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(54) **Magnetic recording medium**

(57) A magnetic recording medium comprises a substrate such as a polyester film coated with a magnetic layer which comprises a magnetic powder and a binder, said binder including a polyester resin having  $-\text{SO}_3\text{Na}$  groups and a polyurethane prepolymer. Other binder components such as a thermoplastic polyurethane polyester, nitrocellulose or a vinyl chloride-vinyl acetate copolymer can be also incorporated with said polyester. A crosslinking agent can be also incorporated to cure said binder.

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## SPECIFICATION

**Magnetic recording medium**

- 5 The present invention relates to a magnetic recording medium of the type comprising a substrate coated with a magnetic layer comprising a magnetic powder dispersed in a binder. 5
- High reproducing output of high frequency wave data is increasingly required of magnetic recording tapes especially magnetic recording tapes for video tape recorders. Various ways of improving the dispersibility and the surface property have been proposed. It has been proposed
- 10 to incorporate a surfactant as a dispersing agent in the binder of the magnetic coating composition applied to the tape or to increase the content of hydrophilic groups such as -OH groups, and -COOH groups, in the binder. In the former method the disadvantages of deterioration of physical properties and variation of properties on aging may be caused by the 10
- 15 satisfactory dispersibility has not been achieved in the case of a binder for a video recording tape or in the case of a magnetic composition comprising a powder having low dispersibility such as carbon black. 15
- The present invention provides a magnetic recording medium comprising a substrate coated with a magnetic layer comprising a binder and a magnetic powder, said binder including a resin
- 20 having -SO<sub>3</sub>Na groups and a polyurethane prepolymer. 20
- Magnetic recording media in accordance with the invention are found to have excellent surface reflectivity and excellent surface properties.
- The magnetic recording media of the invention have an excellent homogeneous magnetic layer in which the magnetic powders are highly dispersed. They also have an excellent S/N
- 25 ratio and excellent physical and electromagnetic characteristics such as high durability and good friction and still characteristics. 25
- The resin having -SO<sub>3</sub>Na groups is preferably a polyester resin. The binder may also include for example a thermoplastic polyurethane, nitrocellulose or a vinyl chloride-vinyl acetate and/or vinyl alcohol copolymer. A polyisocyanate crosslinking agent can be incorporated so as to
- 30 crosslink the binder. Two or more kinds of polyester resins including at least one polyester resin having -SO<sub>3</sub>Na groups can be used in the binder composition. 30
- The inventors have found that when a resin having branched chain groups of great polarity and having excellent softness is used as the binder, the dispersibility of the magnetic and other powders is remarkably high, giving a homogeneous layer, the surface property of the resulting
- 35 magnetic layer is excellent and the surface processibility of the magnetic layer is also excellent. No disadvantage appears to result from the incorporation of a dispersing agent. 35
- The magnetic powder can for example be a magnetic acicular metal or a magnetic acicular oxide.
- Other resins such as nitrocellulose, a vinyl chloridevinyl acetate and/or vinyl alcohol
- 40 copolymer and for a thermoplastic polyurethane prepolymer are preferably incorporated together with the polyester having -SO<sub>3</sub>Na groups. The use of these other resins is known in this field. 40
- The types and quantities of the magnetic powders used are also known.
- Typical resins having -SO<sub>3</sub>Na groups are polyesters of a polyhydric alcohol and a dicarboxylic acid which include a suitable amount of a sulfocarboxylic acid. The molar ratio of sulfocarboxylic
- 45 acid to the total of dicarboxylic acids is usually in a range of 0.2 to 30 mol %, preferably 0.5 to 20 mol % especially 1 to 10 mol % . 45
- The polyhydric alcohols can be glycols such as ethyleneglycol, propyleneglycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentylglycol, diethyleneglycol or dipropyleneglycol and ethyleneoxide adducts or propyleneoxide adducts such as polyethyleneglycol,
- 50 polypropyleneglycol and polytetramethyleneglycol. It is possible to incorporate a small ratio of a triol or a tetraol such as trimethylolpropane, glycerin or pentaerylthritol. 50
- The dicarboxylic acids can be aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, orthophthalic acid and 1,5-naphthalic acid; and aliphatic dicarboxylic acids such as succinic acid, adipic acid, azelaic acid, sebacic acid and suberic acid. It is also possible to
- 55 polycondensate oxycarboxylic acids such as p-oxybenzoic acid or p-(hydroxyethoxy) benzoic acid with a suitable amount of a sulfooxycarboxylic acid. It is possible to incorporate a small amount of a tricarboxylic acid or a tetracarboxylic acid such as trimellitic acid, trimesic acid or pyromellitic acid. 55
- Typical polyesters having -SO<sub>3</sub>Na groups are polyesters of ① a dicarboxylic acid such as
- 60 terephthalic acid, isophthalic acid, adipic acid or sebacic acid with the sodium sulfocarboxylic acid, especially sodium sulfoterephthalic acid or sodium sulfoisophthalic acid, and ② a polyhydric alcohol such as ethyleneglycol. A typical polyester resin having -SO<sub>3</sub>Na groups is commercially available as Vylon-530 (manufactured by Toyo Boseki K.K.) and obtained by the incorporation of -SO<sub>3</sub>Na groups into Vylon-500 (manufactured by Toyo Boseki K.K.). The
- 65 degree of the incorporation of -SO<sub>3</sub>Na groups is such as to impart hydrophilic properties to the 65

resin without making it water soluble. This means that quite a small ratio of  $-SO_3Na$  groups to the resin is satisfactory. The effect of the polyester resin having  $-SO_3Na$  groups is imparted since such resin has remarkable polarity. Other resins having  $-SO_3Na$  groups can also impart the same effect and can be also used in the recording medium of the present invention.

5 Typical polyurethane prepolymers for use in the present invention are reaction products of a diisocyanate and a polyester or a polyether. Typical diisocyanates which can be used are MDI (diphenylmethane diisocyanate); DMDI (dimethyl diphenylmethane diisocyanate); HMDI (hexamethylene diisocyanate); and TDI (tolylene diisocyanate). Typical polyesters are reaction products of an aliphatic dicarboxylic acid and a polyhydric alcohol, wherein the aliphatic dicarboxylic acid can be adipic acid or suberic acid and the polyhydric alcohol can be ethyleneglycol, propylene-  
10 glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentylglycol, diethyleneglycol, dipropyleneglycol, ethyleneoxide adducts or propyleneoxide adducts. The molecular weight of the prepolymer is usually in a range of  $1 \times 10^3$  to  $1 \times 10^5$ , preferably  $1 \times 10^4$  to  $1 \times 10^5$ .

15 The content of the polyester resin having  $-SO_3Na$  groups in the binders is usually in a range of 10 to 99 wt.%, preferably 20 to 90 wt.% based on the binders. The content of the polyurethane prepolymer in the binders is usually 1 to 60 wt.%, preferably 5 to 50 wt.% based on the binders. The remainder is preferably thermoplastic polyurethane, nitrocellulose and/or vinyl chloride-vinyl acetate and/or vinyl alcohol copolymer. It is preferable to incorporate a polyisocyanate as a crosslinking agent when a thermoplastic polyurethane prepolymer is  
20 incorporated. The content of the polyisocyanate to the binder is usually in a range of 1 to 30 wt.%, preferably 5 to 20 wt.%.

Suitable abrasives, carbon black, lubricants and other additives can be incorporated in the magnetic powder compositions of the invention at desired ratios. The magnetic powder  
25 composition is usually prepared with a large amount of an organic solvent such as ketone e.g. methyl ethylene ketone, a hydrocarbon, an ester or an alcohol. It is preferable to incorporate an organic solvent which will dissolve a resin having  $-SO_3Na$  groups. The ratio of the organic solvent used to the magnetic powder composition should be suitable for preparing a pasty magnetic powder composition which will be easily coatable on a substrate such as a polyester  
30 film or a metal plate.

In a preferred process, the magnetic powder and other powders such as carbon black and abrasives are well dispersed to give a homogeneous magnetic layer and the surface property is improved whereby the surface reflectivity, the residual magnetic flux density  $Br/B_m$  and  $Y-S/N$  of the magnetic recording medium are improved. Moreover, when the thermoplastic polyurethane prepolymer or the other resin is crosslinked with the polyisocyanate as the crosslinking  
35 agent, the durability, the running friction and the still time of the magnetic recording medium are improved together in addition to the effects imparted by the resin having  $-SO_3Na$  groups.

The other conditions for preparing the magnetic recording medium can be understood from the descriptions of prior disclosures such as U.S. Patent 4,115,290 G.B. Patent Publications  
40 2,017,117A, 2,021,126A and Patent Applications U.S. SN 109,032, West German P 3,001,451, U.K. 8001322 and Netherland 800061 and Japanese Patent Application 79937/1979.

The present invention will be further illustrated by the following examples and references which are provided for purposes of illustration only.

45 In the tables, the surface reflectivity is shown by the following equation: (decibel) 45

$$\text{Surface reflectivity} = 20 \log \frac{X}{\text{REF}}$$

50 wherein REF designates the reflectivity of an STD plate measured by Type GM5 manufactured by Murakami Color Research Laboratory (Japanese Industrial Standard Z 8741-GS-60-94) and X designates the reflectivity of the sample. 50

The running friction is shown by the tension at an outlet of a head drum of National VHS  
55 Video Tape Recorder NV 8600 which is measured by a tension gauge. 55

The still time was measured by National VHS Video Tape Recorder NV 8600 under a tension of 100g. at 0°C.

The  $Y-S/N$  is  $S/N$  ratio of a white-black picture. (based on Standard Tape (TDK Reference Tape).  
60 60

*Polyester resin having  $-SO_3Na$  groups:*

Polyester of terephthalic acid (45 mol %), isophthalic acid (10 mol %), sebacic acid (32.5 mol %) and sodium sulfoisophthalic acid (2.5 mol %) and ethyleneglycol (50 mol %) and neopentylglycol (50 mol %).

*Polyurethane prepolymer:*

Polyurethane prepolymer of diphenylmethane diisocyanate and butanediol-adipic acid ester (M.W.  $5 \times 10^4$ ).

5	<b>EXAMPLE 1:</b>		5
	A composition of the following components was prepared.		
	Co-adsorbed $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> magnetic powder	: 400 wt.parts	
	Carbon black	: 20 "	
10	Polyester resin having -SO <sub>3</sub> Na groups (Vylon-530 manufactured by Toyo Boseki K.K.)	: 40 "	10
	Nitrocellulose (H-1/2 sec. manufactured by Asahi Kasei K.K.)	: 30 "	
	Thermoplastic polyurethane prepolymer	: 30 "	
15	(Nippolan 2304 manufactured by Nippon Polyurethane Co.)		15
	Lubricant	: 7 "	
	Mixture of methyl ethyl ketone and methyl isobutyl ketone	: 1,000 "	
20	Abrasive	: 20 "	20

The components were charged in a ball mill and thoroughly kneaded to disperse them to prepare a magnetic powder composition. The composition was coated in a thickness of about 5 $\mu$  (in dry) on a polyethyleneterephthalate film having a thickness of 15 $\mu$ . The surface of the dried coated layer was treated by a heated calender roll at about 70°C to carry out a mirror plane processing. The film was cut in a desired width to prepare a magnetic recording tape. The carbon black was incorporated so as to impart a desired antistatic property and the abrasive was incorporated so as to impart a desired wearing resistance.

30	<b>REFERENCE 1:</b>		30
	In accordance with the process of Example 1 except substituting the polyester resin having -SO <sub>3</sub> Na groups (Vylon-530) by polyester resin having no SO <sub>3</sub> Na group (Vylon-500 manufactured by Toyo Boseki K.K.), a magnetic recording tape was prepared.		
35	Certain characteristics of the magnetic recording tapes obtained by Example 1 and Reference 1 were measured. The results are shown in Table 1.		

Table 1

	Example 1	Reference 1	
40	<i>Surface reflectivity:</i>		40
	Before mirror plane processing: (dB)	+ 1.3      - 0.8	
	After mirror plane processing: (dB)	+ 5.2      + 4.8	
	<i>Coercive force:</i> (Oe)	645          640	
45	<i>Residual magnetic flux density:</i> (gauss)	1200          1110	45
	<i>Br/Bm:</i>	0.76          0.74	
	<i>Y-S/N:</i> (white and black picture) (dB)	+ 1.3          0	

50	<b>EXAMPLE 2:</b>		50
	The components used in Example 1 were charged in a ball mill and thoroughly kneaded to disperse them to prepare a magnetic powder composition and then, 15 wt.parts of a crosslinking agent of polyisocyanate (Desmodule L manufactured by Bayer A.G.) was incorporated. The composition was coated in a thickness of about 5 $\mu$ (in dry) on a polyethyleneterephthalate film having a thickness of 15 $\mu$ . The surface of the dried coated layer was treated by a heated calender roll at about 70°C to carry out a mirror plane processing. The film was cut in a desired width to prepare a magnetic recording tape.		
55	Certain characteristics of the magnetic recording tapes obtained in Example 2 and Reference 1 were measured.		
60	The results are shown in Table 2 together with the result of Example 1.		

Table 2

	Example 2	Example 1	Reference 1	
5				5
10				10
15				15
20				20

**EXAMPLE 3:**

A composition of the following components was prepared.

25	Co-adsorbed $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> magnetic powder:	:	400 wt.parts	25
	Carbon black:	:	20 "	
	Polyester resin having -SO <sub>3</sub> Na groups: (Vylon-530 manufactured by Toyo Boseki K.K.)	:	30 "	
30	Vinyl chloride-vinyl acetate copolymer (VAGH manufactured by UCC)	:	50 "	30
	Thermoplastic polyurethane prepolymer (Nippolan 2304 manufactured by Nippon polyurethane Co.)	:	20 "	
35	Lubricant	:	7 "	35
	Abrasive	:	20 "	
	Mixture of methyl ethyl ketone and methyl isobutyl ketone	:	1,000 "	
40	The components were charged in a ball mill and thoroughly kneaded to disperse them to prepare a magnetic powder composition. The composition was coated in a thickness of about 5 $\mu$ (in dry) on a polyethyleneterephthalate film having a thickness of 15 $\mu$ . The surface of the dried coated layer was treated by a heated calender roll at about 70°C to carry out a mirror plane processing. The film was cut in a desired width to prepare a magnetic recording tape. The			40
45	carbon black was incorporated so as to impart a desired antistatic property and the abrasive was incorporated so as to impart a desired wearing resistance.			45

**REFERENCE 2:**

50	In accordance with the process of Example 3 except substituting the polyester resin having -SO <sub>3</sub> Na groups (Vylon-530) by polyester resin having no -SO <sub>3</sub> Na group (Vylon-500 manufac- tured by Toyo Boseki K.K.), a magnetic recording tape was prepared.	50
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Table 4

	Example 4	Example 3	Reference 2	Reference 3	
5	<i>Surface reflectivity:</i>				5
	Before mirror plane processing: (dB)				
	+ 1.0	+ 1.0	- 1.0	- 1.2	
	After mirror plane processing: (dB)				
	+ 5.0	+ 5.0	+ 4.5	+ 4.4	
10	<i>Coercive force: (Oe)</i>				10
	640	640	645	645	
	<i>Residual magnetic flux density: (gauss)</i>				
	1200	1200	1100	1070	
	<i>Br/Bm:</i>				
	0.77	0.77	0.74	0.74	
	<i>Y-S/N: (dB)</i>				
	+ 1.2	+ 1.2	+ 0.3	0	
15	<i>Durability:</i>				15
	no level	level	level	level	
	down in	down in	down in	down in	
	500 times	250 times	250 times	200 times	
	<i>Running friction: (g)</i>				
	77	81	81	82	
	<i>Still time: (min.)</i>				
	>90	60	60	60	
20					20

**EXAMPLE 5:**

A composition of the following components was prepared.

25	Co-adsorbed $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> magnetic powder	:	400 wt.parts	25
	Carbon black:	:	20 "	
	Polyester resin having -SO <sub>3</sub> Na groups (Vylon-530 manufactured by Toyo Boseki K.K.)	:	70 "	
	Thermoplastic polyurethane prepolymer (Nippolan 2304 manufactured by Nippon Polyurethane Co.)	:	30 "	30
	Lubricant	:	7 "	
	Mixture of methyl ethyl ketone and methyl isobutyl ketone	:	1,000 "	
35	Abrasive	:	20 "	35

The components were charged in a ball mill and thoroughly kneaded to disperse them to prepare a magnetic powder composition. The composition was coated in a thickness of about 5 $\mu$  (in dry) on a polyethyleneterephthalate film having a thickness of 15 $\mu$ . The surface of the dried coated layer was treated by a heated calender roll at about 70°C to carry out a mirror plane processing. The film was cut in a desired width to prepare a magnetic recording tape.

The carbon black was incorporated so as to impart a desired antistatic property and the abrasive was incorporated so as to impart a desired wearing resistance.

**45 REFERENCE 4:**

In accordance with the process of Example 5 except substituting the polyester resin having -SO<sub>3</sub>Na groups (Vylon-530) by polyester resin having no SO<sub>3</sub>Na group (Vylon-500 manufactured by Toyo Boseki K.K.) a magnetic recording tape was prepared.

Certain characteristics of the magnetic recording tapes obtained by Example 5 and Reference 4 were measured. The results are shown in Table 5.

50

Table 5

	Example 5	Reference 4	
5			5
	<i>Surface reflectivity:</i>		
	Before mirror plane processing: (dB)	+ 1.1	- 0.8
	After mirror plane processing: (dB)	+ 5.1	+ 4.6
	<i>Coercive force: (Oe)</i>	640	640
10	<i>Residual magnetic flux density: (gauss)</i>	1250	1150
	<i>Br/Bm:</i>	0.78	0.74
	<i>Y-S/N: (dB)</i>	+ 1.3	0

15 **EXAMPLE 6:**

The components used in Example 5 were charged in a ball mill and thoroughly kneaded to disperse them to prepare a magnetic powder composition and then, 15 wt.parts of a crosslinking agent of polyisocyanate (Desmodule L manufactured by Bayer A.G.) was incorporated. The composition was coated in a thickness of about 5 $\mu$  (in dry) on a polyethyleneterephthalate film having a thickness of 15 $\mu$ . The surface of the dried coated layer was treated by a heated calender roll at about 70°C to carry out a mirror plane processing. The film was cut in a desired width to prepare a magnetic recording tape.

Certain characteristics of the magnetic recording tapes obtained in Example 6 and Reference 4 were measured.

25 The results are shown in Table 6 together with the rest of Example 5.

Table 6

	Example 6	Example 5	Reference 4	
30				30
	<i>Surface reflectivity:</i>			
	Before mirror plane processing: (dB)	+ 1.0	+ 1.1	- 0.8
35	After mirror plane processing: (dB)	+ 5.1	+ 5.1	+ 4.6
	<i>Coercive force: (Oe)</i>	640	640	640
	<i>Residual magnetic flux density: (gauss)</i>	1200	1250	1150
	<i>Br/Bm:</i>	0.77	0.78	0.74
40	<i>Y-S/N: (dB)</i>	+ 1.2	+ 1.3	0
	<i>Durability:</i>	no level down in 500 times	level down in 250 times	level down in 250 times
	<i>Running friction: (g)</i>	75	81	80
45	<i>Still time: (min.)</i>	>90	60	60

As can be seen from the Tables, the magnetic recording tapes of the Examples had improved characteristics of surface reflectivity, residual magnetic flux density and S/N ratio. It is considered that such improved characteristics were attributable to the effect of the -SO<sub>3</sub>Na group which imparts high dispersibility to the magnetic powder and other powders such as carbon black to give a homogeneous coated layer. Therefore, the localization of the resin and the powder, causing noise, can be prevented. Moreover, the residual magnetization was large which improved the S/N ratio.

55 On the other hand, when the thermoplastic polyurethane prepolymer was crosslinked with the polyisocyanate, the durability, the running friction and the still time were improved. This effect is achieved by improving the strength of the magnetic layer by means of the crosslinking agent.

## CLAIMS

- 60 1. A magnetic recording medium comprising a substrate coated with a magnetic layer comprising a binder and a magnetic powder, said binder including a resin having -SO<sub>3</sub>Na groups and a polyurethane prepolymer.
2. A magnetic recording medium according to claim 1 wherein said resin having -SO<sub>3</sub>Na groups is a polyester resin.
- 65 3. A magnetic recording medium according to claim 1 or claim 2 wherein a thermoplastic



polyurethane is also incorporated as a part of said binder.

4. A magnetic recording medium according to any preceding claim wherein nitrocellulose is also incorporated as a part of said binder.

5. A magnetic recording medium according to any preceding claim wherein a vinyl chloride-  
5 vinyl acetate and/or vinyl alcohol copolymer is also incorporated as a part of said binder. 5

6. A magnetic recording medium according to any preceding claim wherein a polyester  
having no  $-\text{SO}_3\text{Na}$  group is incorporated as a part of said binder.

7. A magnetic recording medium according to any preceding claim wherein a polyisocyanate  
crosslinking agent is incorporated in the coating composition to cure said magnetic layer.

10 8. A magnetic recording medium according to claim 1, substantially as herein described 10  
with reference to any one of the Examples.