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(54) MAGNETIC RECORDING MEDIUM

(71) We, N.V. PHILIPS' GLOEILAMPEN-FABRIEKEN, a limited liability Company, organised and established under the laws of the Kingdom of the Netherlands, of Emmasingel 29, Eindhoven, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a magnetic recording medium of the kind comprising a carrier and a magnetisable coating provided thereon which comprises a magnetic pigment dispersed in a binder as well as a silane compound.

Such a recording medium is known from U.S. Patent No. 3,996,407. In the known recording medium an alkoxyaminoalkylsilane and in particular the substance γ -aminopropyltriethoxysilane is used as a silane compound.

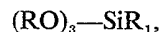
The use of functional organo silanes as coupling agents in compositions of synthetic resins and minerals have been known already since the early seventies. For example, in Applied Polymer Symposium No. 19, pp. 75—90 (1972) is described the reaction mechanism of the silane coupling in synthetic resin-mineral interfaces and in addition many examples are given of silane compounds and the adhesion of a variety of synthetic resins on minerals, for example glass and metal, influenced with said compounds. It appears from this article, and it is also stated as such, that trialkoxy silanes which have an aminoalkyl functional group have the best activity. In this connection, reference may be had in particular to table X on page 89 of the said literature reference in which data are stated of the adhesion of a styrene-butadiene polymer on glass under the influence of various silanes.

It appears from the table that compound

γ -aminopropyltriethoxysilane described in the above-mentioned U.S. Patent belongs to the substances having the best activity.

Contrary to expectations and prejudices it has now been found surprisingly that in a recording medium of the aforesaid kind it is not the silane compounds which have an aminoalkyl functional group, but silanes which has a chlorinated hydrocarbon group that have a considerably improving effect on the mechanical and electromagnetical properties of a magnetic recording medium.

According to the present invention there is provided a magnetic recording medium comprising a carrier and a magnetisable coating provided thereon which comprises a magnetic pigment dispersed in a binder in the ratio of from 1 to 10 parts of magnetic pigment by weight to one part by weight of the binder, as well as a silane compound characterised in that the silane compound satisfies the formula



wherein R is an alkyl group, a cycloalkyl group or an alkoxyalkyl group each of said groups having at most 10 carbon atoms, or a phenyl group or a benzyl group and R_1 is a chloroalkyl, chlorocycloalkyl or chlorophenylalkyl group the alkyl moiety of which groups contains at most 10 carbon atoms.

Silane compounds of the formula $(\text{R}_2\text{O})_3\text{—Si—R}_3$ are suitable in which R_2 is an alkyl group having 1—4 carbon atoms and R_3 is a chloroalkyl group having 1—6 carbon atoms. Particularly interesting is the commercially available and comparatively cheap γ -chloropropyltrimethoxysilane which exerts a very favourable effect on the mechanical and electromagnetical properties of the recording medium.

By using the above-described silanes in

the recording medium according to the invention the recording medium shows improved mechanical properties, such as increased tensile strength and modulus of elasticity, a reduced abrasive resistance, a better surface as well as a better electromagnetic behaviour, particularly under severe climatological conditions.

The quantity of silane in the recording medium of the invention may be between 0.2 and 5% by weight calculated on the quantity of magnetic pigment, and even between 0.5—2% by weight. It has been found that increase of the content of silane above 2% by weight produces no further significant improvement of the properties of the recording medium, so that for considerations of cost-price the above-mentioned maximum content of 2% by weight is satisfactory.

The binder used in the magnetisable coating of the recording medium of the invention is of the conventional type. Examples of suitable binders are polyvinyl chloride, polyvinyl acetate, which may be fully or partly hydrolysed, polyacrylate, polyester, polyesteramide, polyurethane and copolymers of at least two monomers selected from vinyl chloride, vinyl acetate, acrylonitrile, vinyl alcohol, vinyl butyral and vinylidene chloride.

The magnetic pigment in the coating of the recording medium of the invention comprises the usual magnetisable particles, such as metal particles on the basis of iron, cobalt, chromium and/or nickel, $\gamma\text{-Fe}_2\text{O}_3$ particles, magnetic particles and CrO_2 particles. The particles are generally acicular having a length of roughly 0.1—1 μm . The quantity of pigment is related to the quantity of binder and is 1—10 parts by weight, preferably 3—6 parts by weight, of the magnetic pigment per part by weight of the binder.

The pigment is finely distributed in the binder by means of a dispersion agent. The usual dispersion agents, for example, lecithin, if desired in combination with a driving oil, mono- or diesters of phosphoric acid and alcohols and alkylarylsulphonic acids may be used in the recording medium of the invention.

The magnetisable coating of the recording medium of the invention may comprise, in addition to the above-mentioned ingredients, other conventionally used ancillary substances, for example a lubricant. Lubricants which may be used in the recording medium are, for example, oleic acid, stearic acid, silicone oil, fatty acid amides, paraffin, e.g. as the commercially available material known under the Trade Name Vaseline (the word "Vaseline" is a registered Trade Mark) or graphite, and reaction products is isocyanates with aliphatic or olefinic

alcohols, amines and carboxylic acids of which the aliphatic or olefinic hydrocarbon chain contains 12—24 carbon atoms. The latter group of lubricants which are described in the Applicants' United Kingdom Patent Application No. 53932/77 (Serial No. 1,562,670) are particularly suitable.

The non-magnetic carrier present in the magnetic recording medium of the invention usually is in the form of a tape, plate or disk and can be manufactured from a plastics material, such as polyester or polyvinyl chloride. The carrier may also be manufactured from paper, glass or metal.

The recording medium may be manufactured in a usual manner by mixing in a ball mill the ingredients of the magnetisable coating, such as binder, magnetic pigment, silane compound, dispersion agent and possible ancillary substances such as lubricant, in the presence of an organic solvent and grinding and then providing the resulting mixture on the carrier.

According to the present invention there is provided a method of preparing the recording medium characterised in that the magnetic pigment is treated with the aforesaid silane compound, after which the treated pigment together with the binder, a dispersion agent and, if desired, auxiliary substances, are mixed and ground in a ball mill in the presence of an organic solvent for the binder and the resulting mixture is then coated on the carrier.

Suitable solvents for the binder are organic liquids, such as esters, for example ethyl acetate, ethers, for example tetrahydrofuran, ketones, for example methylisobutylketone and cyclohexanone and chlorinated hydrocarbons, for example, 1,2-dichloroethane.

The treatment of the pigment with the silane compound is carried out in the presence of a suitable diluent, for example a mixture of an alcohol in water.

One embodiment of the method of the invention results in a magnetisable recording medium which, when compared with a magnetic recording medium prepared according to the above-mentioned usual method, shows better mechanical properties, such as an improved tensile strength and modulus of elasticity.

After thoroughly grinding the dispersion in the ball mill, the larger magnetisable particles, if any, are sieved out and the mixture is provided on the carrier in a uniform layer. As already noted above, the carrier may have the form of a tape, plate or disk and the like and, depending on the material from which the carrier is manufactured, it may be provided with a suitable adhesive layer for the coating to be provided on the carrier. In addition to the adhesive layer, other layers, such as an antistatic layer,

may also be provided. The whole is then dried, the solvent evaporating and a recording layer having a diameter of 2 to 10 μ remaining on the carrier.

- 5 In order to promote the resistance to abrasion said layer of the recording medium may be cured and, if desired, subjected to a calendering process so that the surface of the layer becomes smoother.

- 10 By way of illustration a number of embodiments of the invention will now be described in more detail with reference to the ensuing specific Examples.

15 EXAMPLES:

1. The following ingredients are provided in a ball mill:

- 96 parts by weight γ -Fe₂O₃
 20 0.96 parts by weight γ -chloropropyltrimethoxysilane
 3.85 parts by weight of lecithin
 40 parts by weight tetrahydrofuran
 15.5 parts by weight cyclohexanone and
 25 64.4 parts by weight methylisobutylketone.

- The ingredients are mixed for two hours and 52.4 parts by weight of a 20% solution of polyurethane resins in a mixture (1:1) of tetrahydrofuran and cyclohexanone, as well as 69.9 parts by weight of a 30% solution of vinylidene chloride-acrylonitrile copolymer (8:2) in a mixture (1:1) of tetrahydrofuran and cyclohexanone, as well as 33.1 parts by weight of methylisobutylketone are added to the resulting mixture. The whole is ground for several hours, e.g. in a ball mill, until a particle size of fineness smaller than 2—3 μ m is obtained. The product was drained, filtered and provided on a 12 μ m thick foil of polyethylene terephthalate. The assembly comprising the carrier foil and magnetisable coating of 6 μ m being ultimately obtained.

- 45 2. A magnetic recording medium was prepared in a similar manner to Example 1 with the exception that the silane compound was provided in the magnetic pigment in a pretreatment and was not provided in the mixture which was ground in a ball mill. For this purpose the γ -Fe₂O₃ was stirred for 1 hour with the γ -chloropropyltrimethoxysilane in a water-alcohol mixture. After this treatment the γ -Fe₂O₃ was filtered,

dried and added to the ball mill together with the other ingredients according to the prescription given in Example 1.

3. A recording medium was prepared in a similar manner as described in Example 1 with the exception that the silane compound was omitted. It should be noted the magnetic recording media referred herein in the tests according to Examples 3, 7 and 8 are for comparison purposes only.

4. The results of experiments carried out with the magnetic recording media obtained according to the Examples 1, 2 and 3 and in particular the magnetisable coating thereof are recorded in Table I.

Column 1 of Table 1 refers to the recording medium by reference to the relevant Example in relation to its preparation. Column 2 describes which silane compound has been used. Column 3 records the breakage strength of the magnetisable coating. For this purpose, the magnetisable coating is not provided on a foil of polyethylene terephthalate (see Examples) but on a non-adhering base, in this case a glass plate. After curing the coating, the base plate is removed and the F-fracture in kg/cm² of the remaining magnetisable coating is determined. The elasticity modulus E is also determined for a magnetisable coating and this is given in column 4 of Table I in kg/cm². Abrasive resistance (expressed in mg) is recorded in column 5. The abrasive resistance was determined according to the standard Tabor-abrasion test in which the magnetisable coating was provided on an Al-plate. The Cs 10-wheels, used in the Tabor-abrasion test, were each loaded with 500 g. and were rotated 1000 times over the surface of the magnetisable coating after which the loss of weight of the magnetisable coating was measured.

The results of a life test are recorded in column 6. According to the life test, a 6.3 kHz signal is recorded on the magnetic tapes manufactured according to the above Examples. The tapes are passed along a Sandust reproduction head at a speed of 4.75 cm/sec. at an ambient temperature of 30°C and a relative humidity of 90%. Column 6 gives the number of times which the tape can be passed along the Sandust head without a signal strength loss exceeding 0.5 dB occurring.

TABLE I

	recording medium Example No.	silane compound used	F.fracture in kg/cm ²	E-modulus in kg/cm ²	abrasive resistance in mg	life test 30°C, 90% relative humidity
5	1	γ -chloropropyl- trimethoxy- silane	200	22000	0.057	>>>100
10	2	γ -chloropropyl- trimethoxy- silane	205	25000	0.063	>>>100
15	3	None	100	15000	0.104	30

5. The following ingredients were provided in a ball mill:

- 231 parts by weight of a 20% solution of a mixture (100:15) of a copolymer vinylchloride - vinyl acetate - vinyl alcohol (mixing ratio 90:4:6) and of polyester in methylolbutylketone.
- 3.9 parts by weight of sodium-lecithin as a dispersion agent.
- 1.3 parts by weight of oleic acid as a lubricant.
- 100 parts by weight of γ -Fe₂O₃
- 30 1 part by weight of γ -chloropropyltrimethoxysilane

The mixture was ground for several hours to a particle size fineness of 2—3 μ m. The product was drained, filtered through an asbestos filter and provided on a 12 μ m thick foil of polyethylene terephthalate. The assembly comprising the carrier foil and magnetisable coating was dried and calendered, the layer thickness of the magnetisable coating being reduced to 6 mm.

6. In an analogous manner as described in Example 5 a magnetic recording medium was manufactured in which the silane compound was provided on the γ -Fe₂O₃ in a pretreatment according to Example 2 instead of being provided as such in the ball mill. The thus pretreated γ -Fe₂O₃ was provided in the ball mill.

7. In a similar manner as described in Example 6, a magnetic recording medium was prepared in which the material γ -aminopropyltriethoxysilane was used as a silane compound.

8. In a similar manner as described in Example 5 a magnetic recording medium was manufactured without a silane compound.

9. The recording media obtained according to Examples 5 to 8 were subjected to tests as regards breakage strength, E-modulus and abrasive resistance according to the methods stated in Example 4. The results are recorded in the Table II below.

TABLE II

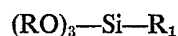
	recording medium Example No.	silane compound used	F-breakage in mg/cm ²	E-modulus in kg/cm ²	abrasive resistance in mg.
65	5	γ -chloropropyltrimethoxy- silane	215	30000	0.080
70	6	γ -chloropropyltrimethoxy- silane	215	32000	0.076
75	7	γ -aminopropyltriethoxy- silane	90	15000	0.110
	8	None	25	8500	0.135

80 WHAT WE CLAIM IS:—

1. A magnetic recording medium comprising a carrier and a magnetisable coating provided thereon which comprises a mag-

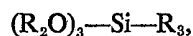
netic pigment dispersed in a binder in the ratio of from 1 to 10 parts of magnetic pigment by weight to one part by weight of the binder, as well as a silane compound

characterised in that the silane compound satisfies the formula



5 where R is an alkyl group, a cycloalkyl group or an alkoxyalkyl group each of said groups having at most 10 carbon atoms, or a phenyl group or a benzyl group and
10 R_1 is a chloroalkyl, chlorocycloalkyl or chlorophenylalkyl group the alkyl moiety of which groups contains at most 10 carbon atoms.

15 2. A magnetic recording medium as claimed in Claim 1, characterised in that the silane compound satisfies the formula



20 where R_2 is an alkyl group having 1—4 carbon atoms and R_3 is a chloroalkyl group having 1—6 carbon atoms.

25 3. A magnetic recording medium as claimed in Claim 2, characterised in that the silane compound is a γ -chloropropyl-trimethoxysilane.

4. A magnetic recording medium as claimed in Claim 1, 2 or 3, characterised

in that the magnetic recording medium contains 0.5—2% by weight of the silane compound calculated on the quantity of magnetic pigment. 30

5. A method of preparing a magnetic recording medium as claimed in any of the preceding Claims 1 to 4, characterised in that the magnetic pigment is treated with a silane compound as defined in any of the preceding Claims after which the treated pigment together with the binder, a dispersing agent and if desired auxiliary substances are mixed and ground in a ball mill in the presence of an organic solvent for the binder and the resulting mixture is then coated on the carrier. 35 40

6. A magnetic recording medium according to claim 1 substantially as hereinbefore described. 45

7. A method of preparing a magnetic recording medium according to Claim 5 substantially as hereinbefore described. 50

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