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[54] **PROTECTIVE COATING ON WIRE**

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[63] Continuation of Ser. No. 20,851, March 18, 1970, abandoned.

[52] **U.S. Cl.** ..... **148/6.24,** 148/6.14 R

[51] **Int. Cl.** **C23f 7/00**

[58] **Field of Search** ..... 117/239, 240, 237; 148/6.14 R, 6.24; 29/191.6; 179/100.2 R; 274/41.4

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[57] **ABSTRACT**

A chemical bath for applying a protective coating on magnetically plated wire during in-line processing, the bath comprising an aqueous alkaline solution including a 0.05 to 0.25 percent concentration of an adsorbable, organic corrosion inhibitor from the class consisting of thiazole, urea and amine compounds; and a 1 to 5 percent concentration of an inorganic, PH stabilizer from the class consisting of borate, benzoate and phosphate salts of sodium and potassium.

6 Claims, No Drawings

PROTECTIVE COATING ON WIRE

This application is a division of application Ser. No. 20,851 filed Mar. 18, 1970, now abandoned.

BACKGROUND OF THE INVENTION

The invention herein described was made in the course of and under a contract, or subcontract thereunder, with the U.S. Strategic Systems Projects Office, Department of the Navy.

This invention is related, generally, to chemical solutions for forming protective coatings on wire and is concerned, more particularly, with a chemical bath for applying a protective coating on plated memory wire during in-line processing.

One exemplary magnetic plating line comprises a spaced, parallel array of chemical cells in colinear alignment with a rotatable spool of wire at one end of the array and a longitudinally disposed, tubular furnace at the other end. The wire, usually, is made of a resilient material having good electrical properties, such as beryllium-copper, for example. In operation, wire feeds continuously off the spool and is drawn longitudinally through the respective cells of the array and the aligned, tubular furnace. Generally, the surface of the wire is cleaned, etched and electropolished while passing through the initial cell stages, and receives a plating of copper, while passing through the intermediate cell stages of the array. Usually, in the final cell stages of the array, the wire is plated with a material having desirable magnetic properties, such as permalloy, for example.

Permalloy is a nickel-iron compound having preferred percentage compositions for plated memory wire which exhibit low magnetostrictive properties when the plated wire is distorted. Another reason permalloy is a preferred plating material for magnetic memory wire is that it acquires uniaxial, anisotropic magnetic properties when influenced by a coaxial magnetic field during the plating process. As a result, an "easy" direction of magnetication is established circumferentially in the plated permalloy film; and an orthogonal "hard" direction of magnetization is established parallel to the axis of the wire. Furthermore, each discrete cylindrical portion of the plated permalloy film has a nearly square hysteresis loop in the easy direction of magnetization and an almost linear hysteresis loop in the hard direction. Thus, any particular portion of the plated permalloy film may be magnetized in the circumferential direction, either clockwise or counterclockwise. Also, the magnetic vector of a selected portion of the plated permalloy film may be switched from one circumferential rest position to the other. Consequently, the two oppositely directed rest positions, usually, are assigned the respective digits, one and zero, of a binary logic system.

In order to avoid deterioration of the described magnetic characteristics, the plated permalloy film is annealed while exposed to the flux of an orienting magnetic field. Therefore, after leaving the final permalloy plating cell in the magnetic plating line, the plated wire, generally, passes through an additional chemical cell containing a pool of conductive liquid, such as mercury, for example. The mercury liquid provides a minimum resistance means for making an electrical connection to the continuously moving wire, without wetting the metallic components of the plated permalloy film.

By means of the mercury contact, an orienting current is passed through the permalloy plated wire while the wire is traveling through the subsequent furnace stage of the magnetic plating line. In the furnace, the wire generally passes through an inert or a reducing gas atmosphere which, usually, is maintained at a temperature greater than 250°C. Thus, the plated permalloy film is annealed while the magnetic vectors of the respective memory cells in the permalloy film are uniformly aligned by a coaxial magnetic field established by the orienting current. After passing through the heat treatment furnace, the wire, generally, is tested as part of the continuous process and cut into segments which, subsequently, are assembled into a memory system.

The plated permalloy film is very thin, generally being about 1 micron in thickness. Consequently, minute holes occur in the film along the length of the continuous wire. It has been found that, when the permalloy plated wire passes through the liquid contact, minute quantities of mercury enter these "pin" holes and amalgamate with the exposed copper material. Consequently, when the permalloy plated wire enters the elevated temperature environment of the heat treatment furnace, the low melting temperature mercury-copper alloy expands radially under the permalloy film. As a result, localized cracking and peeling of the permalloy film were found, at a later time, to have occurred around the respective pin holes and spread radially outward therefrom. Thus, stored memory bits were destroyed and sizable portions of the plated memory wire had become inoperative.

Therefore, in order to ensure long term reliability for plated memory systems, it is imperative that the plated memory wire be protected from the described type of mercury-induced corrosion. Protective coatings applied after the plated wire has been processed and tested will not solve this problem, because the mercury must be prevented from wetting any exposed copper material during processing of the wire. Furthermore, it is essential that the mercury liquid be in electrical contact with the continuously moving wire in order to provide an orienting current during the heat treatment process. Consequently, coatings of insulating material, such as paints, varnishes, resins and the like, are unsuitable for such protective coatings. Also, any coating of protective material applied during processing of the wire must be capable of withstanding the elevated temperature environment of the heat treatment furnace without stressing or otherwise affecting the magnetic properties of the plated permalloy film.

SUMMARY OF THE INVENTION

Accordingly, this invention provides a chemical bath for forming a protective coating on plated memory wire while the wire is moving longitudinally through the bath at plating line velocity. The chemical bath of this invention comprises an aqueous, alkaline solution including 0.05 to 0.25 percent concentration of an adsorbable corrosion inhibitor, and 1 to 5 percent concentration of a PH stabilizer. It was found that members of the thiazole group of compounds, such as thiazole, mercaptothiazole, benzothiazole, for examples, are the most effective adsorbable, corrosion inhibiting agents. However, members of the urea group of compounds, such as thiourea, monotolylthiourea, ditolylthiourea, for examples, and members of the amine group of compounds, such as dibenzlamine, tribenzla-

mine, hexodecylamine, for examples, also are acceptable as adsorbable, corrosion inhibiting agents in the chemical bath of this invention. Sodium borate, sodium benzoate and sodium phosphate are preferred stabilizing agents, although potassium borate, potassium benzoate and potassium phosphate also are acceptable as PH stabilizing agents for this bath.

Since the chemical bath of this invention was developed, specifically, for protecting plated memory wire during in-line processing, it was evaluated in a typical magnetic plating line. The inventive aqueous, alkaline solution was contained in a chemical cell which was disposed between the final cell of the permalloy plating stage and the mercury contact cell. The chemical cell, so disposed, was 3 inches high, 6 inches long, 5 inches wide and contained 750 milliliters of the inventive alkaline solution. During the evaluation tests, the described bath was maintained at a temperature between 20° and 30°C.

The wire used for evaluating this chemical bath was a commercial grade, No. 125 beryllium-copper wire having an initial diameter of about 5.5 mils and a surface finish of about 16 microinches. However, after passing through the etching and electro-polishing cell stages of the magnetic plating line, the diameter of the wire was reduced to about 4.9 mils and the resulting surface finish was about 4 microinches. In the intermediate cell stages of the line, the polished wire received a plating of copper, about 3 microns thick. In the magnetic plating stage of the line, the copper-plated wire received a plating of permalloy material about 1 micron in thickness.

After passing through the chemical bath of this invention, the plated wire passes through the mercury contact cell and then through the heat treatment furnace. One suitable furnace was 4 feet long and was maintained at a temperature between 300° and 400°C. In order to test the quality of the protective coating applied by the chemical bath, an inert or reducing gas atmosphere was not used in the heat treatment stage. Thus, the plated wire was exposed to an air atmosphere at high temperature. Under these conditions, any areas left uncovered by the protective coating will be covered with a black oxide coating. It has been found that wire coated with this black oxide film will not pass electrical test at the end of the plating line. When a portion of the wire fails electrical test, an automatic cutter is triggered which then removes the rejectable portion from the continuous wire.

The compositions of the inventive baths tested under the described conditions are listed below.

Chemical Bath No. 1

Constituent	Conc. Range	Preferable Conc.
Thiazole	.5–2.5 gm/liter	1 gm/liter
Sodium borate	10–50 gm/liter	10 gm/liter
Sodium benzoate	10–50 gm/liter	10 gm/liter
Distilled water	balance	balance

Chemical Bath No. 2

Constituent	Conc. Range	Preferable Conc.
Mercaptothiazole	.5–2.5 gm/liter	1 gm/liter
Sodium benzoate	10–50 gm/liter	10 gm/liter

Chemical Bath No. 3

Constituent	Conc. Range	Preferable Conc.
Benzothiazole	.5–2.5 gm/liter	1 gm/liter
Sodium phosphate	10–50 gm/liter	10 gm/liter

The function of the organic inhibitor, such as thiazole, mercaptothiazole and benzothiazole in the inventive Chemical Baths Nos. 1, 2 and 3, for example, is to coat any exposed copper on the plated wire before it enters the mercury contact cell. These organic inhibitors preferentially wet copper and are adsorbed onto the copper surface, thereby forming an extremely thin layer of organic material, only a few molecules in thickness. This molecular thin layer of inert material is sufficient to prevent mercury wetting of the copper and the resulting formation of low melting mercury copper amalgamines. However, the adsorbed layer of organic material does not interfere with the passage of current from the mercury to the plated wire. Thus, the mercury liquid still retains electrical contact with the surface of the plated wire.

It has been found that if the organic inhibitor concentration is below the specified minimum value, the exposed copper material will not be completely coated with inert material. Consequently, mercury-induced corrosion can take place at the still exposed copper areas and result in damage to the surrounding permalloy film, as previously described. On the other hand, if the organic inhibitor concentration is above the specified maximum value, organic inhibitor material, being solubility sensitive, will precipitate out of the solution. Not all organic inhibitors perform satisfactorily in the chemical bath of this invention. Some organic inhibitors do not preferentially wet exposed copper material, and others contaminate the mercury cell. Some organic inhibitors which may be used, alternatively, in place of those disclosed in respective Chemical Baths 1, 2 and 3 are: mercaptobenzothiazol, 1-2 thiazoldinethione, 2-4 thiazoldenione, 1-(2 thiazolylago-2 napthol), thiourea, monotolylthiourea, ditolylthiourea, dibenzlamine, tribenzylamine and hexodecyclamine.

The function of the PH stabilizer in this novel chemical bath is to maintain the PH value of the bath in the 8–11 alkaline range. Thus, if the concentration of the PH stabilizer is below the specified minimum value, the PH value of the bath will be in the acidic range and will result in pitting of the plated permalloy film. When the PH stabilizer concentration is within the specified limits, the resulting alkaline solution reacts with the plated permalloy material and renders it passive thereby forming an extremely thin layer of nickel-iron oxide, only a few molecules thick, on the surface of the permalloy film. This molecular thin layer of nickel-iron oxide material is not thick enough to interfere with the passage of current from the mercury liquid to the plated wire. However, if the concentration of the PH stabilizer is above the specified maximum value, the PH value of the bath will be above the required 8–11 range. This highly alkaline solution will passivate the surface of the plated permalloy material too deeply. The resulting thick nickel-iron oxide layer will interfere significantly with the passage of current from the mercury liquid to the plated wire core. Consequently, the orienting current required for the heat treatment stage will fluctuate and the resulting magnetic properties of the annealed permalloy film will be erratic. Therefore, the maximum concentration value specified for the PH stabilizer in the bath is extremely critical.

In this chemical bath, sodium borate, sodium benzoate and sodium phosphate are preferred PH stabilizing agents. However, potassium borate, potassium benzoate and potassium phosphate also may be used as PH

stabilizers. Further, these PH stabilizing agents may be used alone or in combination with another one of the designated PH stabilizers to maintain the bath in the desired PH range of 8–11. When at least one of the designated PH stabilizers is present, within the concentration range specified, the resulting alkaline solution reacts with the permalloy plated wire to produce a surface film which, after passing through the subsequent furnace stage, hardens into a characteristic light colored coating. Evaluation studies disclose that a permalloy plated memory wire having this light colored coating has a low failure rate in electrical test and exhibits improved aging properties. It also has been found that the coating action of this inventive bath is practically instantaneous and, therefore, not dependent on the speed of the magnetic plating line.

Thus, there has been disclosed herein a novel chemical bath for applying a protective coating to plated magnetic memory wire during processing of the wire. The bath comprises an aqueous alkaline solution including an organic inhibitor which is adsorbed on the surface of exposed copper material to form a molecular thin film thereon which prevents the copper areas from being wetted by mercury in the subsequent liquid contact cell. The solution also includes at least one PH stabilizer which maintains the solution in the PH range of 8–11. As a result, of passing through this alkaline solution and the subsequent furnace stage, the permalloy plated wire is coated with a protective film which prevents further oxidation of the permalloy plated wire. This protective coating does not adversely affect the magnetic properties of the permalloy plated material but appears to ensure that the permalloy material will retain the magnetic properties required for plated memory systems.

From the foregoing, it will be apparent that various changes may be made by those skilled in the art without departing from the spirit of this invention as expressed in the appended claims. It is to be understood, therefore, that all matter described herein is to be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In combination:

a protective coating on a body comprising a permalloy plated conductor having a coating of magnetic material, said protective coating being applied by a bath comprising an aqueous alkaline solution including an adsorbable, organic corrosion inhibitor comprising thiazole and an inorganic PH stabilizer from the group consisting of borate, benzoate and phosphate salts of sodium and potassium and combinations thereof.

2. The combination as set forth in claim **1** wherein the PH of the bath is maintained at a value between 8 and 11.

3. The combination as set forth in claim **1** wherein the minimum concentration of said organic corrosion inhibitor is about 0.05 percent, and the minimum concentration of said inorganic PH stabilizer is about 1 percent.

4. The combination as set forth in claim **1** wherein the maximum concentration of said corrosion inhibitor is about 0.25 percent and the maximum concentration of said inorganic PH stabilizer is about 5 percent.

5. The combination as set forth in claim **4** wherein said organic corrosion inhibitor is substantially entirely thiazole and said inorganic PH stabilizer is a combination of sodium borate and sodium benzoate.

6. The combination as set forth in claim **5** wherein the concentration of thiazole is about 1 gram per liter, the concentration of sodium borate is about 10 grams per liter, and the concentration of sodium benzoate is about 10 grams per liter.

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