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PROCESS FOR FORMING A METALLIC LAYER ON A SUBSTRATE

Melvin D. Sterman and David J. Genova, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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ABSTRACT OF THE DISCLOSURE

A uniform layer of noble metal on a substrate is formed by reacting a salt of the noble metal with cuprous iodide. The resulting layer is especially useful as a catalytic layer for the formation of a ferromagnetic layer on the substrate by electroless deposition.

BACKGROUND OF THE INVENTION

The present invention relates to a novel process for coating a surface of a substrate, such as plastic tape, with a uniform layer of a noble metal, and particularly to such a process wherein said noble metal layer is then utilized as a catalytic layer for use in the electroless deposition of a ferromagnetic layer on said substrate for use as a magnetic record member.

Processes for forming metallic coatings by electroless deposition on a substrate, for various purposes, have been known, and in fact this general technique has been disclosed for use in the production of magnetic record members. See for example Canadian Pat. 705,366 issued Mar. 9, 1965, which discloses sensitizing a tape support by passing it through a bath containing a reducing agent such as stannous chloride or titanium chloride to leave a residue thereof on the tape, then passing it through a "seeding" solution containing palladium chloride, which reacts with the stannous or titanium chloride to form particles of metallic palladium on the surface of the tape. The "seeded" tape is then passed through a bath containing various cobalt, nickel and phosphorus salts which are catalytically reduced by the palladium to form the final magnetic recording surface.

While quite effective record members can be made in this way it has been found extremely difficult to obtain that degree of uniformity of magnetic characteristics which is essential for high quality magnetic tapes. We have found that this problem arises primarily due to uneven distribution of the particles of catalytic metal, e.g. palladium, etc., on the substrate prior to deposition of the magnetic material. This unevenness appears to be caused by a combination of two factors: the difficulty of obtaining a truly uniform coating of any material merely by dipping techniques, and a tendency for stannous and titanium chloride particles to agglomerate, as evidenced by a somewhat mottled appearance of a tape coated therewith, whether by dipping or by some other coating technique. This known process also has the objection that the substrate will be coated on both sides whereas it is normally desired to have the magnetic layer on but one face of a record member.

It is therefore an object of this invention to provide a process for use in the production of magnetic records by electroless deposition techniques that will overcome these problems.

SUMMARY OF THE INVENTION

We have found, surprisingly, that by forming the catalytic noble layer by employing the substantially unrelated compound, cuprous iodide, which is not normally classified as a reducing agent, instead of the prior art chloride reducing agents previously utilized, these problems are effectively overcome. Moreover when thus using cuprous chloride, conventional high-precision coating techniques such as are used in manufacture of photographic film materials can conveniently be used to produce a catalytic layer of extremely fine particles of palladium or other noble metal uniformly distributed over the desired surface only of the substrate. The improvement appears in part at least to be caused by the fact that the particles of noble metal produced as a result of reaction with cuprous iodide tend to be much smaller and more uniform in size than when the prior art chloride reducing agents are used. While preferably the cuprous iodide is first applied to the substrate surface and then the noble metal salt applied thereto for reaction in situ, some of the advantages of our invention are still retained even when the cuprous iodide and noble metal salt are reacted together to produce the noble metal particles prior to application thereof to the substrate.

Thus, in the preferred embodiment of our invention, cuprous iodide is first deposited, with or without a binder, as a uniform layer on a suitable substrate such as paper or plastic sheet or tape material. When the cuprous iodide layer is dry, the noble metal salt is brought into contact with the cuprous iodide layer as by progressively traversing the substrate through a liquid bath of the noble metal salt, advantageously an aqueous solution thereof. Then the coated substrate is washed thoroughly with water to remove undesired reactants such as copper chloride or other salts that may be present, and, upon drying, the substrate will be found to have an extremely uniform, thin layer of the noble metal thereon in a state suitable to act as a catalyst for the subsequent deposition of a ferromagnetic metal on the substrate.

In a second embodiment for preparing a noble metal layer on the substrate in accordance with our invention, a dispersion of the noble metal in a liquid medium containing a binder is first prepared by mixing together the cuprous iodide, the noble metal salt, and the binder with the necessary liquid ingredients, thereby forming a dispersion of fine metal particles which is then coated onto the surface of the support and dried thereon by heating at an elevated temperature.

Regardless of which method is employed for producing the uniform noble metal coating, the deposition of another metal such as a ferromagnetic metal as a layer on the substrate is accomplished by bringing into contact with the noble metal layer a preferably aqueous solution of a reducing agent and a compound of the ferromagnetic metal. The ferromagnetic metal compound should, of course, be one which is relatively readily reduced in the presence of the noble metal, thereby forming a ferromagnetic layer on the substrate. For example, the ferromagnetic metal can be cobalt, nickel, iron, or alloys of two or more of these metals with one another; and the compound which is reduced can be any suitable salt such as cobalt chloride hexahydrate, etc.

DETAILED DESCRIPTION

The following examples illustrate details of how the invention is carried out successfully:

Example I

A poly(ethylene terephthalate) film support subcoated with a terpolymer composed of methyl acrylate, vinylidene chloride and itaconic acid is overcoated on one side

by spreading on the subcoat a solution containing 3% by weight of cuprous iodide and 0.5% of a poly(vinyl formal) binder containing 5 to 7 mole percent of vinyl alcohol and 20 to 27 mole percent of vinyl acetate residues, dissolved in acetonitrile. Upon drying, the coating is found to be extremely smooth and uniform and to contain 10 mg. of cuprous iodide per square foot of substrate.

The coated substrate is next immersed for two minutes in a bath of an aqueous solution containing 0.5 g./l. (grams per liter) of palladium chloride and 0.06 mole/l. of hydrochloric acid (for dissolving the palladium chloride), the solution being at a temperature of 60° C. Upon removal from the solution the coated substrate is thoroughly rinsed with distilled water and that side of the substrate which carries the cuprous iodide is found to have a correspondingly smooth, uniform layer of palladium metal thereon.

The palladium-coated substrate is next immersed for twenty minutes in an aqueous solution containing 0.03 mole/l. of cobalt chloride hexahydrate, 0.06 mole/l. of sodium hypophosphite monohydrate (a reducing agent), 0.23 mol/l. of ammonium chloride, and 0.09 mole/l. of sodium citrate dihydrate (a complexing and solubilizing agent), the solution being at a temperature of 90° C. and having a pH of 9, maintained with ammonium hydroxide.

A continuous, coherent coating of cobalt (alloyed with a small amount of phosphorus derived from breakdown of the reducing agent) is obtained, with a coverage of 550 mg. of cobalt per square foot of substrate. The cobalt-phosphorus coating is then washed in distilled water and air-dried. The dried coating is found to be extremely smooth and uniform and to be firmly bonded to the substrate; it cannot be readily rubbed, abraded, or scratched off, nor can it be pulled off with adhesive tape. The magnetic, audio and digital properties of the resulting tape are measured and found to be well adapted for both digital data storage and sound transcription. The data show that this tape has higher coercivity, better squareness, and better frequency response characteristics than conventional magnetic iron oxide tapes, and superior characteristics for digital uses. Furthermore, the required thickness of the cobalt coating for equivalency to magnetic iron oxide tapes is between 1/10 and 1/20 that of an iron oxide coating. Both the print-through and wear properties of the cobalt tape are superior to those of magnetic iron oxide tape.

Example II

A coating dispersion of cuprous iodide in a water-soluble polymer binder is prepared using 65 ml. of an aqueous solution containing 1.55% by weight of sodium salt of a resinous carboxy ester lactone (see U.S. Pat. 3,169,946) at a pH of 7, to which is added, while stirring in a suitable mixer, 35 ml. of a solution of 3% by weight of cuprous iodide in acetonitrile. 1 ml. of an aqueous solution containing 5% by weight of hexa[1-aziridine]triphosphatriazine is added just prior to the coating operation to function as a crosslinking agent for the binder. The resulting dispersion is coated on several poly(ethylene terephthalate) film substrates, some having subcoatings of the terpolymer of Example I and some having gelatin subcoatings, as well as on a cellulose acetate substrate.

After drying these cuprous iodide dispersion coatings, each of the coated substrates is dipped for two minutes into an aqueous solution containing 0.5 g./l. of palladium chloride and 0.06 mol/l. of hydrochloric acid, the solution being at a temperature of 60° C.

Each of the coated substrates is then thoroughly rinsed with distilled water, after which a cobalt-phosphorus layer is deposited on the palladium layer following the procedure described in Example I to give a magnetic tape having the superior properties described in Example I.

Example III

A dispersion of fine particles of palladium metal is prepared in association with a water soluble polymeric binder by first preparing 65 ml. of an aqueous solution containing 1 g. of poly(vinyl alchol), 0.25 g. of palladium chloride, and 0.03 mole of hydrochloric acid in a suitable mixer. To this solution is added, with continuous mixing, 35 ml. of acetonitrile solution containing 0.6 g. of cuprous iodide to react with the palladium chloride and form the dispersion of fine particles of palladium metal. Then 1 ml. of a 10% aqueous glyoxal solution is added to the dispersion to function as a crosslinking agent for the poly(vinyl alcohol), and the dispersion is promptly coated on poly(ethylene terephthalate) substrates subbed as described in Example II, as well as on cellulose acetate substrates, and dried by heating the coating. Then a cobalt-phosphorus layer is deposited on the substrates as described in connection with Example I to produce magnetic tapes having superior properties comparable to those of Example I.

Example IV

A coating solution containing (by weight) 1% cuprous iodide, 2.5% of poly(methyl acrylate-vinyl chloride-acrylic acid (50:46:4)), as a binder, and 2.5% trimethyl phosphate, as a solubilizing agent, is prepared in a 9:1 solvent mixture of methyl ethyl ketone and cyclohexanone. The resulting solution is coated onto one side of a poly(ethylene terephthalate) film support and dried by blowing hot air over the support to yield a dry coverage of approximately 10 mg. of cuprous iodide per square foot of coating.

The cuprous-iodide-coated element is dipped for two minutes into an aqueous solution maintained at 80° C. containing 0.5 g./l. of palladium chloride and 0.06 mole/l. of hydrochloric acid. The element is removed from the bath, rinsed thoroughly with distilled water, and found to have a uniform, smooth catalytic layer of palladium nuclei on the coated side of the support.

The support with its layer of palladium catalytic nuclei is next immersed in an aqueous solution maintained at a temperature of 95° C. and a pH of 10.5, containing 0.03 mole/l. of cobaltous chloride hexahydrate, 0.07 mole/l. of sodium hydrophosphite monohydrate, and 0.15 mole/l. of aspartic acid. After five minutes immersion time, a continuous, uniform coating of cobalt alloyed with phosphorous has formed on the side of the support containing the catalytic nuclei.

Thorough rinsing with distilled water provides a magnetic tape element which, again, exhibits good adhesion and magnetic properties.

Example V

A coating solution containing, by weight, 1% cuprous iodide, 2.5% du Pont Polyester Adhesive # 49,000 (a tough, hard, amber-colored, non-tacky polyester having an average specific gravity of 1.33 and an average melting range of 245–275° F.), and 2.5% trimethyl phosphite is prepared in a 1:1 solvent mixture of methylene chloride and ethylene chloride. This solution is coated onto one side of a poly(ethylene terephthalate) film base and dried by blowing hot air over the support. The coating is treated as in Example IV with a palladium chloride solution, and then with a cobaltous chloride hexahydrate solution. A magnetic element is thus produced having good adhesion of a continuous, uniform cobalt-phosphorus metallic layer displaying good magnetic properties.

While the invention has been illustrated above by means of specific examples, it is evident that certain variations in the process can be employed within the scope of the invention. Thus, the cuprous iodide coverage can be varied over a wide range and still react with sufficient palladium to provide an effective catalytic layer; for example, it can be as low as 2 mg. per square foot, although 10 mg. per square foot is advantageous for economy and efficiency.

Variations in the coverage may be secured by either reducing or increasing the wet coverage of the cuprous iodide coating solution of a given concentration applied to the substrate, or by varying the cuprous iodide concentration of the coating solution while maintaining the wet coverage at a constant value. The couprous iodide can be in aqueous solution, or in a non-aqueous solvent such as acetonitrile or propionitrile. Cuprous iodide advantageously is present in the solution in an amount between 0.005 and 5%, preferably between 1.0 and 3.0% by weight; and when a film-forming binder is used the latter can be between 0.1 and 5%, preferably between 0.4 and 2.5%.

The concentration of the noble metal salt solution can also be varied considerably while still producing a satisfactory layer. Instead of the hydrochloric acid, other solubilizing agents such as alkali metal halides, ammonium chloride or the like may be used to dissolve the noble metal salt initially. Furthermore, the temperature of the noble metal salt bath may be varied over a wide range, such as 20° to 98° C., with the rapidity of the reaction increasing as the temperature is increased, 60° to 98° C. giving particularly good results. A more uniform layer of noble metal results from the higher temperatures. While the noble metal is perhaps most conveniently palladium, other noble metals such as gold, platinum, or the like can be used. Moreover, while the chlorides are convenient salts to be used, other noble metal salts can obviously be utilized. Complex salts such as platinum or palladium hydrogen chloride, palladium or platinum potassium chloride, etc. can likewise be used.

The conditions under which the ferromagnetic metal reduction is carried out can also be varied. Advantageously, but not necessarily, the temperature of the plating solution should be between 80° and 99° C., preferably between 90° and 99° C., and the pH of the solution between 8 and 11, preferably 9 or above. There is also considerable latitude in the composition of the bath, with the cobalt chloride hexahydrate composition concentration advantageously being between 0.005 and 0.12 mole/l., preferably between 0.02 and 0.06, most desirably about 0.03 mole/l. The sodium hypophosphite monohydrate reducing agent con centration may be varied from 0.005 to 0.24 mole/l., preferably between 0.04 and 0.14 mole/liter, most desirably about 0.07 mole/liter; the ammonium chloride concentration from 0.04 to 1.0 mole/l., preferably between 0.10 and 1.0 mole/liter, most desirably about 0.23 mole/liter; and the sodium citrate dihydrate complexing and solubilizing agent concentration from 0.03 to 0.20 mole/l., preferably between .05 and 0.15 mole/liter, most desirably about 0.09 mole/liter.

In this invention it is desirable, although not necessary, to use a binder to improve adhesion when applying the cuprous iodide layer to the support. Polymers soluble in organic solvents, including vinyl polymers and polyesters, are well adapted for this purpose; for example, polymers of vinylidene chloride, acrylic esters, and itaconic acid; vinylidene chloride and acrylonitrile; vinyl chloride and vinyl acetate; butadiene and acrylonitrile; poly(vinyl formals); and the like. Alternatively polyesters such as those derived from poly(methylene glycols) and terephthalic acid may be employed. Examples of useful polyesters are the Vitel resins sold by Goodyear Tire and Rubber Company and the Du Pont Polyester Adhesives 49,000 49,001, 49,002 and 49,003.

In addition, water-soluble polymers such as poly(vinyl alcohols) and the sodium salts of resinous carboxy esterlactones may be used.

Organic solvents which are useful in these binder formulations are acetonitrile, propionitrile, the ketone solvents, e.g., methyl ethyl ketone, halogenated solvents, and mixtures of ketone solvents, alcohols, and halogenated solvents such as methyl ethyl ketone and acetone, methyl ethyl ketone and ethyl alcohol, methyl ethyl ketone and methyl isobutyl ketone, methyl ethyl ketone and tetrachloroethane, and methylene chloride and ethylene chloride.

When a binder solution comprising an organic solvent is used, it is advantageous to employ a solubilizing agent for the cuprous iodide. Examples of such agents are trimethyl phosphite, diethyl sulfide and amines, e.g., triethylamine and trimethylamine. In certain cases (e.g. where acetonitrile or propionitrile is used as the solvent) no additional solubilizing agent is needed since the cuprous iodide is sufficiently soluble therein without such agent.

The magnetic recording elements of this invention can be further improved by the use of an adhesive subbing composition. Particularly useful for this purpose are polymers of vinylidene chloride, acrylic esters and itaconic acid; vinylidene chloride and acrylonitrile, poly(methylene glycols) and terephthalic acid, vinyl chloride and vinyl acetate, butadiene and acrylonitrile, and the like.

The invention has been described in considerable detail with particular reference to certain preferred embodiments theerof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

We claim:

1. In a process for forming on a surface of a substrate an adherent coating comprising extremely fine particles of a noble metal uniformly distributed over said surface, the improvement comprising:

the step of reacting cuprous iodide with a solution containing a soluble salt of said noble metal to produce said fine particles of noble metal.

2. The invention of claim **1**, wherein said soluble noble metal salt is a halide.

3. The invention of claim **1**, wherein said noble metal is palladium.

4. The invention of claim **1**, wherein said cuprous iodide and noble metal salt solution are reacted together on said substrate to form said particles in situ.

5. The invention of claim **4**, wherein said cuprous iodide is deposited as a layer on said substrate, and said noble metal salt solution is thereafter brought into contact therewith.

6. The invention of claim **4**, wherein said cuprous iodide is deposited by applying to said substrate a solution in an organic solvent, of cuprous iodide and a polymeric binder.

7. The invention of claim **4**, wherein said cuprous iodide is deposited by applying to said substrate a solution, in an organic solvent, of cuprous iodide, a polymeric binder and a solubilizing agent for the cuprous iodide.

8. The invention of claim **7**, wherein said solubilizing agent is selected from the group comprising trimethyl phosphite, diethyl sulfide, triethylamine, and trimethylamine.

9. The invention of claim **1**, wherein said cuprous iodide and noble metal salt are reacted together prior to application of either to said substrate.

10. The invention of claim **9**, wherein said cuprous iodide and noble metal salt are reacted together in a liquid medium containing a binder to form a dispersion of noble metal particles in said binder, and said dispersion is thereafter coated on said substrate.

11. In a process for forming an adherent metallic coating on a surface of a substrate by electroless deposition of a metal in situ on said surface by catalytic reduction from a solution containing a soluble salt of said metal, and which process includes forming on said surface, prior to application of said metal solution thereto, a layer of a noble metal, catalytic to said first mentioned metal, the improvement comprising:

forming said noble metal layer on said surface by reacting cuprous iodide with a solution containing a soluble salt of said noble metal to produce extremely fine particles of said noble metal uniformly distributed over said surface.

12. In a process for forming an adherent ferromagnetic coating on a surface of a substrate by electroless deposition of a ferromagnetic metal in situ on said surface by catalytic reduction from a solution containing a soluble salt of said ferromagnetic metal, and which process includes forming on said surface, prior to application of said ferromagnetic metal solution thereto, a layer of a noble metal, catalytic to said ferromagnetic metal, the improvement comprising:

forming said noble metal layer on said surface by reacting cuprous iodide with a solution containing a soluble salt of said noble metal to produce extremely fine particles of said noble metal uniformly distributed over said surface.

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ALFRED L. LEAVITT, Primary Examiner

J. A. BELL, Assistant Examiner

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