PATENT SPECIFICATION (11) 1 569 489

1 569 489

(21) Application No. 52437/77 (22) Filed 16 Dec. 1977 (19)

(31) Convention Application No. 7614182 (32) Filed 21 Dec. 1976 in

(33) Netherlands (NL)

(44) Complete Specification Published 18 Jun. 1980

(51) INT. CL.[3] C07F 9/09
G11B 5/70

(52) Index at Acceptance
C2P 3B11B 3B15A 3B19C 3B21 5A 7 9 D
C3V DE
C3W 100 204 221C 301 302C
C3Y B262 B284 B390 B392 F250 G320
H800

(54) MAGNETIC RECORDING TAPES CONTAINING A PHOSPHORIC ACID ESTER DISPERSANT

(71) We, N.V. PHILIPS' GLOEILAMPFABRIEKEN, 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 element of the kind which is provided with a carrier having a magnetic recording medium provided thereon.

The carrier is usually manufactured from a plastics material consisting of, for example polyester or polyvinyl chloride or alternatively it may consist of paper, glass or metal. The carrier may have the physical form of a tape, plate or disk.

The magnetic recording medium comprises a binder in which magnetisable particles are finely distributed by using a dispersion agent.

In order to obtain a good recording density and hence a faithful reproduction or recording of signals, it is of great importance that the magnetisable particles should be dispersed optimally in the binder.

The dispersion agents conventionally used for this purpose can be described as falling into two groups, namely, low-molecular and high-molecular dispersion agents. The low-molecular agents, for example, the natural product lecithin, have the disadvantage that an excess is necessary to fully cover the particles dispersed. Additional substances have to be added so as to counteract migration of said excess. It is furthermore difficult to find out whether the additional substances produce a desired immobilising effect. The said addition of the extra substances, for example a drying oil, is described *inter alia* in the United States Patent Specification 3,471,415.

The high-molecular dispersion agents, for example as described in United States Patent No. 3,460,984 have the disadvantage that, due to their poor wetting properties, agglomerates of particles may be formed which are also covered with dispersion agent. It is not readily possible, or is possible only by the expenditure of a relatively large amount of energy, to disintegrate said agglomerates to form individual particles.

United Kingdom Patent No. 766,484 in the name of Applicants suggests the general use of mono- or diphosphoric acid esters of "lower" alcohols as dispersion agents. However, these substances in general have the disadvantage that they are moisture-sensitive, that they can hydrolise the binder, and that furthermore they react with certain types of magnetisable particles, for example, with magnetisable iron oxide. Also, the particles to be dispersed should have acid-burning properties.

Netherlands Patent Application No. 73.13546 laid open to public inspection discloses a two-components dispersion agent which may comprise mono- and diesters of phosphoric acid in addition to alkylaryl sulphonic acids. In this case the same disadvantages as described above with respect to United Kingdom Patent No. 766484 apply.

One object of the present invention is to provide a recording element of the aforesaid kind which mitigates the above-mentioned disadvantages.

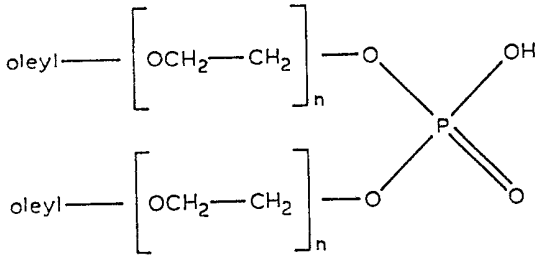
According to the present invention there is provided a magnetic recording element comprising a carrier having a magnetic recording medium thereon, which medium comprises a binder in which a dispersion agent and finely distributed magnetisable particles are present characterised in that the dispersion agent is a salt of an amine and a mono- and/or a diester of phosphoric acid in which said ester contains as the ester group or groups the residue of a higher olefinic alcohol or an alkoxylated derivative thereof.

For the purpose of the present invention the expression, "higher olefinic alcohol or an alkoxylated derivative thereof," refers to those organic compounds which contain at least 12 carbon atoms per molecule. The electromagnetic properties of the recording element of the invention enable a faithful recording or reproduction of signals to be made. Furthermore, the acid sensitivity of the dispersion agent used in the recording medium is considerably reduced. Still further, the rheological character of the binder with the magnetisable particles dispersed therein, and hence the rheological character of the dispersion, is improved namely, the dispersion is less viscous and less thixotropic. The improved characteristics result in an optimum degree of distribution of the particles in the binder and hence in an improved electromagnetic quality of the recording medium present in the recording element.

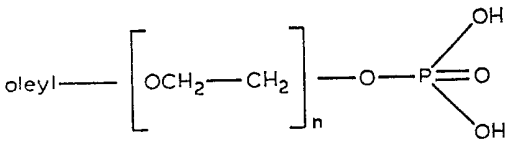
Suitable mono- and/or diesters of phosphoric acid are those in which ortho-phosphoric acid (H_3PO_4) is partially esterified with a higher olefinic alcohol or an alkoxylated derivative thereof containing from 12 - 22 carbon atoms and wherein the alcohol is ethoxylated with up to 30 ethoxy groups. Other alkoxy groups may be present instead of ethoxy groups, for example propoxy groups, in which case it is understood that, for example, a propoxy group is slightly more hydrophobic than an ethoxy group.

Examples of the above alcohols which are readily usable are unsaturated aliphatic alcohols such as, oleyl alcohol.

Particularly good results are obtained with acid esters of ortho-phosphoric acid which correspond to the formula



or



wherein n has the value 0 - 20 and in particular has the value 5 - 18.

The amine present in the dispersion agent may be an organic compound having at least 3 carbon atoms which comprises one or more primary, secondary or tertiary amino groups. Thus, primary, secondary or tertiary amines with a wide variety of properties may be used. In order to illustrate the wide range of amines which are suitable, the following amines are given as examples: saturated and unsaturated aliphatic amines having an alkyl radical, such as, linoleylamine, oleylamine, laurylamine, palmitylamine, stearylamine, amylamine and coconut fat amine; heterocyclic amines, for example, morpholine and morpholine substituted with alkyl; compounds which contain per molecule several amino groups, such as, hexamethylene tetramine; aromatic amines, such as, alkyl-substituted aniline and tertiary amines, such as, triethylamine, trioctylamine and triethanolamine.

Saturated aliphatic and olefinically unsaturated amines in which the alkyl group contains from 12 - 22 carbon atoms as well as triethanolamine are very suitable.

The wide freedom of choice of both the ester of phosphoric acid and the amine has the result that a variety of compositions of the dispersion agent can be selected within of course, the limits as defined hereinbefore and in Claim 1. It is therefore possible to influence the

properties of the dispersion agent, for example, in accordance with the effect of the dispersion agent on the rheologic behaviour of the magnetic dispersion. For example, those skilled in the art can compose a dispersion agent by a suitable choice of a phosphoric acid ester and an amine which satisfies specific requirements imposed by them and which furthermore has the advantages as stated above.

Good results have been obtained, with dispersion agents consisting of salts of triethanolamine, oleylamine or coconut fat amine with phosphoric acid esters which correspond to the above formulae.

An extra advantage is obtained surprisingly if the dispersion agent contains an excess of amine, that is larger than the stoichiometric amount of amine that is necessary to form a salt with the phosphoric acid ester. It has been found that a dispersion agent of such a composition will also fulfil the function of a lubricant. This results in the obvious practical advantage that migration, if any, of the dispersion agent which normally has a detrimental influence on the quality of the recording medium, is no longer a disadvantage and, on the contrary can be advantageous for the transport and detrition properties of the carrier with the recording medium provided thereon. The quantity of dispersion agent in the magnetic recording medium is not restricted to narrow limits and will as a rule be between 1 - 10% by weight calculated on the quantity of magnetisable particles, 2 - 5% by weight being preferably used.

According to the present invention there is also provided a dispersion agent which is suitable for use in a recording element which comprises a dispersion agent consisting of a salt of an amine and a mono- of d- ester of phosphoric acid in which the ester contains as the ester group or groups the residue of a higher olefinic alcohol or an alkoxylated derivative thereof.

The invention also relates to a method of manufacturing said substances.

The substances may be obtained by treating a mono- and/or diester of phosphoric acid with the higher olefinic alcohol or alkoxylated derivative thereof as hereinbefore described with at least an equivalent quantity or an amine.

The phosphoric acid ester starting produce can be prepared, for example, by treating the higher olefinic alcohol, or alkoxylated derivative thereof formed by reaction with an alkylene oxide, with phosphorus pentoxide. The reaction is carried out in the presence of a solvent, for example a hydrocarbon, for example toluene.

The binders to be used in the recording element are of the conventional nature. Examples of suitable binders are, for example, polyvinyl chloride, polyvinyl acetate, polyacrylates, polyester, polyester amides, polyurethanes and copolymers of at least two monomers selected from the group consisting of vinyl chloride, vinyl acetate, acrylonitrile, vinyl alcohol, vinyl butyral and vinylidene chloride. Readily usable binders are in particular polyurethanes and partially hydrolised copolymers of vinyl chloride and vinyl acetate.

The magnetisable particles present in the binder are also of the usual type. As magnetisable particles may be used, for example Fe Powder Fe_2O_3 particles and CrO_2 particles.

The particles are generally acicular and have a length of 0.1 - 1μ and a thickness of 0.01 - 0.2μ.

In addition to the magnetisable particles and the dispersion agent, other ancillary substances may be dissolved or dispersed in the binder, for example a lubricant. Useful lubricants are, for example, oleic acid, mineral oils, fatty acid amides or mixtures thereof.

The preparation of the recording medium may be carried out in the usual manner, for example, by thoroughly mixing the magnetisable particules, the dispersion agent and a part of the binder in a solvent for the binder by means of a ball mill. The remainder of the binder dissolved in a suitable solvent and the lubricant are then added and the whole is ground for another few hours in the ball mill. As solvents for the binder may be used organic liquids, such as esters, for example ethyl acetate, ethers for example, tetrahydrofuran, ketones, such as methyl ketone and chlorinated hydrocarbons, for example 1,2-dichloroethane.

After throughly grinding the dispersion in the ball mill, the larger magnetisable particles possibly present are sieved out and the mixture is provided on the carrier in a uniform layer. As already noted above, the carrier may be in the form of a tape, plate or disk and, dependent on the material from which the carrier is manufactured, may possibly be provided with a suitable adhesive layer for the recording medium to be provided on the carrier. In addition to the adhesive layer, other layers may be provided, for example an anti static layer. The assembly is then dried, the solvent evaporating and a recording layer remaining on the carrier in a thickness of 2 to 10μm.

In order to promote the resistance to detrition, said layer of recording medium may be hardened, if desired, and in addition be subjected to a calendering process in which the surface of the layer becomes smoother.

The invention will be illustrated with reference to the ensuing examples.

EXAMPLES:

1. Preparation of dispersion agent.

A few drops of concentrated hydrochloric acid are added to a stirred solution of 267 g of oleyl alcohol in dry toluene. A solution of 220 g of ethylene oxide in dry toluene is then added dropwise at room temperature. When everything has been added, stirring is continued for approximately another hour. The solvent is evaporated and the resulting reaction product, an ethoxylated oleyl alcohol contaning 5 ethylene oxide groups per molecule, is examined by means of a gel permeation chromatograph and tested for purity. Depending on the added quantity of ethylene oxide, oleyl alcohols having, for example, 8, 10, 15 and 20 ethylene oxide groups, can be prepared in the same manner. 710 g of phosphorus pentoxide are than added to a solution of the above-mentioned ethoxylated oleyl alcohol in toluene while stirring continuously. After complete dissolution of the oxide, stirring is continued for another hour. The reaction mixture is then poured in a large quantity of water. The organic layer is separated and dried with anhydrous $MgSO_4$. The solvent is then removed by evaporation. The resulting reaction product is a mixture of mono- and di- phosphoric acid esters of ethoxylated oleyl alcohol. In the same manner, the above-mentioned ethoxylated oleyl alcohol with different numbers of ethylene oxide groups as well as oleyl alcohol itself can be converted into the phosphoric acid esters. The neutralisation equivalent of the resulting phosphoric acid esters of ethoxylated oleyl alcohol is then determined after which the esters are neutralised with an amine, for example triethanol amine, coconut fat amine or oleylamine. The resulting amine salts of the phosphoric acid esters of ethoxylated oleyl alcohol have been used as dispersion agents in the recording element according to Example 2.

2. Preparation of magnetic recording element.

A magnetic recording medium was prepared by bringing the following ingredients in a pearl mill which contains 600 glass pearls having a diameter of 1 - 2 mm: 100 parts by weight of γ-Fe_2O_3 particles, 3 parts by weight of dispersion agent consisting of the salt of coconut fat amine and phosphoric acid ester of ethoxylated oleyl alcohol containing 5 ethylene oxide groups per molecule. 30 parts by weight of partially hydrolized copolymer of vinyl chloride and vinyl acetate. (Marketed by Union Carbide under the trade name VAGH). 2.5 parts by weight of acetonitrile rubber (marketed by Union Carbide under the trade name HYCAR. The word, HYCAR is a registered Trade Mark). 7.5 parts by weight of solid acid ester (softener). 250 parts by weight of a mixture (1:1) of methyl isobutyl-ketone and toluene.

The mixture of ingredients is mixed completely for 2 to 3 hours at a high speed of rotation of the pearl mill. The resulting recording medium is then passed through a filter having a mesh width of 3μ and provided on a polyester foil having a thickness of 12μ. After drying and calendering, a recording element was obtained in which the carrier (polyester foil) is provided with a recording medium having a layer thickness of approximately 5 microns.

In the same manner a series of magnetic recording elements were manufactured (magnetic tapes) which differ mutually only in the choice of the dispersion agent used in the recording medium.

With each of the manufactured tapes the usual electromagnetic standard measurements were performed. The results of these measurements are recorded in the following table in column 3. The measurements comprise a determination of the maximum output level at 333 Hz and 3% distortion; saturation of 8 kHz; relative tape sensitivity at 333 Hz and 10 kHz; bias noise. The result of each measurement is compared with that of a DIN standard reference tape, the difference being expressed in αB's. The sum of the α B differences of all tests is recorded in column 3 under the heading ER (electro acoustical response). This ER value represents a full picture of the electro acoustical properties of the tape. A higher ER value means a higher (better) level of electro acoustical properties.

In column 2 the composition of the magnetic tape is stated by stating the dispersion agent used.

Table of electro-acoustical properties

Tape ref. No.	Dispersion agent	ER-value
1	salt of oleylamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol	+ 2.2
2	salt of coconut fat amine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 5 ethylene oxide groups	+ 3.6
3	salt of oleylamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 5 ethylene oxide groups	+ 2.8
4	salt of triethanolamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 5 ethylene oxide groups	+ 5.1
5	salt of coconut fat amine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 8 ethylene oxide groups	+ 3.1
6	salt of oleylamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 8 ethylene oxide groups	+ 3.8
7	salt of triethanolamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 8 ethylene oxide groups	+ 5.4
8	salt of coconut fat amine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 10 ethylene oxide groups	+5.2
9	salt of oleylamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 10 ethylene oxide groups	+ 4.1

Table of electro-acoustical properties (Cont)

Tape ref. No.	Dispersion agent	
10	salt of triethanolamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 10 ethylene oxide groups	+ 5.9
11	salt of coconut fat amine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 15 ethylene oxide groups	+ 4.5
12	salt of oleylamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 15 ethylene oxide groups	+ 4.2
13	salt of triethanolamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 15 ethylene oxide groups	+ 3.7
14	salt of coconut fat amine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 20 ethylene oxide groups	+ 4.2
15	salt of oleylamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 20 ethylene oxide groups	+ 3.8
16	salt of triethanolamine and a mixture of mono- and di-phosphoric acid esters of oleyl alcohol with 20 ethylene oxide groups	+ 5.0
A	soya-lecithin	+ 1.8

It is to be noted that in the magnetic tape having reference number A a very usual and known dispersion agent is used, namely soya-lecithin. Upon playing back, said tape showed "squeel" which did not occur in the other tapes.

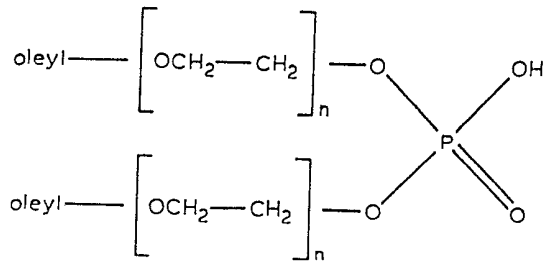
By the addition of extra amine (10-20% of the quantity of amine required for neutralisation) the coefficient of friction of the tapes was reduced from approximately 0.30 to approximately 0.20.

WHAT WE CLAIM IS:-

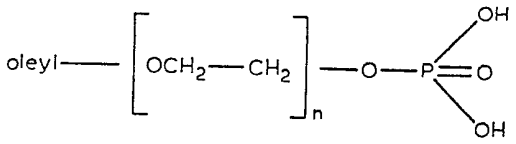
1. A magnetic recording element comprising a carrier having a magnetic recording medium thereon which medium comprises a binder in which a dispersion agent and finely distributed magnetisable particles are present, characterised in that the dispersion agent is a salt of an amine and a mono- and/or a diester of phosphoric acid in which the ester contains as the ester group or groups the residue of a higher olefinic alcohol containing at least 12 carbon atoms alkoxylated derivative thereof.

2. A magnetic recording element as claimed in Claim 1, characterised in that the higher olefinic alcohol or alkoxylated derivative thereof contains 12-22 C atoms and is ethoxylated with up to 30 ethoxy groups.

3. A magnetic recording element as claimed in Claim 2, characterised in that the acid ester of phosphoric acid is represented by the formula



or



wherein n = 5-18.

4. A magnetic recording element as claimed in Claim 1, 2 or 3, characterised in that the amine is an organic compound having at least 3 C-atoms which comprises one or more primary, secondary or tertiary amino groups.

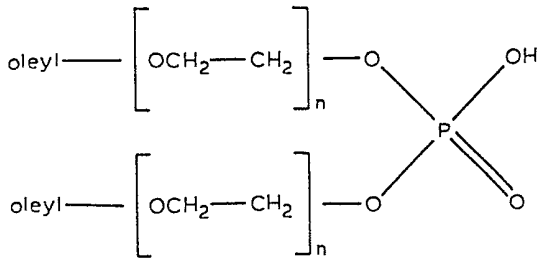
5. A magnetic recording element as claimed in any of the preceding Claims, characterised in that the dispersion agent contains an excess of the amine over the stoichiometric amount necessary to form the salt.

6. A dispersion agent for a magnetic recording element according to claim 1, characterised in that the dispersion agent comprises a salt of an amine and a mono- or diester of phosphoric acid with a higher olefinic alcohol containing at least 12 carbon atoms or an alkoxylated derivative thereof.

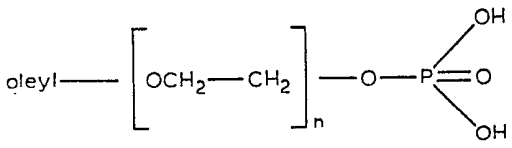
7. A dispersion agent as claimed in Claim 6, characterised in that the higher olefinic alcohol or alkoxylated derivative thereof contains from 12-22 C atoms and is ethoxylated with up to 30 ethoxy groups.

8. A dispersion agent as claimed in Claim 6, characterised in that the amine is an organic compound having at least 3 C-atoms which contains one or several primary, secondary or tertiary amino groups.

9. A dispersion agent as claimed in Claim 6, characterised in that the acid ester of phosphoric acid is represented by the formula



or



wherein n = 5-18.

10. A method of preparing a dispersion agent as claimed in Claim 6, characterised in that the dispersion agent is prepared by reacting a mono- and/or diester of phosphoric acid in which the ester group or groups is the residue a higher olefinic alcohol as hereinbefore defined or an alkoxylated derivative thereof, with at least an equivalent quantity of an amine.

11. A magnetic recording element as claimed in claim 1 substantially as hereinbefore described.

12. A method of preparing a dispersion agent for use in a magnetic recording element as claimed in claim 10 substantially as hereinbefore described.

13. A dispersion agent suitable for use in a magnetic recording element as claimed in claim 6 substantially as hereinbefore described.

R.J. BOXALL,
Chartered Patent Agent,
Berkshire House,
168-173 High Holborn,
London WC1V 7AQ.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,from
which copies may be obtained.