(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 997 918 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.05.2000 Bulletin 2000/18

(51) Int. Cl.^{7}: **H01F 41/02**, H01F 1/00,
G08B 13/24

(21) Application number: **99201371.4**

(22) Date of filing: **29.04.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **26.10.1998 EP 98203868**

(71) Applicant: **AGFA-GEVAERT N.V.**
2640 Mortsel (BE)

(72) Inventors:
- **Andriessen, Hieronymus**
  2640 Mortsel (BE)
- **Lezy, Steven**
  2640 Mortsel (BE)

(74) Representative:
Ramon, Charles Lucien et al
Agfa-Gevaert N.V.
Dienst Intellectuele Eigendom 3800
Septestraat 27
2640 Mortsel (BE)

(54) Preparation of a magnetic layer

(57) A process is disclosed for the preparation of semi-soft or soft magnetic layers. The process involves chemical reduction in aqueous medium of one or more types of metal ions including nickel ions, washing the resulting dispersion of metal particles, and coating this dispersion onto a support.

The resulting magnetic layers can be used in an anti-theft system.

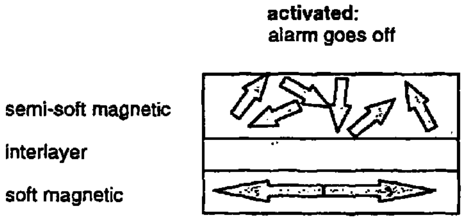

Fig. 2

EP 0 997 918 A1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to the preparation of particular types of magnetic layers and to their use in an anti-theft system.

BACKGROUND OF THE INVENTION

[0002] The lagging of magnetization behind the magnetizing force as the magnetic condition of a ferromagnetic material is changed, e.g. when applying an alternating external field, is called magnetic hysteresis. When a ferromagnetic sample that is initially demagnetized is subjected to an increasing external magnetic field H it reaches a particular flux density B_{sat} at the maximum value of H. When the value of H is decreased again the decreasing flux density does not follow the path of increase but decreases at a rate less than that at which it rose. When H has reached zero again the value of B is not reduced to zero but to a value called the retentivity or remanence. The sample has retained a permanent magnetization. The value of B may be reduced to zero by reversing th magnetic field to negative and increasing its value to the so-called coercive force or coercivity. By further increasing H to negative values and then again reversing its direction a hysteresis loop as represented in fig. 1 is completed.

[0003] We define in this curve :

- the saturation magnetization B_{sat} which is proportional to the amount of material;
- the coercive force C_M which is dependent on the chemical composition, the particle size, the temperature, etc.;
- the magnetic permeability (susceptibility or permitivity) P_M which is dependent on the chemical composition, the degree of deformation of the material, etc..

[0004] A so-called soft ferromagnetic material shows a rather low coercive force ; a so-called semi-soft ferromagnetic material shows a rather high coercive force. This properties are used in a special type of anti-theft labels, e.g. for preventing the theft from clothes out of shops, called EM-EAS labels (Electro Magnetic Electronic Article Surveillance). The principle works as follows. A label carrier is covered on one side with a soft magnetic layer having a coercive force of about 0.5 Oe, and on the other side with a semi-soft magnetic layer having a coercive force of about 100 Oe. The detection zone consists of a transmitter which transmits an alternating magnetic field with a force Z_M positioned between 0.5 and 100 Oe, and of a receiver.

[0005] Under normal conditions the soft magnetic material will follow the alternating magnetic field. This is the case when the semi-soft layer is not magnetized (active situation). When one walks with this label through the detection zone the reversing of the magnetic dipole due to the high permeability (>40,000) will be detected by the receiver and as a consequence an alarm will go off. On the contrary, when the semi-soft layer is magnetized the soft material will be magnetized as well in the opposite sense. The transmitter is in this case not able to influence the soft magnetic material since the field strenght of the semi-soft material is larger than the strenght of the transmitted alternating field. As a consequence nothing is detected. The situations explained are briefly summarized in fig. 2.

[0006] For a particular brand of commercially available labels the semi-soft magnetic layer consists of a nickel mesh, and the soft magnetic layer consists of a complex alloy of $Ni_aFe_bCo_c(Mo)_dB_e$. The problem with these magnetic layers is the fact that they are nowadays applied by means of sputtering in vacuo, a cumbersome and expensive technique.

OBJECTS OF THE INVENTION

[0007] It is an object of the present invention to provide a simple and cheap method for producing soft and semi-soft magnetic layers.

[0008] It is a further object of the invention to provide a use for such magnetic layers in the design of EM-EAS labels.

SUMMARY OF THE INVENTION

[0009] The above mentioned objects are realised by providing a process for the preparation of a magnetic element comprising a support and at least one magnetic layer, said process comprising the steps of :

(1) preparing an aqueous solution containing one or more type of metal ions including nickel ions,
(2) chemically reducing said one or more metal ions by means of a reducing agent thus forming an aqueous dis-

persion of metal particles including nickel,

(3) removing all superfluous ions from said aqueous dispersion by means of a washing step, preferably an ultrafiltration and/or diafiltration step, or by means of centrifugation,

(4) coating the resulting aqueous dispersion onto a support.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The present invention will now be explained on the hand of a preferred embodiment whereby the metal ios undergoing reduction are solely nickel(II) ions.

[0011] In a first step an aqueous solution of nickel(II) ions is prepared. A most suitable salt is $Ni(NO_3)_2.6H_2O$. The solution is acidified with a small amount of nitric acid.

[0012] In a following step the nickel ions in the solution are reduced to highly dispersed metallic nickel particles of nanosize by means of the addition of a reducing agent. A preferred reducing agent is KBH_4. The reducing agent can be added to the original nickel salt solution as a solid powder. More preferably, the reducing agent may be dissolved separately in a second aqueous medium and added to the nickel salt solution according to a single jet or a double jet procedure. Preferably, according to the double jet principle, the aqueous medium containing the nickel ions and the second solution containing the reducing agent are added together to a third aqueous medium.

[0013] The second aqueous solution comprising the reducing agent preferably also contains sulphite ions which strongly enhance the chemical stability of this solution.

[0014] In order to keep the nickel nanoparticles formed by reduction in colloidal dispersion a protective binder is preferably added to one or more of the three aqueous solutions involved. Preferably, this protective binder is added to the third aqueous medium wherein both others are jetted. A particularly preferred protective binder is carboxymethylcellulose (CMC). Other possible binders include gelatin, arabic gum, poly(acrylic acid), cellulose derivatives and other polysaccharides.

[0015] Preferably also a complexing agent is present in one of the three aqueous media described above. A preferred complexant is simply the well-known ethylenediaminetetraacetic acid (EDTA) or a homologous compound or a salt thereof. Another preferred one is citrate, e.g. triammonium citrate. Other suitable complexants include diethylenetriamine-pentaacetic acid (DTPA), trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA), ethyleneglycol-O,O'-bis(2-aminoethyl)-N,N,N',N'-tetraacetic acid (EGTA), N-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetic acid (HEDTA), etc.. The complexing agent is preferably present in the third aqueous medium to which the other solutions are added according to the double jet principle.

[0016] In a following step 3 of the present invention the superfluous salts are first removed from the aqueous medium by a washing process, preferably involving ultrafiltration and/or diafiltration. Additionally or alternatively centrifugation can be used.

[0017] In any of the solutions involved in the preparation a so-called dispersing aid can be present. In a preferred embodiment this compound is added to the diafiltration liquid at the last stage of the preparation. Suitable dispersing aids in the case of nickel are phosphates, more particularly a hexametaphosphate such as sodium hexametaphosphate. Probably, the hexametaphosphate adsorbs to the surface of the alloy particles so that they become negatively charged. By electrostatic repulsion they are kept in dispersion. Also the phosphate inhibits further oxidation of the surface of the formed nanoparticles. In other words, the thin nickel oxide shell that will be formed inevitably around the nanoparticles since the reducing medium disappears during the washing step will be passivated by the hexametaphosphate. So in a preferred embodiment the nickel particles are ultrafiltrated e.g. through a Fresenius F60 cartridge and subsequently diafiltrated against a solution of sodium hexametaphosphate in water/ethanol (98.5/1.5). Apart from the diafiltration liquid the hexametaphosphate is also preferably added to the third aqueous solution.

[0018] Preferably after the addition of one or more coating agents the obtained final colloidal composition is coated on the substrate by means of a conventional coating technique, such as slide hopper, curtain coating and air-knife coating.

[0019] Suitable coating agents include non-ionic agents such as saponins, alkylene oxides e.g. polyethylene glycol, polyethylene glycol/polypropylen glycol condensation products, polyethylene glycol alkyl esters or polyethylene glycol alkylaryl esters, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivaties, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agenst comprising an acid group such as a carboxy, sulpho, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as aklylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Other suitable surfactants include perfluorinated compounds.

[0020] Useful transparent organic resin supports include e.g. cellulose nitrate film, cellulose acetate film, polyvinylacetal film, polystyrene film, polyethylene terephthalate film, polycarbonate film, polyvinylchloride film or poly-α-olefin films such as polyethylene or polypropylene film. The thickness of such organic resin film is preferably comprised between 0.05 and 0.35 mm. In a most preferred embodiment of the present invention the support is a polyethylene terephthalate layer provided with a subbing layer. This subbing layer can be applied before or after stretching of the polyester film support. The polyester film support is preferably biaxially stretched at an elevated temperature of e.g. 70-120°C, reducing its thickness by about 1/2 to 1/9 or more and increasing its area 2 to 9 times. The stretching may be accomplished in two stages, transversal and longitudinal in either order or simultaneously. The subbing layer, when present, is preferably applied by aqueous coating between the longitudinal and transversal stretch, in a thickness of 0.1 to 5 mm. In case of a nickel magnetic recording layer the subbing layer preferably contains, as described in EP 0 464 906, a homopolymer or copolymer of a monomer comprising covalently bound chlorine. Examples of said homopolymers or copolymers suitable for use in the subbing layer are e.g. polyvinyl chloride; polyvinylidene chloride; a copolymer of vinylidene chloride, an acrylic ester and itaconic acid; a copolymer of vinyl chloride and vinylidene chloride; a copolymer of vinyl chloride and vinyl acetate; a copolymer of butylacrylate, vinyl acetate and vinyl chloride or vinylidene chloride; a copolymer of vinyl chloride, vinylidene chloride and itaconic acid; a copolymer of vinyl chloride, vinyl acetate and vinyl alcohol, etc.. Polymers that are water dispersable are preferred since they allow aqueous coating of the subbing layer which is ecologically advantageous.

[0021] Alternatively, the support may be opaque, such as a paper support, e.g. a plain paper support or a polyolefin coated paper. Furtheron glass, e.g. thin glass packed on roll can be used.

[0022] The coated substantially pure nickel layer is ferromagnetic of the so-called semi-soft type.

[0023] In a further important embodiment of the present invention the nickel ions are not the sole ion type undergoing reduction but they are mixed with one or more other types of ions. Preferred types of salts for admixture with the nickel salt are iron salts, cobalt salts or molybdene salts, or mixtures of those.

[0024] By choosing the appropriate type(s) of ions and the appropriate admixture ratio(s) so-called soft magnetic layers can be prepared.

[0025] In a particular embodiment of the present invention a support, preferably a paper support, is coated on one side with a semi-soft magnetic layer based on substantially pure nickel prepared according to the present invention, and on the opposite side with a soft magnetic layer based on an admixture of nickel particles with other metal particles prepared according to the present invention. When this material is cut into small dimensions the resulting labels can be used in a EM-EAS system (Electro Magnetic Electronic Article Surveillance). Furtheron, such a label can also be produced when a semi-soft magnetic layer prepared according to the present invention is applied to a commercially available soft magnetic layer on a support. Examples of such commercial products are PERMALLOY (trade mark of Western Electric), METGLAS (trade mark of Allied Signal Co.), and ATALANTE (trade mark of IST/Bekaert). Particularly useful METGLAS products are type 2705M, consisting of $Co_{69}Fe_4Ni_1B_{12}Si_{12}$, and type 2826MB, consisting of $Fe_{40}Ni_{38}Mo_4B_{12}$. Vice versa, such a label can also be produced when a soft magnetic layer prepared according to the present invention is applied to a commercially available semi-soft magnetic layer on a support. Examples of such commercial products are VICALLOY (trade mark of Telecon Metals Ltd.), AMOKROME (trade mark of Arnold Engineering), and CROVAK (trade mark of Vacuumschmelze GmbH).

[0026] The present invention will now be illustrated by the following examples without however being limited thereto.

Examples

Example 1

Preparation of a magnetic material (NiFe).

[0027] The following solutions were prepared:

Solution 1	
$Ni(NO_3)_2.6H_2O$	41.8 g
$Fe(SO_4)_2.6H_2O$	14.3 g
water to	150 ml
HNO_3	3ml

Solution 2	
Water	150 ml
NH_3 (26% in water)	0.5 ml
KBH_4	10 g
Na_2SO_3	2 g

Solution 3	
Na6P6O18 (2% in water/ethanol (85/15)	100 ml
Triammoniumcitrate (70% in water)	9.1 ml
Carboxymethylcellulose (3% in water)	25.5 ml

[0028] The Ni-Fe-dispersion was prepared as follows:

[0029] To solution 3, held at room temperature and stirred at 300 rpm, solution 1 at a flow rate of 12.4 ml/min was simultaneously added with solution 2 at 12.4 ml /min. After the reduction, the NiFe dispersion was ultrafiltrated through a Fresenius F60 cartridge and diafiltrated with a 0.36 % solution of sodium hexametaphosphate in water/ethanol (98.5/1.5).
The dispersion was stirred and 10 ml of a 12.5% solution of Saponine Quillaya (Schmittmann) in water/ethanol (80/20) was added. This is the Ni-Fe dispersion.
The dispersion was analysed for its particle size distribution (weight average d_{wa}) with the Disc Centrifuge Photosedimentometer BROOKHAVEN BI-DCP. A d_{wa} of 56 nm (s_{wa} = 10) was obtained.
Subsequently this dispersion was coated on a substrated PET foil so that an amount of 0.90 g/m^2 was obtained.
A Squid magnetometer was used to measure the magnetic properties. A coercive field of 110 Oe was measured.

Claims

1. Process for the preparation of a magnetic element comprising a support and at least one magnetic layer, said process comprising the steps of :

    (1) preparing an aqueous solution containing one or more type of metal ions including nickel(II) ions,
    (2) chemically reducing said one or more metal ions by means of a reducing agent thus forming a aqueous dispersion of metal particles including nickel,
    (3) removing all superfluous ions from said aqueous dispersion by means of a washing step or by means of centrifugation,
    (4) coating the resulting aqueous dispersion onto a support.

2. Process according to claim 1 wherein said reducing agent is added by means of a separate second aqueous solution.

3. Process according to claim 2 wherein said separate second aqueous solution further contains sulphite ions.

4. Process according to any of claims 1 to 3 wherein said reducing agent is KBH_4.

5. Process according to any of claims 1 to 4 wherein said washing step involves an ultrafiltration and/or diafiltration step.

6. Process according to claim 5 wherein a phosphate is present as dispersing aid during the ultrafiltration and/or dia-

filtration step.

7. Process according to claim 6 wherein said phosphate is a hexametaphosphate.

8. Process according to any of claims 1 to 7 wherein said metal ions are substantially solely nickel(II) ions thus giving rise after completing steps (1) to (4) to a semi-soft magnetic layer.

9. Process according to any of claims 1 to 7 wherein said metal ions beside nickel ions further comprise iron ions, cobalt ions or molybdene ions, or mixtures of those, thus giving rise afer completing steps (1) to (4) to a soft magnetic layer.

10. Magnetic material comprising a support and on one side of said support a semi-soft magnetic layer prepared according to the process of claim 8, and on the other side of said support a soft magnetic layer.

11. Magnetic material comprising a support and on one side of said support a semi-soft magnetic layer, and on the other side of said support a soft magnetic layer prepared according to the process of claim 9.

12. Magnetic material comprising a support and on one side of said support a semi-soft magnetic layer prepared according to the process of claim 8, and on the other side of said support a soft magnetic layer prepared according to the process of claim 9.

13. Use of a magnetic material according to any of claims 10 to 12 as a label in a EM-EAS system (Electro Magnetic Electronic Article Surveillance).

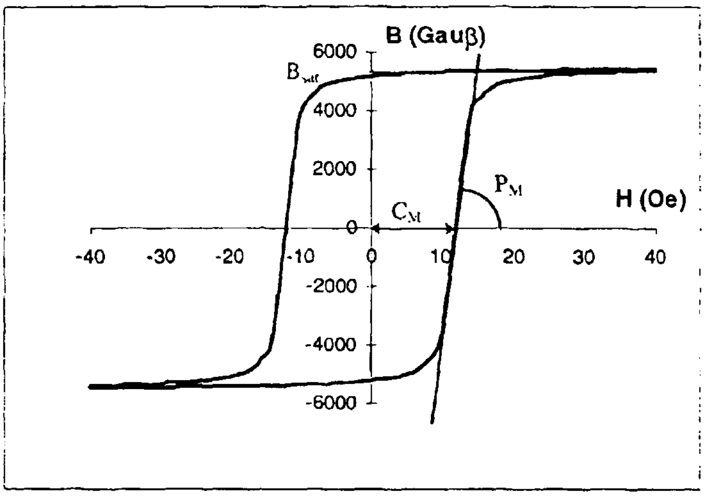
B (Gauβ)
6000
4000
2000
0
-2000
-4000
-6000
Bsat
PM
CM
H (Oe)
-40
-30
-20
-10
0
10
20
30
40

Fig. 1

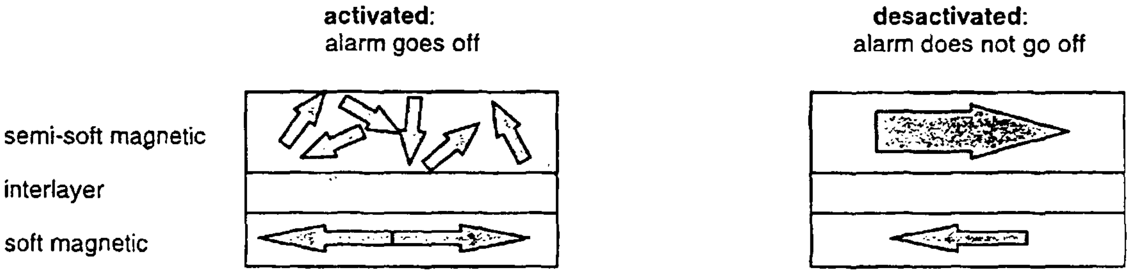
activated:
alarm goes off
desactivated:
alarm does not go off
semi-soft magnetic
interlayer
soft magnetic

Fig. 2

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 1371

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 007, no. 069 (C-158), 23 March 1983 (1983-03-23) & JP 58 003963 A (NIPPON DENKI KK), 10 January 1983 (1983-01-10) * abstract * ---	1,9	H01F41/02 H01F1/00 G08B13/24
A	PATENT ABSTRACTS OF JAPAN vol. 006, no. 143 (C-117), 3 August 1982 (1982-08-03) & JP 57 067156 A (NEC CORP), 23 April 1982 (1982-04-23) * abstract * ---	1,9-11	
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 325 (P-1075), 12 July 1990 (1990-07-12) & JP 02 108221 A (MITSUBISHI KASEI CORP), 20 April 1990 (1990-04-20) * abstract * ---	1,4,9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	EP 0 793 242 A (UNITIKA LTD) 3 September 1997 (1997-09-03) -----		H01F G08B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 January 2000	Decanniere, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 20 1371

14-01-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 58003963 A	10-01-1983	JP 1613936 C	15-08-1991
		JP 2029753 B	02-07-1990
JP 57067156 A	23-04-1982	JP 1021227 B	20-04-1989
		JP 1546136 C	28-02-1990
JP 02108221 A	20-04-1990	NONE	
EP 0793242 A	03-09-1997	JP 9232142 A	05-09-1997
		CA 2198810 A	28-08-1997
		US 5932310 A	03-08-1999