

Jan. 10, 1956

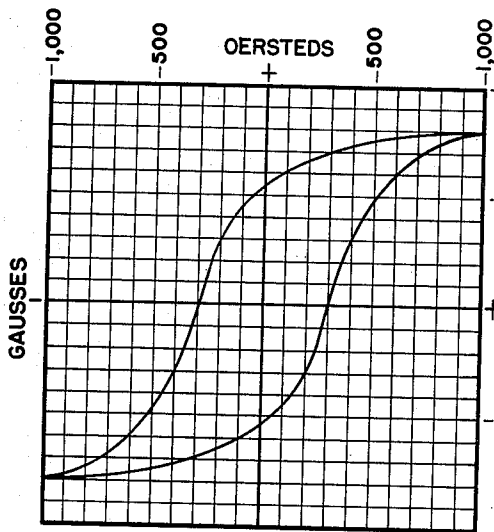
W. E. MOLINE ET AL

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METHOD OF ELECTROPLATING COBALT-NICKEL COMPOSITION

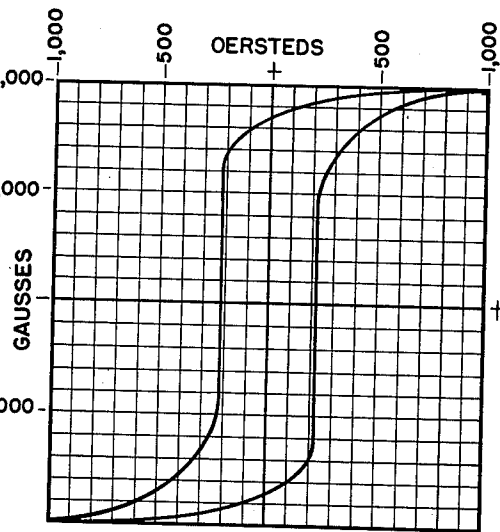
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WITHOUT ADDITION AGENTS

FIG. 1



WITH ADDITION AGENTS

FIG. 2

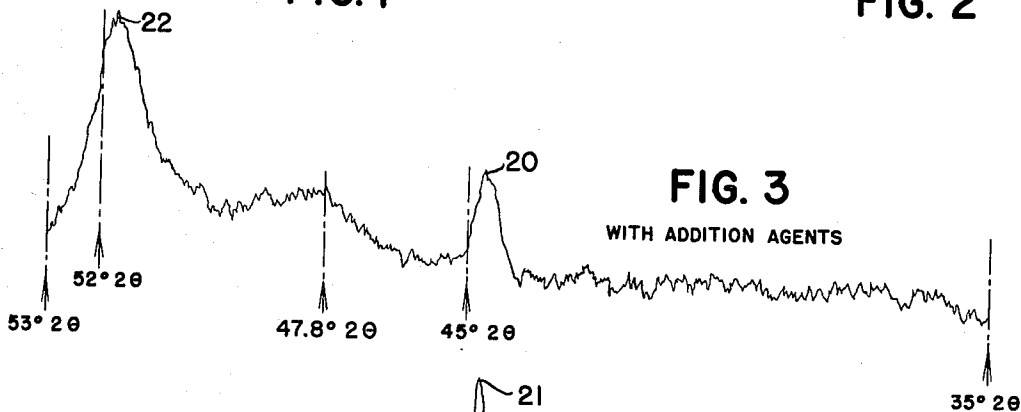


FIG. 3

WITH ADDITION AGENTS

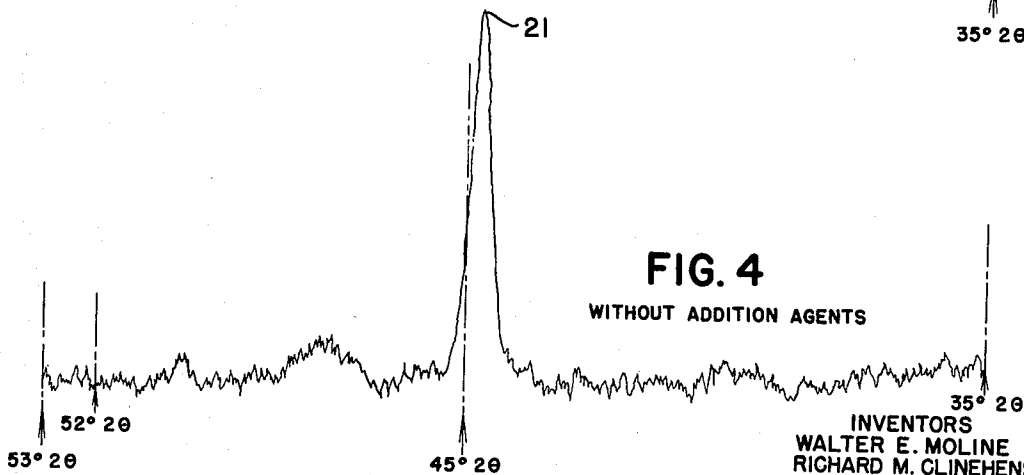


FIG. 4

WITHOUT ADDITION AGENTS

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FIG. 6

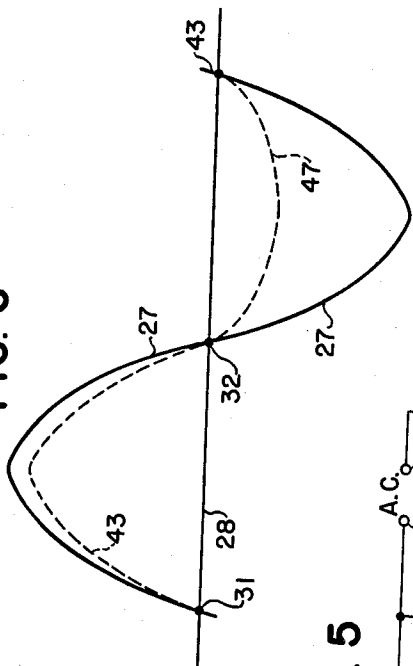
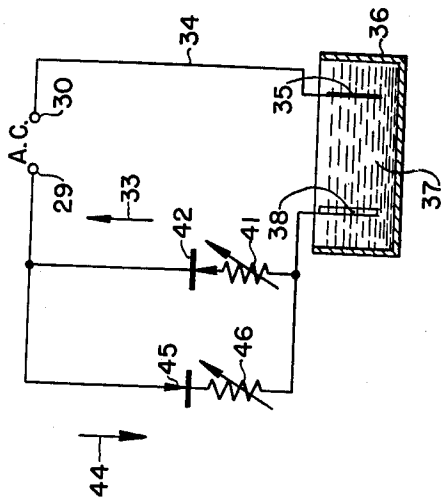


FIG. 5



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METHOD OF ELECTROPLATING COBALT-NICKEL COMPOSITION

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6 Claims. (Cl. 204—43)

This invention relates to the method of electro-plating a cobalt-nickel composition on a metal base whereby the electro-plate has high quality magnetic recording characteristics. More particularly, the process pertains to such a method in which the metal base used is non-magnetic and wherein the electro-plate preferably is of a thickness ranging from .00025 of an inch to .0015 of an inch.

The plating, for recording use, preferably is applied to a flexible tape of the selected metal base, as such tape is well adapted to be supported and moved upon drums or reels relative to a pick-up or recording station, although wire, sheet, disc-like or cylindrical base members may be so plated. Brass may be used, but it is inferior because the novel plating process, unless preceded by a short direct current plating period, tends to pit the surface of the brass by removal of zinc therefrom and requires pre-plating with cobalt-nickel, copper or nickel to prevent pitting.

Ordinary aqueous cobalt-nickel alloy plating solutions of the chloride type, as will be specified, are used in conjunction with novel addition agents to be described, which addition agents render the electro-plating, produced by the novel process of this invention, better in magnetic recording characteristics than cobalt-nickel alloy plating compositions made without the use of the novel addition agents. As is the practice in the plating of cobalt-nickel alloys, to increase magnetic recording properties, this process uses a plating current having a plating-phase and a reverse or deplating-phase, a novel current controlling device supplying the particular wave form preferably being used. This novel current control device is connected to an alternating current source. One lead of the alternating current source is connected directly to a plating electrode and the other lead is connected to two half-wave rectifiers of opposite phase connected in parallel and containing circuit elements which cause them to be unbalanced as to output so that the average plating-phase current density is less than 10 times and more than one time the average deplating phase current density. The current density during the plating phase may range from 100 to 1400 amperes per square foot and the current density during the deplating phase may range from 32 to 480 amperes per square foot. The plating current may be obtained in any other manner than that specified as preferred, as, for instance, by super-imposing alternating current on direct current.

A superior grade of Phosphor-bronze suitable for making the base tape or other base forms is one having, in percentage, by weight,

3.50-5.80 tin
.03-.35 phosphorous
.01 iron maximum
.05 lead maximum
.30 zinc maximum
99.50 minimum for copper, tin, lead and zinc-combined.

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The percentages given for the Phosphor-bronze ingredients may vary considerably without impairing the results obtained by the novel plating process. The Phosphor-bronze of the type specified above as a preferred example is suitable for flexing about the drums or reels of supporting and driving members of a magnetic signal recording or reproducing machine.

The process, as before stated, utilizes certain addition agents, and these are in the form of chemical compounds which are necessary to the process; these addition agents including, first, either ortho-toluene sulfonamide or para-toluene sulfonamide or a mixture of them, and, second, boric acid.

As is common practice in nickel or cobalt plating or a nickel-cobalt plating, to prevent pitting of the plated surface, a wetting agent, such as sodium lauryl sulfate, is added in small quantity to the electrolyte.

Therefore, it is an object of the invention to provide a process for making a superior cobalt-nickel electro-plate on a non-magnetic base material.

Another object of the invention is to provide such a process in which the superior electro-plating is brought about by the addition of certain chemical compounds to ordinary cobalt-nickel plating solutions.

With these and incidental objects in view, the invention includes certain novel steps and ingredients, a preferred embodiment of the process being hereinafter described with reference to a drawing which accompanies and forms a part of this specification.

In the drawing:

Fig. 1 is a reproduction of the hysteresis loop traced by the beam of a cathode ray tube used to examine the magnetic characteristics of a Phosphor-bronze tape .001 of an inch in thickness and electro-plated with cobalt-nickel composition to a thickness of .0004 of an inch on each side, without the use of the addition agents used in the novel process of this invention.

Fig. 2 is a reproduction of the hysteresis loop traced by the beam of a cathode ray tube used to examine, under the same circumstance as the tape of Fig. 1, the magnetic characteristics of a tape similar to the tape of Fig. 1 except that the plating bath contained the addition agents used in the novel process of this invention.

Fig. 3 is a reproduction of the trace made by a recording X-ray diffraction spectrometer instrument using a copper radiation and examining a cobalt-nickel electro-plated Phosphor-bronze tape of the type shown in Fig. 2, that is to say, one made with the use of the novel addition agents provided by the process of this invention.

Fig. 4 is a reproduction of the trace made with the same instrument as made the trace of Fig. 3 and with a similar tape and under the same conditions, except that the tape had been electro-plated in a bath not containing the novel addition agents provided by this process.

Fig. 5 is a circuit diagram for controlling the energy supply to an electrolytic bath, the dotted waveform of Fig. 6 being derived from this circuit.

Fig. 6 shows an alternating current wave symmetrical with respect to its axis, and also shows in dotted outline the plating and deplating phases thereof.

There, next, will be described, in detail, a preferred form of electro-plating cobalt-nickel according to the process of this invention.

Into a rubber-lined steel plating tank, or equivalent inert container, is introduced an electrolyte consisting of the following ingredients given in grams per liter of aqueous solution.

Cobalt, as cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$)	25 to 75
Nickel, as nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	10 to 75
Boric acid	5 to 45.0
Addition agents	1 to 3

The addition agents, ortho-toluene sulfonamide and para-toluene sulfonamide may be used in a mixture of any proportions or either may be used alone.

It has been found by applicants that an alloy of cobalt-nickel of 80%-85% cobalt content and the remainder nickel is superior magnetically. The anode, therefore, preferably is an alloy of cobalt and nickel in the proportion of 80%-85%, by weight, of cobalt and 20%-15%, by weight, of nickel.

It is desirable to adjust the pH of the bath to between 1 to 5.5 and to have the bath temperature between 100° and 200° F.

To prevent pitting of the electro-plate by clinging of hydrogen bubbles to the cathode, the wetting agent is specified. For instance, the aforementioned sodium lauryl sulfate may be used in an amount of 0.002 to 0.003 gram per liter of solution. As is common practice, the anodes are bagged with cotton goods, or equivalent, to prevent the contamination of the electrolyte bath with particles of sludge formed as an undesirable product of the corrosion of the anode. The total effective area of the anodes, generally speaking, should be equal to the area of the cathode material undergoing plating. In processing a tape, the tape is passed through the bath in a continuous run, the tape entering the bath at one side of the tank, looping through the bath and leaving it on the other side of the tank, the anodes being disposed so both sides of the tape receive an equal amount of deposit.

It has been found that a tape of the dimension given, plated on each side to a thickness of .0004 of an inch seems to have excellent magnetic and physical characteristics. To so plate a tape of Phosphor bronze of .001 of an inch in thickness, the tape may be in the bath for approximately six minutes during which time it is subjected to, on the plating phase, preferably, a current density of 480 amperes per square foot and is subject to, on the reverse or deplating phase, a current density of 160 amperes per square foot, with a 60-cycle frequency, although the latter may be varied between 25 and 400 cycles. Because the current density used is so high there is a consequent danger of burning the metal tape being plated. Therefore, in order to keep it cool the energized portion of the tape may be submerged in the electrolyte with the contacts protected from being plated by use of physical shielding. The shielding may be in the form of a submerged cell which has an entrant slot and an exit slot through which the tape passes, yet affording an access to the electrolyte fluid which acts as a coolant. Such cells may be made of plastic resinous material such as methyl methacrylate. The cooling may also be accomplished, in case non-submerged contacts are used, by flowing electrolyte over the entrant tape between the contacts and the bath.

The metal base strip or tape may be subjected to a conventional cleaning bath before it is introduced into the plating bath. On emergence from the plating bath the tape is rinsed and dried. If it is found that the edges of the tape have a bead of the plating material formed along them, the bead may be cut off by a slitting machine which acts as an edge trimmer.

The plated tape made according to the above process is exceptionally adapted for having recorded thereon magnetic signals in the form of spots, although it is useful for receiving audio signals as well. According to Fig. 2, the tape, so plated, according to the preferred embodiment of this invention as just specified, has a remanence of approximately 8700 Gauss and a coercivity of approximately 230 Oersteds, as compared with similar plating made in a bath without the special addition agents, as shown in Fig. 1, where the remanence is only 5460 Gauss and the coercivity is 300 Oersteds. This means that the novel tape of this invention is easier to impress with a magnetic signal and it reproduces a larger signal than tapes made by similar electro-plating

but without the use of the specified novel addition agents provided by this process.

Figs. 3 and 4 show that the plating made on the tape represented by the hysteresis loop of Fig. 2 has a different lattice structure than the plating made on the tape represented by the hysteresis loop of Fig. 1. These X-ray diffraction spectrometer traces are taken between 35° 2θ and 53° 2θ as it is in that region that the difference in lattice structure is most noticeable. The peak 20 near 45° 2θ having a "d" value of 2.04 is smaller in Fig. 3 than the corresponding peak 21 in Fig. 4 and the peak 22 at 52° 2θ in Fig. 3 representing the "d" value of 1.76 is absent in Fig. 4. Also the presence of the high level around 47.8° 2θ is indicative of superior magnetic quantities. The difference between Figs. 3 and 4 positively indicates that there is a difference in the crystal structure of the plating produced by this novel process over plating made without the addition agent specified and stands as proof of the fact that the process of this invention provides a novel product.

The circuit of Fig. 5 permits independent adjustment of the plating and deplating current. The input to this circuit is represented by the typical alternating current wave 27 of Fig. 6, symmetrical with respect to the alternating current time axis 28. The alternating current input is applied to the control circuit between terminals 29 and 30. During the positive half cycle, illustrated between points 31 and 32 (Fig. 6), terminal 30 is positive with respect to terminal 29, and the plating current flows from the positive terminal along conductor 34 to the anode or plating electrode 35, located in the inert tank 36, containing solution 37. Since the cathode electrode 38, representing the work or plating recipient, is negative with respect to the anode electrode 35, plating is effected during this half cycle. The plating current, represented by the arrow 33, is returned to the other input terminal 29 by way of a path including an adjustable resistor 41 and a rectifier 42. The current which is actually effective in providing the plating action is represented by the dotted voltage waveform 43 of Fig. 6. The amplitude difference between the input wave 27 and the useful wave 43 is occasioned by the voltage drop across the resistor 41, neglecting, of course, any slight loss across the rectifier 42. Consequently, by adjusting the value of resistor 41, the magnitude of plating current can be selected as desired.

The deplating phase is established between points 32 and 43 of the time axis of Fig. 6. Reversal of the alternating current input wave 27 causes terminal 29 to become positive with respect to terminal 30. The deplating current, represented by the arrow 44, flows through rectifier 45 and adjustable resistor 46, from the cathode 38 to the anode 35, effecting the desired deplating of the recipient 38, and is returned over lead 34 to the now negative terminal 30. The amplitude of this current during the deplating interval is represented by the dotted wave 47 of Fig. 6. The amplitude is independently adjusted by resistor 46, the value of which usually greatly exceeds that of resistor 41. The ratio of plating to deplating current can be selected as desired, the resistor 41 usually being adjusted to zero or very nearly so, in order that the plating current approaches its maximum value and the resistor 48 set to a high value to provide a ratio within the range aforesaid.

As has been said, the process may be used to make platings of different thicknesses depending upon the use to which they may be put and the process may be used within the limits specified, to plate any form of base material, with comparable results.

While the process herein described is admirably adapted to fulfill the objects primarily stated, it is to be understood that it is not intended to confine the invention to the particular preferred embodiment disclosed for it is susceptible of variation without departing from the essence of the invention.

What is claimed is:

1. The process of electro-plating a base metal with a nickel-cobalt composition including the steps of preparing an electrolyte consisting of an aqueous vehicle in which has been dissolved nickel and cobalt salts so that the nickel content is from 10 to 75 grams per liter of solution and the cobalt content is from 25 to 75 grams per liter of solution and in which has been dissolved between 1 and 3 grams of a toluene sulfonamide per liter of solution, said toluene sulfonamide being taken from the group consisting of ortho-toluene sulfonamide and paratoluene sulfonamide, and boric acid in the amount of 5 to 45.0 grams per liter of solution; introducing the base metal into said electrolyte as the cathode; introducing an anode into the electrolyte; and passing, from an alternating current source, an alternating current between the electrodes, the connection from one electrode to the alternating current source being a direct connection, and the connection from the other electrode to the alternating current source being divided into two parallel branches, one branch containing a first half-wave rectifier and a first impedance and the other branch containing a second half-wave rectifier oriented electrically to pass current in a direction opposite to that of the first rectifier and also containing a second impedance of a value different from the first so that there is a plating phase and

a deplating phase, said impedances being so selected that the average plating current density is less than 10 and more than one times the average deplating current density.

2. The process of claim 1 in which the nickel salt is nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$).

3. The process of claim 1 in which the cobalt salt is cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$).

4. The process of claim 1 in which the nickel and cobalt salts are, respectively, nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$).

5. The process of claim 4 in which the average current density during the plating phase may range from 100 to 1400 amperes per square foot and the average current density during the deplating phase may range from 32 to 480 amperes per square foot.

6. The process of claim 1 in which the average current density during the plating phase may range from 100 to 1400 amperes per square foot and the average current density during the deplating phase may range from 32 to 480 amperes per square foot.

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