



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US84/01381 <b>(22) International Filing Date:</b> 30 August 1984 (30.08.84)  <b>(31) Priority Application Number:</b> 528,045 <b>(32) Priority Date:</b> 31 August 1983 (31.08.83) <b>(33) Priority Country:</b> US  <b>(71) Applicant:</b> DeSOTO, INC. [US/US]; 1700 South Mt. Prospect Road, Des Plaines, IL 60018 (US). <b>(72) Inventors:</b> BROWN, Wallace, H. ; 1308 Gilbert, Downers Grove, IL 60515 (US). ANSEL, Robert, E. ; 1440 Caldwell Lane, Rolling Meadows, IL 60194 (US). <b>(74) Agents:</b> GULKO, Arnold, G. et al.; Dressler, Goldsmith, Shore, Sutker & Milnamow, Ltd., 1800 Prudential Plaza, Chicago, IL 60601 (US).		<b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> MAGNETIC RECORDING STRUCTURE AND PROCESS		
<b>(57) Abstract</b>  Magnetic recording structure and a process for producing magnetic recording structures having a greater concentration of magnetizable particles in which a layer of magnetizable particles of reduced thickness is provided by coating a substrate with a liquid coating composition which is substantially free of magnetizable particles and which provides a tacky surface adapted to bond to magnetizable particles, magnetizable particles are applied to the tacky surface which is then solidified with the particles thereon.		

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## MAGNETIC RECORDING STRUCTURE AND PROCESS.

DESCRIPTION5 Field of the Invention

This invention relates to the production of magnetic recording structures, especially tapes, in which a layer of magnetizable particles of reduced thickness, preferably only one or two particles  
10 thick, is applied to a nonmagnetizable substrate.

Background Art

The production of magnetic recording structures, such as tapes and discs, is known. In these known processes, a liquid coating composition  
15 which has been pigmented with particles having the capacity to retain a magnetic orientation, referred to hereinafter as magnetizable particles, is applied to an appropriate nonmagnetizable substrate. The pigmented coating is then baked to solidify the  
20 coating and fix the magnetizable particles in place within the coating. In the known processes, the magnetizable particles are used in admixture with a nonmagnetizable binder (which may be thermoplastic or thermosetting) and a volatile solvent to provide a  
25 pigmented coating composition which is applied as a thin coating upon the substrate which is then baked to remove the solvent and to cure the binder if it is curable. Such a process is illustrated in U. S. Patent No. 4,246,316. However, this process produces  
30 a coated substrate in which the magnetizable particles are dispersed throughout the layer of binder, and this layer is normally thick enough to accommodate many layers of particles. As a result, a great many magnetizable particles are used and the  
35 final product is heavier and more expensive than



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desired. Also, the thinner and more concentrated the magnetizable particle layer, the better the recording performance, so this provides a further reason for making the distribution of particles as narrow as possible.

Description of the Invention

In accordance with this invention, a substrate is first coated with a liquid coating composition which is substantially free of magnetizable particles and which provides a tacky surface having the capacity to bond to magnetizable particles applied to the tacky surface thereof. Magnetizable particles are then applied to the exposed tacky surface of the applied coating, and this may be done by dusting a dry powder or by spraying on a suspension of the particles in a volatile organic solvent or by transferring dry powder that has previously been coated on a smooth surface that will readily release the dry pigment. The coated substrate with the particles thereon is then solidified, as by heating or exposure to radiation when the binder is radiation-curable.

The substrate is normally nonmagnetizable, as when Mylar is used, but any substrate can be used. If orientation of the magnetizable particles is desired, the coated substrate with the particles adhered to its exposed surface is passed through a magnetic field, which may be vertical or horizontal, as desired, and the coating is preferably solidified while the coating is within this magnetic field. This expedient of solidifying the coating while it is within the magnetic field is the subject of a commonly owned application, or if it is not used, the particles can be oriented and then transferred to the tacky surface.



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The objective of this invention is to adhere to the binder-coated substrate as close to a single layer of particles as possible. Excess particles which are not bound by the binder may be blown or  
5 brushed off prior to or after solidification of the wet coating or thereafter. In this invention, the applied magnetizable particles are concentrated by being confined to the surface of the previously applied coating and are prevented from becoming  
10 dispersed in that coating.

The process of this invention produces a magnetic recording structure having a higher recording density and improved recording characteristics because the magnetizable particles  
15 are more densely packed and confined to a thinner layer. More particularly, many of the magnetizable particles are only partially embedded in the upper surface of the layer of nonmagnetizable resin, and this structure distinguishes the products of this  
20 invention from the magnetic recording structures previously available. This also provides a desirable economy.

The final structure may be overcoated to protect the magnetizable particles, but this is not  
25 essential for in some systems, there is no contact between the recording head and the upper surface of the layer which is intended to receive the magnetic image.

The selection of magnetizable particles is  
30 not an aspect of this invention. These are illustrated by acicular gamma- $\text{Fe}_2\text{O}_3$  particles of pigment grade which may be modified with cobalt oxide. The coercivity of these particles is a variable, and the appropriate selection of this  
35 factor is known in the art. U. S. Patent No.



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4,246,316 contains an extensive disclosure of suitable magnetizable particles.

The preferred substrate is commonly biaxially oriented polyethylene terephthalate when that substrate is to form part of the final magnetic recording structure, but the choice of the nonmagnetizable substrate and its thickness are known to the art. Also, temporary substrates can be used, such as polytetrafluorethylene, commercially available under the name Teflon, when laminating processes are employed, as will be illustrated in the examples herein. The Teflon facilitates removal of the temporary substrate after the resin layer with the magnetizable pigment bonded to one surface thereof has been removed.

Any liquid coating composition which will adhere to the substrate and which will provide a tacky surface (or which can be partially dried to provide a tacky surface) may be employed. Since conventional thermoplastic and thermosetting binders are nonmagnetizable, any of these may be used, normal application being from a solution in a volatile organic solvent. However, and since all that is desired is adhesion to the substrate and an adherent surface, one may also employ aqueous coatings, including aqueous latices of thermoplastic emulsion copolymers.

One may also employ a liquid radiation-curable polyethylenically unsaturated coating composition for these are also generally nonmagnetizable. Polyacrylates are particularly preferred and will be illustrated herein. Electron beam radiation is preferred for curing these polyacrylate coating compositions since the pigment which is associated with the predeposited layer of



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coating does not interfere greatly with the penetration of this radiation.

Referring more particularly to the radiation curable coatings which may be used herein, these are  
5 subject to wide variation because any electron beam-curable coating composition is theoretically useful. However, it is preferred to employ liquid solvent solution coatings which contain at least one viscous nonpourable liquid to normally solid  
10 polyethylenically unsaturated compound having at least 2.5 repeating units (preferably at least 4) held together by linkages selected from the group consisting of urethane groups, urea groups, thiocarbamate groups, and mixtures thereof, and there  
15 is an average of one ethylenically unsaturated group per from 750 to 10,000 units of molecular weight. The repeating units preferably have a molecular weight in the range of 60-2000, more preferably from 200-1500, and the groups containing the ethylenic  
20 unsaturation are not counted as repeating units. The liquid vehicle has low viscosity to enable coating, and the status of the unsaturated compound is noted at 25°C. The solvent may be ethylenically unsaturated, and hence reactive during the electron  
25 beam cure, or it can be nonreactive, e.g., an ordinary organic solvent. If the wet-coated substrate contains a volatile nonreactive solvent, this volatile solvent is removed, as by vaporization at room or slightly elevated temperature so that the  
30 surface is tacky. After the process of this invention has been carried out, the coating with the layer of magnetizable particles adhered thereto is exposed to electron beam radiation to convert the unsaturated compound into a solid thermoset coating  
35 having a layer of magnetizable particles confined to



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the upper surface thereof with some of these particles being partially embedded in the cured coating.

The polyethylenically unsaturated compounds are formed to contain a plurality of repeating units which are held together by certain selected groups, as previously set forth. To illustrate how this is done, one can take a diol, such as 1,4-butane diol, and react it with a diisocyanate, like isophorone diisocyanate, to provide a linear oligomer which may be either isocyanate-terminated or hydroxy terminated, depending upon which functional group is in excess. By varying proportions, e.g., by using a 3:2 or 4:3 equivalent ratio between the functional groups which are interreacted, several repeating groups will be formed, and they will be linked by urethane groups.

Correspondingly, and by using a diamine, like hexamethylene diamine, in place of the diol noted above, one will obtain an oligomer in which the repeating units are linked together by urea groups instead of urethane groups.

It will be understood that if a mixture of diamine and diol is used, that the linking groups in the oligomer which is formed will contain some urea groups and some urethane groups.

On the same basis, one can use a dimercaptan, like 1,6-hexane dimercaptan, in place of the diol discussed previously, and the product will now be an oligomer in which the repeating units are thiocarbamate groups.

While difunctional materials have been illustrated above, higher functional materials are also useful to form oligomers which are branched instead of linear. These higher functional materials





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are illustrated by trimethylol propane or pentaerythritol. Triisocyanates, like the biuret of hexamethylene diisocyanate, are also useful.

The plurality of linkages of the type noted  
5 provides the oligomer with improved toughness, and the many variations which are permissible will be evident to those skilled in the art and are illustrated more fully in commonly owned application serial No. 473,544 filed Mar. 9, 1983.

10 Of course, the oligomers described above are terminated with unsaturated groups, preferably with acrylate groups. This is easily done by using either hydroxyethyl acrylate or its reaction product with one molar proportion of a diisocyanate, like  
15 isophorone diisocyanate, to provide an unsaturated monoisocyanate. The hydroxyethyl acrylate is selected as the reactant when the oligomer is terminated with isocyanate functionality. The monoisocyanate is selected when the oligomer is  
20 terminated with isocyanate-reactive groups.

These oligomers are diluted to coating viscosity by the inclusion of reactive solvents, like trimethylol propane triacrylate, or by the presence of a monoethylenically unsaturated monomer, like  
25 N-vinyl pyrrolidone, or by the presence of a volatile nonreactive solvent, like methyl ethyl ketone. In this invention it is only necessary to have enough volatile material present so that the removal of volatiles will provide a solid to semi-solid layer  
30 having a tacky surface which will permit the magnetizable particles to adhere to it.

The electron beam-curable coatings of this invention possess superior toughness enabling satisfactory magnetic recording structures of good  
35 quality to be rapidly produced.



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In the examples which follow, the radiation-curable resin employed is of the type described above, and is a mixture of an ethylenically unsaturated polymer prepared from 4,4'-methylene bis phenyl isocyanate, poly tetramethylene glycol of average molecular weight 650 and 2-hydroxyethyl acrylate at a mole ratio of 6 to 5 to 2 (50% solution in methyl ethyl ketone), 2-isophorone diisocyanate trimer-2-hydroxyethyl acrylate adduct (60% solution in methyl ethyl ketone) and N-vinyl pyrrolidone at a 70/20/10 weight ratio based on solids. The resulting resinous solution at 54% reactive material had a viscosity of 1200 centipoises.

Example 1

15 A thin layer of magnetic pigment is deposited on a tacky, uncured but curable resin coated onto a polyethylene terephthalate substrate in the following manner.

The 54% solution of radiation curable resin dissolved in methyl ethyl ketone described previously, essentially free of pigment, was coated out on a polyethylene terephthalate sheet and the solvent was evaporated, resulting in a smooth, clear, tacky layer of uncured resin about 1 mil thick. A layer of magnetic pigment was deposited on the surface by dusting with an air gun. This pigment had been previously treated with a dilute solution of Dow Corning Z-6032 to enhance the wetting of the surface of the pigment by the resin and to help to promote 30 adhesion between the pigment and the resin.

The resin coated substrate with magnetic pigment on the surface was then passed through an electron beam processor and cured using a dose of 10 megarads

35 The resulting coated sheet was then



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burnished with burnishing paper to remove excess pigment from the surface and to smooth and polish the surface.

The result was a magnetic media that had a  
5 very thin, highly concentrated layer of magnetic oxide on the surface, approximately 2,000 - 4,000 angstroms thick. The particles were random oriented.

The same system in which the magnetic pigment was electrostatically sprayed on the surface  
10 of the uncured resin, resulted in a pigment surface of between 6,000 and 20,000 angstroms thick, with the particles oriented in the vertical direction.

#### Example 2

The same resin, essentially free of pigment,  
15 was coated onto the same base to provide an uncured film of tacky, mobile resin, 1 mil in thickness. A sheet of Teflon was coated with a very thin layer of magnetic pigment that had been treated with Dow Corning 2-6030 to enhance the pigment's ability to be  
20 wet and be bound by the resin.

The two films described above were then pressed together, the uncured resin in contact with the dry magnetic pigment. Light pressure was applied using a roller to get good, uniform contact over the  
25 entire surface of the sheet.

The laminated mass was then cured in an electron beam processor using a dose of 10 megarads. The Teflon film was peeled away, leaving a film constituted by a polyethylene terephthalate base  
30 coated with a film of cured resin having a thin layer of magnetic oxide embedded on the surface of the cured resin. The pigmented surface was then burnished with paper to remove the excess unadhered pigment and to smooth and polish the surface.

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Example 3

A thin layer of magnetic oxide that had been treated with Dow Corning 2-6032 was coated by means of a drawdown bar onto a smooth, chrome-plated sheet. This pigment-coated sheet was then passed through a curtain coater and a 1 mil thick layer of pigment-free resin was laid down over the thin layer of dry pigment.

At this point a polyethylene terephthalate sheet can be laminated to the uncured resin surface, or the coated chrome sheet can be processed as is. In either case the coated sheet is then put into an electron beam processor and exposed to a dose of 10 megarads.

The cured coating is then removed from the chrome base and burnished with paper to remove excess magnetic pigment and to smooth the surface.

The resulting film is a magnetic media with a thin (2,000 angstrom), highly concentrated layer of magnetic pigment on the surface.

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## WHAT IS CLAIMED IS:

1. A process for producing magnetic recording structures having a layer of magnetizable particles of reduced thickness comprising, coating a substrate with a liquid coating composition which is substantially free of magnetizable particles and which provides a tacky surface adapted to bond to magnetizable particles applied thereto, applying magnetizable particles to the exposed tacky surface of said substrate, solidifying said coating with said particles thereon, and removing excess particles from said exposed surface.
2. The coating process recited in claim 1 in which said liquid coating composition is applied to a nonmagnetizable substrate to which it is adherent.
3. The coating process recited in claim 1 in which said particles are supported on a substrate which is removed after the coating is solidified.
4. The coating process recited in claim 1 in which said liquid coating is solidified by heating.
5. The coating process recited in claim 1 in which said liquid coating is radiation-curable and is solidified by exposure to radiation.
6. The coating process recited in claim 5 in which said radiation is electron beam radiation.
7. The coating process recited in claim 1 in which said magnetizable particles are applied as a dry powder.
8. The coating process recited in claim 1 in which said magnetizable particles are suspended in a volatile organic solvent and are applied by spraying.
9. The coating process recited in claim 1 in which said magnetizable particles on said tacky surface are passed through a magnetic field to orient



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said magnetizable particles prior to solidifying said coating.

10. The coating process recited in claim 9 in which said coating is solidified while it is in  
5 said magnetic field.

11. The coating process recited in claim 1 in which said cured coating with the magnetizable particles bonded to the surface thereof is burnished to remove excess particles.

10 12. The coating process recited in claim 1 in which said liquid coating composition comprises an electron beam-curable polyethylenically unsaturated oligomer and a volatile organic solvent, and said solvent is evaporated to provide a solid to  
15 semi-solid curable layer having a tacky surface.

13. A magnetic recording structure comprising a solid layer of coating which is substantially free of magnetizable particles and a thin layer of magnetizable particles bonded to the  
20 upper surface of said layer, at least some of said particles being only partially embedded in the upper surface of said layer.

14. The coating process recited in claim 1 in which said magnetizable particles are oxide  
25 particles.

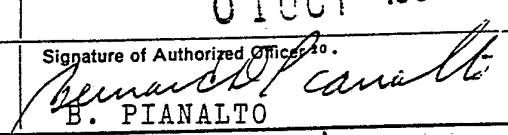
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# INTERNATIONAL SEARCH REPORT

International Application No PCT/US84/01381

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. <sup>9</sup> H01F 10/10		
U.S. CL. 427-44		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
U.S.	427-48, 130, 131, 385.5, 427 428-69, 900	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category *	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
P, Y	US, A, 4,410,565 PUBLISHED 18 OCTOBER 1983 KITAMOTO ET. AL	1-4, 13
A	US, A, 3,398,011 PUBLISHED 20 AUGUST 1968 G. NEIROTTI, ET AL	11
A	US, A, 3,649,358 PUBLISHED 14 MARCH 1972 H. K. JOHNSTON, II	8, 14
A	US, A, 4,335,183 PUBLISHED 15 JUNE 1982 HOSAKA	5-6, 7, 12
A	US, A, 2,857,879 PUBLISHED 28 OCTOBER 1958 W. L. JOHNSON	1
Y	N, IBM TECHNICAL DISCLOSURE BULLETIN ISSUED DECEMBER 1966, H. FRIEDMAN ET AL, LUBRICANTS FOR MAGNETIC RECORDING MEDIA, SEE PAGE 779, VOL. NO. 7	1
A	US, A, 2,161,083, PUBLISHED 14 JUNE 1973 DR. HANS-JURGEN MICHEL	9, 10
<p>* Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>3</sup>	Date of Mailing of this International Search Report <sup>2</sup>	
19 SEPTEMBER 1984	01 OCT 1984	
International Searching Authority <sup>1</sup>	Signature of Authorized Officer <sup>10</sup>	
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