLE IV.—AMOUNT REDUCTION ACCORDING TO BATH TYPE, OPTIMUM CD

	To remove, mil	Optimum CD (ma./cm.²)	Smoothness
Bath:			
1_C	0.5	100	Satisfactory.
1_C	1.1	400	Do.
1_C	1.7	850	Do.
1_A	1	600	Do.
1_{B-3}	2	500	Do.
1_{A-1}	3	500	Do.
1_{A-2}	3	500	Do.
1_{B-1}	4	600	Do.
1_{A-1}	(4)	(800)	Unsatisfactory.
1_{A-2}	(4)	(800)	Do.

Summarizing the results of the novel drawing method, according to the invention, it will be clearly evident from Table IV that addition of the halogen additives greatly increases drawing efficiency while maintaining satisfactory smoothness (as indicated for baths 1_{A-1}, 1_{A-2}, 1_{B-1}); and that consistent with current density adjustments different baths may be used in a given electrolytic drawing arrangement to provide different optimum thickness reductions. Maximum CD's will be kept in mind, since, for instance, increasing current density for either of baths 1_{A-1} or 1_{A-2} from about 500 to about 800 ma./cm.² produces an unsatisfactory rough surface, although it increases the drawing rate. While this drawing treatment is specified as apt for copper alloy type substrates, it will be understood that, with modifications known to those skilled in the art, it may be applied to other related alloys such as silver or the like.

REBUILDING

Following the above-indicated electrolytic drawing treatments, it is preferred to rebuild the wire replacing a substantial portion of the removed thickness with a layer of deposited metal, most often a different metal

from that of the wire core. The object of such a replacement deposit is to bring the wire up to a larger prescribed diameter and to derive the advantages of a surface metal without using it, disadvantageously, for the wire core. For instance, a thick layer of copper may be deposited onto the electrolytically reduced beryllium copper wire to form a substrate for deposition of a thin magnetic film. Dual advantages are thereby derived. Beryllium-copper is best for a core material since it is readily obtainable, very strong and adapted to be electrolytically drawn; but it is very unsuitable as a substrate for plating of thin magnetic films. However, the metallurgical, mechanical and magnetic properties of the copper coating make it advantageous as such a substrate, although the copper is poor as core material, being mechanically weak, etc. Thus, when a wire is required having particular surface characteristics for certain applications and having particular, different, characteristics for the core, one metal, being inapt to satisfy both sets of characteristics, a method is taught for forming a wire of core material and covering it with surface material. For instance, a core filament may be continuously advanced through the aforementioned electrolytic drawing station then rinsed, cleaned and thereafter moved through a copper plating station to deposit a very substantial layer of copper very quickly and very smoothly, both to improve the "plate-ability" of the beryllium copper wire substrate and to improve the magnetic characteristics thereof. Typically, this thick copper layer may be as thick as about one-half mil or more. The details of such a copper plating are completely and particularly described in a co-pending application, commonly assigned with the instant application and entitled "Improved Copper Coating" by Semienko et al.; incorporated by reference herein. It will be found that such coppering is especially apt for applications such as for the deposition of thin magnetic films for which good (e.g. Be–Cu) core material is so inapt that a mere surface etching, smoothing, etc. thereof will not remove sufficient subsurface imperfections, discontinuities, etc. as to provide a proper plated wire. For instance, in the aforementioned application to Semienko up to about one mil of copper is electroplated onto a beryllium-copper core with a relatively high degree of smoothness, the copper layer being thereafter polished, for instance, by electro-polishing as indicated below, to form an outstandingly suitable substrate for plating thin magnetic films. While the novel copper plating can provide control over roughness of the plated copper, a finer control will at times be employed supplementarily.

ELECTRO-POLISHING

Subsequent to the drawing and copper coating treatments above, it is preferred to electro-polish the coated (rebuilt) filament, also continuously, since the coating may not be smooth enough for certain applications, such as depositing thin magnetic films. It is especially preferred to electro-polish with a novel sulfamic acid type bath, particularly when the filament is to be used as a substrate in sulfamate type magnetic plating solutions. The current density will be varied according to the amount of polishing desired.

The copper-plated wire is therefore next continually advanced past the coppering station through a clean water rinse and beyond to an electro-polishing station, where the copper finish may be finally smoothed and also be sensitized for subsequent magnetic plating. The electropolish is performed by a smoothing electrolysis using an aqueous phosphoric acid-sulfamic acid bath, such as indicated in Examples II, III or IV below. A sulfamic electropolish bath is provided according to the invention to polish both smoothly and efficiently, while also reducing contamination of subsequent sulfamate containing (plating) solutions. For instance, eliminating the sulfamic acid constituent from a phosphoric acid bath has been found to induce the formation of oxidation sites (blocking subse-

quent plating). Similarly, using sulfuric acid alone corrodes the copper layer catastrophically, leaving intolerable discontinuities therein. The "sulfamic type" baths act to reduce the activity of the polishing bath and inhibit post-copper-plating oxidation (which degrades subsequent magnetic plating), thus providing the best control over "plateable" surface finishing at a minimum loss of plated copper thickness. For instance, they can produce a reproducible surface-leveling of from 1 to 300 micro-inch RMS for "drop-out free" magnetic plating. The preferred electropolishing conditions are indicated for Examples II, III, IV below wherein it will be presumed that the abovementioned "on-line" wire treating conditions apply, such as advancing the wire at five-inches per minute and wherein the cell used is understood to include a cylindrical lead polishing cathode as known in the art.

[Bath at room temperature]

	Examples			
	II	III (Preferred)	IV	Range
Bath:				
Orthophosphoric acid, ml	100	300	400	200–400
Water, ml	300	200	100	100–300
Sulfamic acid, gm	[1] 1–15	[2] 1–10	[3] 1–5	[4] 1–15
Current density-time immersed	2–50 ma./cm.^{2} (pref. 12) for 50 sec			

[1] Preferred 6 gm.
[2] Preferred 4 gm.
[3] Preferred 2 gm.
[4] Preferred 2–6 gm (under about 50 gm./l. water).

Sulfamic acid may be used up to the solubility limit of concentration to maintain smoothness, but about 20 gm. sulfamic acid per liter water is preferred.

The above polishing steps have achieved a surprising smoothness when used with the copper plated wire aforementioned, reducing roughness a predetermined controlled amount for instance from #40 (STM smoothness; micro-inches, peak-to-peak) to as little as #1. Any desired smoothness on the order of up to 3% of a typical plated thickness (about one micron, i.e. 40 micro-inches) has been achieved. For instance, with Example IV above, a current density of 50 ma./cm.^{2} will level a 4 micron copper coating on 5 to 8 mil wire to about #4 STM roughness, reducing its thickness only about 1 micron.

The acid concentrations and other polishing conditions may be varied as understood by those skilled in the art. This electro-polishing step may also be applied to other metal (coatings) substrates from the copper family, such as copper alloys, silver alloys etc. It is not applicable for such metals as nickel, iron or their alloys, however.

The drawn, copper-plated, electro-polished wire is now ready for use being made strong, homogeneously surfaced and subsurfaced and polished to controlled smoothness according to the invention. For instance, the wire may be further continually advanced through a following clean water rinse and thence to a magnetic plating station for providing a thin magnetic film of a few microns, such as by electroplating a nickel-iron magnetic film from a sulfamate type solution.

It will be apparent to those skilled in the art that the principles of the present invention may be applied to different embodiments from that shown; for instance to other types of filamentary substrates for improving the smooth reduction thereof to a controlled diameter. Likewise, the described electro-polishing step may be used to subsequently smooth other similar types of substrates. While in accordance with the provisions of the statutes, there have been illustrated and described the best forms of the invention known, it will be apparent to those skilled in the art that changes may be made in the conditions of the processes disclosed without departing from the spirit of the invention as set forth in the appended claims and that, in some cases, certain features of the invention may be used to advantage without a corresponding use of other features.

Having now described the invention, what is claimed as new and for which it is desired to secure Letters Patent is:

1. In the manufacture of a plated wire memory element having a magnetic information-storing layer on a conductive non-magnetic rod-like substrate, the substrate preparing steps of

(A) providing a mechanically-drawn beryllium-copper rod element having an outer layer of surface and subsurface material discontinuities including mechanical drawing discontinuities,

(B) providing an electrolytic cell containing an acid electrolytic drawing bath,

(C) electrolytically drawing said rod element with said bath in said cell to remove a significant portion of the thickness of said rod element, thereby to remove said outer layer of discontinuities, and

(D) rebuilding at least a portion of the removed thickness of the electrolytically drawn rod element by depositing a continuous layer of copper material onto it thereby to provide a surface for receiving said magnetic layer.

2. A method for manufacturing a plated wire memory element as defined in claim **1** comprising the further step of depositing said magnetic information-storing layer onto said deposited copper material of said rebuilt rod element.

3. The method defined in claim **1** in which the steps of providing said electrolytic cell containing an acid electrolytic drawing bath includes providing said drawing bath to consist essentially of phosphoric acid, a lesser amount of chromic acid and a lesser amount of halogen material selected from the group consisting of chlorine, bromine and fluorine materials.

4. The method defined in claim **1** in which the step of providing said electrolytic cell provides said drawing bath consisting essentially of a major portion of phosphoric acid, a lesser portion of chromic acid, and a lesser portion of sulphuric acid.

5. A method as defined in claim **4** in which cell providing step includes

(A) providing said phosphoric acid in an amount substantially between 600 and 800 milliliters per liter,

(B) providing said sulfuric acid in an amount substantially between 2 and 8 milliliters per liter, and

(C) providing said chromic acid in an amount substantially between 30 and 64 grams per liter.

6. In the manufacture of a memory element having a magnetic information-storing layer on a conductive, non-magnetic substrate, the steps of

(A) providing a mechanically drawn beryllium-copper wire having an outer layer of surface and subsurface discontinuities,

(B) providing an electrolytic cell containing a drawing bath consisting essentially of a major amount of orth-phosphoric acid, a lesser amount of chromic acid, and a lesser amount of halogen material selected from the group consisting of chlorine, bromine and fluorine materials,

(C) electrolytically drawing said wire with said bath in said cell to remove a significant portion of the diameter of said wire, thereby to remove said outer layer of discontinuities,

(D) rebuilding at least a portion of the removed diameter of the electrolytically drawn wire by depositing a continuous layer of copper onto it; and

(E) depositing said information-storing layer onto said deposited copper.

7. A method as defined in claim **6** in which said halogen material is provided by introducing halogen materials selected from the group consisting of hydrochloric acid, hydrobromic acid, stannous chloride and ammonium acid fluoride salt.

8. A method as defined in claim **6** in which said halogen material is selected from the group consisting of

(1) hydrobromic acid in a concentration of about 8 to 10 grams per liter,

(2) hydrochloric acid in a concentration of about 1.1 to 1.4 grams per liter and stannous chloride in a concentration of about 5 to 20 grams per liter, and

(3) ammonium acid fluoride salt in a concentration of about 10 to 12.5 grams per liter.

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