Description

Technical Field

The invention concerns a magnetic recording medium, the magnetizable coating of which is protected by an adherent covering which acts as a lubricant and can also act as a barrier against air if the magnetizable coating is subject to oxidiation. The invention especially concerns protective coverings for metallic thin-film magnetic recording media.

Background Art

While the magnetizable coatings of virtually all magnetic recording media now in use comprise magnetizable particles dispersed in organic binder, the amount of information that can be recorded on any such medium is reaching the theoretical limit. It is known that information can be recorded more compactly on metallic thin-film magnetic recording media, but such media are highly susceptible to abrasion when moved across a magnetic recording head. Hence, such media require some sort of protective covering which should also protect the metallic thin-film coating against corrosion upon exposure to air.

U.S. Patents No. 2,644,787 (Bonn et al.), No. 3,138,479 (Foley), No. 3,350,180 (Croll), and No. 4,210,946 (Iwaskai et al.) disclose various types of metallic thin-film magnetic recording media. U.S. Patent No. 3,973,072 (Anderson) discloses a nonmetallic thin-film magnetic recording medium for which a protective covering would also be especially useful. Unlike particulate magnetizable coatings, thin-film coatings do not have pores into which conventional lubricants may be adsorbed and hence they are more easily moved by or transferred to recording heads.

U.S. Patent No. 3,531,322 (Kefalos et al.) discloses a protective covering for metallic, thin-film magnetic recording media which it calls a "pseudo-film". This "pseudo-film" is similar in metallurgical properties to the magnetic layer, e.g., a nonmagnetic Ni-alloy is provided as a protective covering over a magnetic Ni-alloy. A level of hardness approximating that of the magnetic layer is described as providing a two- or threefold increase in useful life, as defined by a drop in readout signal of no more than a few percent. The "pseudo-film" is also said to offer an improvement in corrosion resistance. However, hard protective coverings cause an undesirable degree of wear of the recording head. If of sufficient thickness to be effective, they may produce an undesirably large spacing between the recording head and the magnetic coating. Also, if applied as disclosed in the patent, the hard protective coverings may not have sufficiently uniform thicknesses to insure recording uniformity over the entire magnetic coating.

Lubicants such as are commonly used on particulate magnetizable coatings have also been used in efforts to prevent damage to metallic thin-film magnetic coatings. Among a wide variety of lubricants developed for particulate magentic recording media are fluoroinated polyethers disclosed in U.S. Patents No. 4,268,556 (Pedrotty) and No. 4,237,139 (Schaefer et al.). The paragraph bridging columns 6 and 7 of the former discloses that such lubricants were applied to the nonmetallic thin-film magnetic recording coating of U.S. Patent No. 3,973,072 (Anderson). However, it is believed that no material which has been suggested as a magnetic recording lubricant would adequately protect metallic thin-film magnetic recording coatings against abrasion, much less effectively protect against corrosion from exposure to air.

While thin-film magnetic recording media involve special problems as discussed above, there is a continuing need for improving the durability of particulate-type magnetic recording coatings, especially for stop-action use in video recorders.

Disclosure of Invention

The present invention comrpises a composite, low surface energy, adherent covering which protects metallic thin-film magnetic recording media from abrasion and corrosion far more effectively than do coverings which have been disclosed in the prior art. The novel coverings also provide improved lubrication of particulate-type magnetic coatings.

According to a first aspect of the present invention there is provided a magnetic recording medium having a magnetizable coating, the face of which is covered by a covering, characterized in that said covering comprises an inner layer of polymer, insoluble in methyl ethyl ketone, being coated onto said magnetizable coating, said polymer being made from 80 to 95 parts by weight of a film-forming aromatic or heterocyclic polymerizable monomer having a plurality of polymerizable, ethylenically unsaturated groups and correspondingly 20 to 5 parts by weight of vinyl aromatic comonomer, and an outer layer of polymer, insoluble in 1,1,2-trichloro-2,2,1-trifluoroethane, in contiguous relationship with said inner layer, said polymer of said outer layer being made from perfluoropolyether monomer co-polymerizable with the monomers of said first layer, and having a perfluoropolymer segment which comprises a plurality of $-C_aF_{2a}O-$ repeating units, where subscript a is independently in each such unit an integer from 1 to 4, the thickness of said covering not exceeding 200 nm, said monomers of the two layers being polymerized in situ after being applied to said magnetic coating.

By polymerizing the monomers of both layers while they are in their contiguous relationship, the perfluoropolyether segments of the polymeric coating have significantly greater adherence to the magnetizable coating than they would have had the perfluoropolyether monomer been applied directly to the magnetizable coating and then polymerized *in situ*. By virtue of that greater adhesion, the perfluoropolyether segments tend to remain in place and to resist being moved about by or transferred to recording

heads, the composite covering being thus durable.

The composite, low surface energy covering of the invention is very thin, and can approach monomolecularity, thereby minimizing head spacing losses. While being exceedingly difficult to measure, preferred thicknesses of the composite low surface energy coverings of the invention are in the approximate range of 5 to 200 nm, more preferably within 10 to 100 nm. Even at thicknesses of the order of 10 nm, the novel low surface energy covering provides adequate lubricity for sufficiently long periods of time. Increased thicknesses up to 200 nm may provide somewhat longer life where the recording medium is in rugged service, e.g. repeated stop-action at the same frame of a video tape. At thicknesses much greater than 200 nm, spacing losses would become undesirably large.

According to a second aspect of the invention there is provided a method of making the recording medium referred to above characterized by the steps of

(a) coating onto the face of the magentizable coating of said medium, a first solution of from 80 to 95 parts of said film-forming aromatic or heterocyclic polymerizable monomer, and correspondingly from 20 to 5 parts by weight of said vinyl aromatic monomer to provide an inner coating,

(b) coating over the inner coating a second solution of said perfluoropolyether monomer said perfluoropolyether segment thereof comprising a plurality of $-C_aF_{2a}O-$ repeating units, where subscript a is independently in each such unit an integer from 1 to 4, to provide an outer coating, and

(c) drying said coatings and polymerizing said monomers.

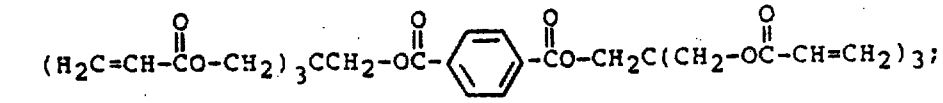
Ultraviolet radiation can be used to effect polymerization of the monomers of the two coatings, preferably in an inert atmosphere without the use of a photoinitiator. Although the rate of polymerization is enhanced by photoinitators or sensitizers such as benzophenone and benzoin, adequate rates can be attained without their use; and they preferably are not used because their presence in the low surface energy covering tends to weaken it. Ultraviolet radiation is especially effective and economical for polymerizing the monomers to provide composite low surface energy coverings up to about 100 nm in thickness.

By covering the magnetizable coating with the composite covering in the manner described above, no siginficant dimensional changes in the recording medium occur, which will be particularly important where such recording medium is very thin, as in the case of a metallic thin-film recording tape.

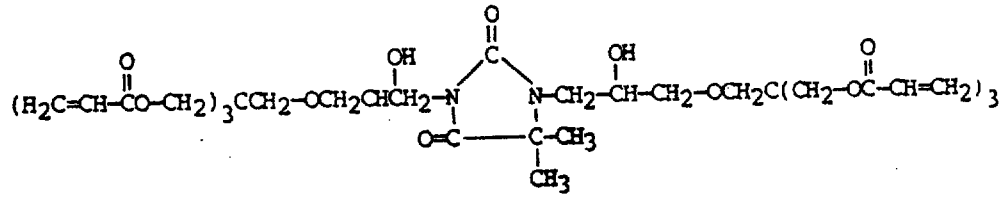
The polymers of the inner and outer layers are insoluble, that is, crosslinked, the polymer of the inner layer being insoluble in common organic solvants, e.g. methyl ethyl ketone, and the polymer of the outer layer being insoluble in 1,1,2-trichloro-2,2,1-trifluoroethane ("Freon" 113).

The thickness of the composite covering is conveniently controlled by the proportion of solvent in the two dilute solutions. Coating techniques for in-line processing include brushing, wire or knife coating, spraying, curtain coating and gravure coating. Curtain coating permits essentially simultaneous application of both solutions. If the coating technique used for applying the second solution of perfluoropolyether monomer involves mechanical contact of the underlying or inner coating, e.g., gravure coating, the inner coating should first be dried, and the solvent of the second solution should not be a solvent for the material deposited from the first solution.

Polyfunctional, ethylenically-unsaturated, film-forming aromatic or heterocyclic monomers useful for making the inner layer include polyester acrylates of aromatic dicarboxylic acid such as



acrylate esters of heterocyclic polyols such as



for brevity termed "hydantoin hexaacrylate"; polyacrylate esters of polyhydric phenols such as dimethacrylate of hydroxypropylated bisphenol A and alkoxylated hydroxypropylbisphenol A dimethacrylate.

Vinyl aromatic monomers useful for making the inner layer include styrene, alpha-methylstyrene, alpha-chlorostyrene, alpha-bromostyrene, 2,4-dimethylstyrene, 2,4-dichlorostyrene. These have the function of ensuring that the first layer uniformly covers the entire face of the magnetizable coating. In the absence of a vinyl monomer, there might be minute voids in the composite low-energy layer through which atmospheric air could pass to corrode a metallic thin film coating. Particularly preferred are styrenes, especially alpha-methylstyrene.

If either more than 20 parts or less than 5 parts of the vinyl monomer were used in making the inner

layer, the composite low-energy covering would have less endurance upon rpeated passes across recording heads. Best results are obtained with approximately equi-molar amounts, e.g., a 16 to 84 weight ratio when using the preferred alpha-methyl styrene and hydantoin hexaacrylate.

Preferably the sum of the weights of said monomers used for the inner layer is employed in amounts ranging from 1 to 40 parts per part by weight of the perfluoropolyether monomer. If that ratio were less than about 1 to 1, the conesiveness and the adhesion to the underlying substrate and hence the endurance would be noticeably reduced. Use of a weight ratio greater than about 40 to 1 would be inefficient of the raw material for the inner layer.

Perfluoropolyether monomers preferred for making the outer layer of the composite low surface energy covering of the invention have the formula

$$Q\text{—}(C_aF_{2a}O)_k\text{—}C_aF_{2a}\text{—}Z \qquad (a)$$

wherein Q comprises a polymerizable group attached to a chain of randomly distributed perfluoroalkylene oxide, $—C_aF_{2a}O—$, repeating units, in each of which a is independently an integer of 1 to 4, k is the number of such repeating units and it has a value from 1 to 300 such that the segment preferably has a number average molecular weight of 500 to 20,000, and Z is $—OC_aF_{2a-1}$ or Q. If Z is not Q, it preferably is $—OCF_3$, $—OCF_2CF_3$, or $OCF(CF_3)CF_3$. Typically the perfluoroalkylene oxide units will be $—CF_2O—$, $—C_2F_4O—$, and/or $—C_3F_6O—$.

It is preferred that the perfluoropolyether monomers have functionalities within the range of 1.5 to 2.0 in order to provide covalent bonding at both ends of most of the segments.

Preferred perfluoropolyether monomers are the ethylenically-unsaturated monomers disclosed in U.S. Patent No. 3,810,874 (Mitsch et al.) and U.S. Patent No. 4,321,404 (Williams et al.) wherein Q of the above Formula A is selected from

(a) $H_2C{=}C(R)C(=O)O—$, (b) $H_2C{=}C(R)C(=O)NH—$,

(c) $H_2C{=}C(R)CH_2O—$, and (d) $H_2C{=}C(R)CH_2NH—$

where R is hydrogen or methyl.

These preferred ethylenically-unsaturated perfluoropolyethyer monomers which have the formula

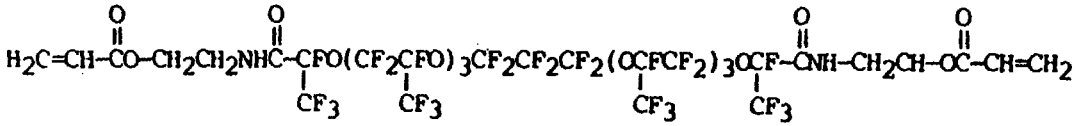
$$Q\text{—}CF_2O(CF_2CF_2O)_m(CF_2O)_nCF_2\text{—}Q \qquad (B)$$

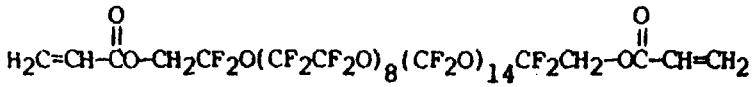
wherein Q is as defined above and m and n designate the number of randomly distributed perfluoroethyleneoxy and perfluoromethylene oxy backbone repeating units, respectively, n and m having independently values, for example, from 1 to 200, and the ratio m/n is 0.2/1 to 5/1.

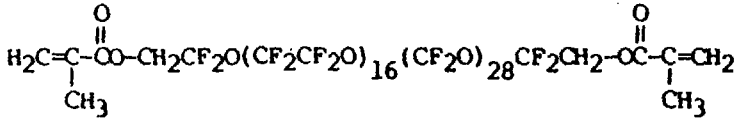
Examples of polymerizable perfluoropolyether monomers of Formula A useful for making the low surface energy covering of the invention are those of the following formulas where here again, as elsewhere, the perfluoroalkylene oxide units are randomly distributed, the given number (a subscript) of which are average values.

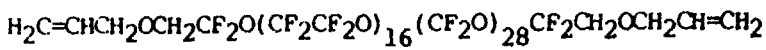
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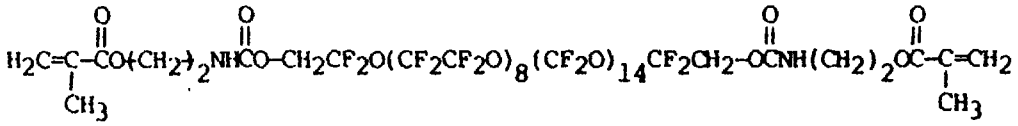
Perfluoropolyether Monomer

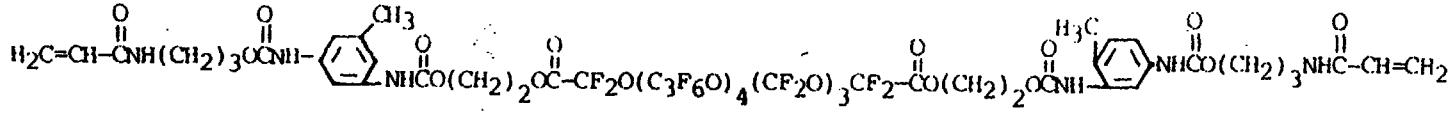
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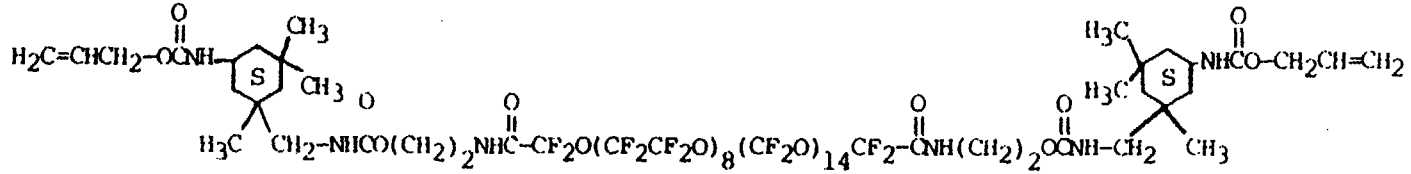
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III 

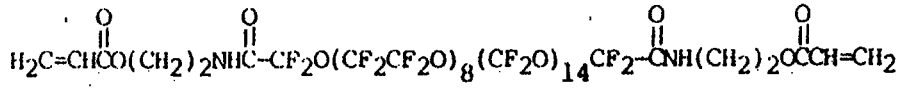
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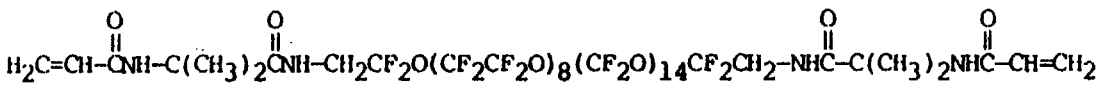
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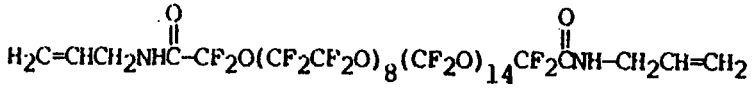
VI 

VII 

Perfluoropolyether Monomer

VIII 

IX 

X 

In addition to the perfluoropolyether monomer, the solution used to apply the outer coating may contain one or more copolymerizable monomers of other types in amounts up to about 20% by weight of the outer layer. However, the composite low surface energy covering is most effective if at least 75% of the weight of the outer layer is provided by perfluoropolyether segments. Useful copolymerizable monomers of this purpose include acrylic and methacrylic esters, amides, and urethanes, and vinyl ethers, esters, and heterocycles.

The magnetic recording medium according to the invention may be further characterized by the feature that said inner layer is an insoluble polymer made of 80 to 95 parts by weight 1,3-bis 3-[2,2,2-(triacryloxyloxymethyl)ethoxy]-2-hydroxypropyl-5,5-dimethyl-2,4-imidazolidinedione of the dimethacrylate of hydroxypropoxylated bisphenol A and 20 to 5 parts by weight alpha-methyl styrene, and said outer layer is an insoluble polymer made from monomer having a perfluoropolyether segment which is

$$CF_2O(CF_2CF_2O)_m(CF_2O)_nCF_2—$$

wherein m and n denote randomly distributed repeating units, the ratio m/n is in the range of 0.2/1 to 5/1, the number average molecular weight of said segment is in the range of 800 to 10,000, and at least 75 weight percent of said outer layer is said segments, the weight of said inner layer being from 1 to 40 times that of said outer layer, and the thickness of said covering being in the range of 10 to 100 nm.

Examples

The invention is illustrated in the following examples. In these examples, a "Corrosion Test" and a "Scratch Resistance Test" were used to evaluate samples.

In the "Corrosion Test", pieces of magnetic recording media 5 cm in length are placed in a chamber at 90% RH and 60°C for 48 hours and are then examined under a microscope for evidence of corrosion. If the low surface energy covering of a metallic thin-film magetic recording medium is not fully effective, corrosion will be present and appear as tiny color discontinuities. In the absence of any protective coating, a metallic thin-film magnetic recording medium would experience a general color change indicative of overall corrosion.

In the "Scratch Resistance Test", a test piece of a magnetic recording medium is mounted on a microscope slide and contacted by a 1.5-mm-diameter sapphire bead under a load of 85 g while being oscillated at a frequency of 100 cycles/minute (1.67 Hz) and a stroke length of 4 cm. Time to failure is indicated when a scratch first becomes visible to the naked eye.

Each of the examples employed the same magnetic recording medium 1.3 cm in width which had a biaxially-oriented poly(ethyleneterephthalate) film backing having a thickness of about 0.02 mm and an aluminum thin-film coating on one face. Over that coating was vapor-deposited a cobalt-nickel-titanium alloy to a thickness of about 100 nm to provide a magnetizable coating. In each example, the materials used to make the low surface energy covering were applied by dip coating as described by C. C. Yang et al., *Thin Solid Films*, Volume 74, pages 117—127 (1980). In each example, the second solution contained 0.1 g of Perfluoropolyether II per 100 ml of solvent.

For purposes of comparison, samples of covered magnetic recording media were prepared using first solutions with and without the vinyl aromatic monomer (viz. alpha methyl styrene) required by this invention.

In the examples, all parts are given by weight.

Examples 1 and 1A

	Example	
First solution:	1	1A
dimethacrylate of hydroxypropoxylated bisphenol A	0.44 g	0.50 g
alpha-methylsytrene	0.06 g	0
methylisobutyl ketone	100 ml	100 ml

The magnetic recording medium was dip-coated in the first solution and, after being allowed to dry for a few seconds, was dip-coated in the second solution. After a few more seconds for drying, these coatings were subjected to ultraviolet radiation in a vacuum using a BTC Ascor Vacuum Printer 1601—11 (Berkey Technical, Burbank, California) using a 2 kw Addalux medium-pressure mercury lamp No. 1406—02. Ascor and Addalux are trademarks. This polymerized the coatings to provide a composite low surface energy covering of about 30 nm thickness.

Examples 2 and 2A

First solution:	Example 2	Example 2A
dimethacrylate of hydroxypropoxylated isophthalic acid	0.45 g	0.50 g
alpha-methylsytrene	0.05 g	0
methylisobutyl ketone	100 ml	100 ml

Examples 3 and 3A

First solution:	Example 3	Example 3a
hydantoin hexacrylate	0.44 g	0.50 g
alpha-methylsytrene	0.06 g	0
methylisobutyl ketone	100 ml	100 ml

Examples 4 and 4A

First solution:	Example 4	Example 4A
dimethacrylate of ethoxylated bisphenol A	0.475 g	0.50 g
alpha-methylsytrene	0.025 g	0
methylisobutyl ketone	100 ml	100 ml

The resultant magnetic recording media of the foregoing examples were subjected to the "Corrosion Test" and the "Scratch Resistance Test" with the following results. Each "Scratch Resistance" value is an average of six tests.

Example	Results of Scratch Resistance Test (Time in secondd to failure)	Results of Corrosion (Presence of corrosion)
1	320	None
1A	112	Some
2	393	None
2A	148	Some
3	86	None
3A	3	Some
4	273	None
4A	232	Some

Each of the eight media of the foregoing examples has a coefficient of friction of 0.2 or less as measured by the Inclined Standard Method ANSI PH1.47—1972 of American National Standards Institute.

Comparative Examples

Instead of being provided with a composite low surface energy covering as in the foregoing examples, a piece of metallic thin-film magnetic recording medium was dip-coated with a lithium oleate lubricant in the same manner as in the foregoing examples lithium oleate being a well-known lubricant for particulate magentic recording media. This conventionally lubricated recording medium had "Scratch Resistance" of 75 seconds, and showed corrosion over all its surface in the "Corrosion Test". Its coefficient of friction was 0.29 to 0.32.

To another piece of the same metallic thin-film magnetic recording medium was applied by dip-coating a solution of the hydroxy-terminated perfluoropolyether polymer of Example 1 of U.S. Patent No. 4,267,238. This covered recorded medium has a "Scratch Resistance" of about one second.

Claims

1. A magnetic recording medium having a magnetizable coating, the face of which is covered by a covering, characterized in that said covering comprises an inner layer of polymer, insoluble in methyl ethyl ketone, being coated onto said magnetizable coating, said polymer being made from 80 to 95 parts by weight of a film-forming aromatic or heterocyclic polymerizable monomer having a plurality of polymerizable, ethylenically unsaturated groups and correspondingly 20 to 5 parts by weight of vinyl aromatic comonomer, and an outer layer of polymer, insoluble in 1,1,2-trichloro-2,2,1-trifluoroethane, in contiguous relationship with said inner layer, said polymer of said outer layer being made from perfluoropolyether monomer co-polymerizable with the monomers of said first layer, and having a perfluoropolymer segment which comprises a plurality of $-C_aF_{2a}O-$ repeating units, where subscript a is independently in each such unit an integer from 1 to 4, the thickness of said covering not exceeding 200 nm, said monomers of the two layers being polymerized in situ after being applied to said magnetic coating.

2. A magnetic recording medium as defined in claim 1 further characterized by the feature that said perfoluropolyether segments comprises

$$-(C_aF_{2a}O)_k-C_aF_{2a}-$$

that is a chain of randomly distributed $-C_aF_{2a}O-$ repeating units, where subscript a is independently in each such unit an integer of 1 to 4, and k is such that the segment has a number average molecular weight of 500 to 20,000.

3. A magnetic recording medium as defined in claim 3 further characterized by the feature that said perfluoropolyether segment is

$$-CF_2O-(CF_2CF_2O)_m-(CF_2O)_n-CF_2-$$

wherein m and n denote randomly distributed repeating units and the ratio m/n is 0.2/1 to 5/1, and the number average molecular weight of said segment is 800 to 10,000.

4. A magnetic recording medium as defined in claim 1 further characterized by the feature that said vinyl aromatic monomer is a styrene.

5. A magnetic recording medium as defined in claim 6 further characterized by the feature that said styrene is alpha-methyl styrene.

6. A magnetic recording medium as defined in claim 1 further characterized by the feature that the perfluoropolyether segments comprise at least 75% by weight of the outer layer.

7. A magnetic recording medium as defined in claim 1 further characterized by the feature that said magnetizable coating is a metallic thin-film coating.

8. A magnetic recording medium as defined in claim 1 further characterized by the feature that said magnetizable coating comprises magnetizable particles in an organic binder.

9. A magnetic recording medium as defined in claim 1 further characterized by the feature that said perfluoropolyether monomer has a functionality of 1.5 to 20.0 ethylenically unsaturated polymerizable groups, and by the feature that the amount of said aromatic or heterocyclic monomer used for said inner layer is 1 to 40 parts by weight per part by weight of said perfluoropolyether monomer used in said outer layer.

10. A magnetic recording medium as defined in claim 1 further characterized by the feature that said isoluble polymer of said inner layer is made of 80 to 95 parts by weight 1,3-bis 3-[2,2,2-(triacryloyloxy-methyl)ethoxy]-2-hydroxypropyl -5,5-dimethyl-2,4-imidazolidinedione or the dimethacrylate of hydroxy-propoxylated bisphenol A and 20 to 5 parts by weight alpha-methyl styrene, and said insoluble polymer of said outer layer is made from monomer having a perfluoropolyether segmengt which is

Each of the eight media of the foregoing examples has a coefficient of friction of 0.2 or less as measured by the Inclined Standard Method ANSI PH1.47—1972 of American National Standards Institute.

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To another piece of the same metallic thin-film magnetic recording medium was applied by dip-coating a solution of the hydroxy-terminated perfluoropolyether polymer of Example 1 of U.S. Patent No. 4,267,238. This covered recorded medium has a "Scratch Resistance" of about one second.

Claims

1. A magnetic recording medium having a magnetizable coating, the face of which is covered by a covering, characterized in that said covering comprises an inner layer of polymer, insoluble in methyl ethyl ketone, being coated onto said magnetizable coating, said polymer being made from 80 to 95 parts by weight of a film-forming aromatic or heterocyclic polymerizable monomer having a plurality of polymerizable, ethylenically unsaturated groups and correspondingly 20 to 5 parts by weight of vinyl aromatic comonomer, and an outer layer of polymer, insoluble in 1,1,2-trichloro-2,2,1-trifluoroethane, in contiguous relationship with said inner layer, said polymer of said outer layer being made from perfluoropolyether monomer co-polymerizable with the monomers of said first layer, and having a perfluoropolymer segment which comprises a plurality of $-C_aF_{2a}O-$ repeating units, where subscript a is independently in each such unit an integer from 1 to 4, the thickness of said covering not exceeding 200 nm, said monomers of the two layers being polymerized in situ after being applied to said magnetic coating.

2. A magnetic recording medium as defined in claim 1 further characterized by the feature that said perfoluropolyether segments comprises

$$-(C_aF_{2a}O)_k-C_aF_{2a}-$$

that is a chain of randomly distributed $-C_aF_{2a}O-$ repeating units, where subscript a is independently in each such unit an integer of 1 to 4, and k is such that the segment has a number average molecular weight of 500 to 20,000.

3. A magnetic recording medium as defined in claim 3 further characterized by the feature that said perfluoropolyether segment is

$$-CF_2O-(CF_2CF_2O)_m-(CF_2O)_n-CF_2-$$

wherein m and n denote randomly distributed repeating units and the ratio m/n is 0.2/1 to 5/1, and the number average molecular weight of said segment is 800 to 10,000.

4. A magnetic recording medium as defined in claim 1 further characterized by the feature that said vinyl aromatic monomer is a styrene.

5. A magnetic recording medium as defined in claim 6 further characterized by the feature that said styrene is alpha-methyl styrene.

6. A magnetic recording medium as defined in claim 1 further characterized by the feature that the perfluoropolyether segments comprise at least 75% by weight of the outer layer.

7. A magnetic recording medium as defined in claim 1 further characterized by the feature that said magnetizable coating is a metallic thin-film coating.

8. A magnetic recording medium as defined in claim 1 further characterized by the feature that said magnetizable coating comprises magnetizable particles in an organic binder.

9. A magnetic recording medium as defined in claim 1 further characterized by the feature that said perfluoropolyether monomer has a functionality of 1.5 to 20.0 ethylenically unsaturated polymerizable groups, and by the feature that the amount of said aromatic or heterocyclic monomer used for said inner layer is 1 to 40 parts by weight per part by weight of said perfluoropolyether monomer used in said outer layer.

10. A magnetic recording medium as defined in claim 1 further characterized by the feature that said isoluble polymer of said inner layer is made of 80 to 95 parts by weight 1,3-bis 3-[2,2,2-(triacryloyloxy-methyl)ethoxy]-2-hydroxypropyl -5,5-dimethyl-2,4-imidazolidinedione or the dimethacrylate of hydroxy-propoxylated bisphenol A and 20 to 5 parts by weight alpha-methyl styrene, and said insoluble polymer of said outer layer is made from monomer having a perfluoropolyether segmengt which is

* C L M S *

$$—CF_2O(CF_2CF_2O)_m(CF_2O)_nCF_2—$$

wherein m and n denote randomly distributed repeating units, the ratio m/n is in the range of 0.2/1 to 5/1, the number average molecular weight of said segment is in the range of 800 to 10,000, and at least 75 weight percent of said outer layer is said segments.

11. Method of making the magnetic recording medium of claim 1 further characterized by the steps of

(a) coating onto the face of the magnetizable coating of said medium, a first solution of from 80 to 95 parts of said film-forming aromatic or heterocyclic polymerizable monomer, and correspondingly from 20 to 5 parts by weight of said vinyl aromatic monomer to provide an inner coating,

(b) coating over the inner coating a second solution of said perfluoropolyether monomer said perfluoropolyether segment thereof comprising a plurality of $—C_aF_{2a}O—$ repeating units, where subscript a is independently in each such unit an integer from 1 to 4, to provide an outer coating, and

(c) drying said coatings and polymerizing said monomers.

12. Method as defined in claim 11 further characterized by the feature that coating step (a) is followed by drying to provide a dry inner coating before coating step (b).

13. Method as defined in claims 11 or 12 further characterized by the feature that step (c) involves exposing the two coatings to ultraviolet radiation.

14. Method as defined in claim 13 further characterized by the feature that the irradiation is carried out in an inert atmosphere.

15. Method as defined in claim 11 further characterized by the feature that said vinyl aromatic monomer is a styrene.

16. Method as defined in claim 11 further characterized by the feature that said styrene is alpha-methyl styrene.

17. Method as defined in claim 12 further characterized by the feature that said perfluoropolyether monomer has the formula

$$Q—(C_aF_{2a}O)_kC_aF_{2a}—Z$$

wherein Q comprises a polymerizable ethylenically-unsaturated group attached to a chain of k randomly distributed $—C_aF_{2a}O—$ units, where subscript a is independently in each such unit an integer of 1 to 4, and k is a number from 1 to 300 and Z is selected from Q, $—OCF_3$, $—OCF_2CF_3$ and $—OCF(CF_3)CF_3$.

Patentansprüche

1. Magnetischer Aufzeichnungsträger mit einem magnetisierbaren Überzug, der auf seiner Oberfläche mit einer Abcleckung bedeckt ist, dadurch gekennzeichnet, daß die Abdeckung einer innere Schicht aus einem Polymer besitzt, ds in Methylethylketon unlöslich und das auf den magnetisierbaren Überzug aufgetragen ist und aus 80 bis 95 Gewichtsteilen eines filmbildenden aromatischen oder heterozyklischen polymerisierbaren Monomers mit einer Mehrzahl von polymerisierbaren, ethylenisch ungesättigten Gruppen hergestellt ist, und einer entsprechenden Menge von 20 bis 5 Gewichtsteilen eines vinylaromatischen Comonomers, sowie eine äußere Schicht aus einem Polymer, das in 1,1,2-Trichloro 2,2,1-trifluoroethan unlöslich ist, an der inneren Schicht anliegt und aus einem Perfluoropolyethermonomer hergestellt ist, das mit den Monomeren der inneren Schicht copolymersierbar ist und ein Perfluoropolyethersegment besitzt, das eine Mehrzahl von wiederkehrenden $—C_aF_{2a}O—$ -Einheiten besitzt, wobei der Index a in jeder Einheit unabhängig von den anderen eine ganze Zahl von 1 bis 4 ist, die Dicke der Abdeckung nicht größer ist als 200 nm und die Monomere der beiden Schichten nach dem Auftragen auf den magentisierbaren Überzug in situ polymerisiert sind.

2. Magnetischer Aufzeichnungsträger nach Anspruch 1, dadurch gekennzeichnet, daß das Perfluorpolyethersegment mindestens teilweise aus

$$-(C_aF_{2a}O)_kC_aF_{2a}—$$

besteht, d.h. aus einer Kette von zufällig verteilten, wiederkehrenden $—C_aF_{2a}O—$ -Einheiten, wobei der Index a in jeder Einheit unabhängig von den anderen eine ganze Zahl von 1 bis 4 ist und k so gewählt ist, daß das Segment ein zahlenmäßig durchschnittliches Molekulargewicht von 500 bis 20 000 hat.

3. Magnetischer Aufzeichnungsträger nach Anspruch 3, dadurch gekennzeichnet, daß das Perfluorpolyethersegment aus

$$—CF_2O-(CF_2CF_2O)_m-(CF_2O)_n-CF_2—$$

besteht, wobei m und n zufällig verteilte wiederkehrende Einheiten bezeichnen, das Verhältnis m/n 0,2/1 bis 5/1 beträgt und das Segment ein zahlenmäßig durchschnittliches Molekulargewicht von 800 bis 10 000 hat.

4. Magnetischer Aufzeichnungsträger nach Anspruch 1, dadurch gekennzeichnet, daß das vinylaromatische Monomer ein Styrol ist.

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5. Magnetischer Aufzeichnungsträger nach Anspruch 6, dadurch gekennzeichnet, daß das Styrol α-Methylstyrol ist.

6. Magnetischer Aufzeichnungsträger nach Anspruch 1, dadurch gekennzeichnet, daß die Perfluoropolyethersegmente mindestens 75 Gew.% der äußeren Schicht ausmachen.

7. Magnetischer Aufzeichnungsträger nach Anspruch 1, dadurch gekennzeichnet, daß der magnetisierbare Überzug ein metallischer Dünnschichtüberzug ist.

8. Magnetischer Aufzeichnungsträger nach Anspruch 1, dadurch gekennzeichnet, daß der magnetisierbare Überzug magnetisierbare Teilchen in einem organischen Bindemittel enthält.

9. Magnetischer Aufzeichnungsträger nach Anspruch 1, dadurch gekennzeichnet, daß das Perfluorpolyethermonomer eine Funktionalität von 1,5 bis 20,0 ethylenisch ungesättigten polymerisierbaren Gruppen besitzt und daß die Menge des für die innere Schicht verwendeten aromatischen oder heterozyklischen Monomers 1 bis 40 Gewichtsprozent des in der äußeren Schicht verwendeten Perfluorpolyethermonomers beträgt.

10. Magnetischer Aufzeichnungsträger nach Anspruch 1, dadurch gekennzeichnet, daß das unlösliche Polymer der inneren Schicht aus 80 bis 95 Gewichtsteilen 1,3-bis-{3-[2.2.2-(triacryloyloxymethyl)ethoxyl]2-hydroxypropyl}-5,5-dimethyl-2,4-imidazolidindion oder dem Dimethacrylat des hydroxypropoxylierten Bisphenols A und 20 bis 5 Gewichtsteilen α-Methylstyrol hergestellt ist und das unlösliche Polymer der äußeren Schicht aus einem Monomer hergestellt ist, das ein Perfluoropolyethersegment besitzt, das aus

$$—CF_2OCF_2CF_2)_m(CF_2O)_nCF_2—$$

besteht, wobei m und n zufällig verteilte wiederkehrende Einheiten bezeichnen, das Verhältnis m/n im Bereich von 0,2/1 zu 5/1 liegt, das zahlenmäßig durchschnittliche Molekulargewicht des genannten Segmentes im Bereich von 800 bis 10 000 liegt und die äußere Schicht zu mindestens 75 Gew.% aus den genannten Segmenten besteht.

11. Verfahren zum Herstellen des magentischen Aufzeichnungsträgers nach Anspruch 1, gekennzeichnet durch folgende Schritte:

(a) zur Bildung eines inneren Überzuges wird auf die Oberfläche des magnetisierbaren Überzuges des Trägers eine erste Lösung von 80 bis 95 Gewichtsteilen eines filmbildenden aromatischen oder heterozyklischen polymerisierbaren Monomers und einer entsprechenden Menge von 20 bis 5 Gewichtsteilen eines vinylaromatischen Comonomers aufgetragen,

(b) zur Bildung eines äußeren Überzuges wird auf den inneren Überezug eine zweite Lösung des Perfluorpolyethermonomers aufgetragen, in dem das Perfluorpolyethersegment eine Mehrazahl von wiederkehrenden $—C_aF_{2a}O—$ -Einheiten enthält, wobei der Index a in jeder dieser Einheiten unabhängig von den anderen eine ganze Zahl von 1 bis 4 ist, und

(c) die Überzüge werden getrocknet, und die Monomere werden polymerisiert.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß vor dem Auftrageschritt (b) nach dem Auftrageschritt (a) unter Bildung eines trockenen inneren Überzuges getrocknet wird.

13. Verfahren nach Anspruch 11 oder 12, dadurch gekennzeichnet, daß in dem Schritt (c) die beiden Überzüge einer Ultraviolettstrahlung ausgesetzt werden.

14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß die Bestrahlung in einer Inertatmosphäre durchgeführt wird.

15. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das vinylaromatische Monomer ein Styrol ist.

16. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das Styrol α-Methylstyrol ist.

17. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das Perfluoropolyethermonomer die Formel

$$Q—(C_aF_{2a}O)_kC_aF_{2a}—Z$$

hat, in der Q mindestens teilweise aus einer polymerisierbaren ethylenisch ungesättigten Gruppe besteht, die an einer Kette von k zufällig verteilen $—C_aF_{2a}O—$ -Einheiten angelagert ist, wobei der Index a in jeder dieser Einheiten unabhängig von den anderen eine ganze Zahl von 1 bis 4 ist, k eine Zahl von 1 bis 300 ist und Z aus Q, $—OCF_3$, $—OCF_2CF_3$ und $—OCF(CF_3)CF_3$ ausgewählt ist.

Revendications

1. Matériel d'enregistrement magnétique comportant une couche magnétisable, dont la surface est couverte par un revêtement, caractérisé en ce que ce revêtement comprend une couche interne de polymère, insoluble dans la méthyl éthyl cétone, en étant enrobée sur la couche magnétisable susdite, ce polymère étant constitué de 80 à 95 parties en poids d'un monomère polymérisable, aromatique ou hétérocyclique, filmogène, comportant une série de groupes éthyléniquement insaturés, polymérisables, et, de façon correspondante, de 20 à 5 parties en poids d'un comonomère aromatique vinylique, et une couche externe de polymère, insoluble dans le 1,1,2-trichloro-2,2,1-trifluoréthane, cette couche externe

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étant contiguë à la couche interne, le polymère de la couche externe étant formé d'un monomère de perfluoropolyéther copolymérisable avec les monomères de la première couche et comportant un segment de perfluorpolyéther qui comprend une série de chaînons de $—C_aF_{2a}O—$ où la lettre *a* désigne indépendamment, dans chaque chaîon, un nombre entier de 1 à 4, l'épaisseur du revêtement ne dépassant pas 200 nm, les monomères des deux couches étant polymérisés in situ après application à la couche magnétique.

2. Matériel d'enregistrement mangétique suivant la revendication 1, caractérisé en outre en ce que le segment de perfluoropolyéther comprend:

$$—(C_aF_{2a}O)_k—C_aF_{2a}—$$

c'est-à-dire une chaîne de chaînons de $—C_aF_{2a}O—$ répartis de façon désordonnée, où la lettre *a* désigne indépendamment, dans chaque chaînon, un nombre entier de 1 à 4, et *k* est tel que le segment présente un poids moléculaire numérique moyen de 500 à 20.000.

3. Matériel d'enregistrement mangétique suivant la revendication 3, caractérisé en outre en ce que le segment de perfluoropolyéther est:

$$—CF_2O—(CF_2CF_2O)_m—(CF_2O)_n—CF_2—$$

où *m* et *n* désignent des chaînons répartis de façon désordonnée, et la rapport m/n est de 0,2/1 à 5/1, et le poids moléculaire numérique moyen d'un tel segment est de 800 à 10.000.

4. Matériel d'enregistrement mangétique suivant la revendication 1, caractérisé en outre en ce que le monomère aromatique vinylique est un styrène.

5. Matériel d'enregistrement mangétique suivant la revendication 6, caractérisé en outre en ce que le styrène est de l'alpha-méthylstyrène.

6. Matériel d'enregistrement mangétique suivant la revendication 1, caractérisé en outre en ce que les segments de perfluoropolyther constituent au moins 75% en poids de la couche externe.

7. Matériel d'enregistrement mangétique suivant la revendication 1, caractérisé en outre en ce que la couche megnétisable est une couche à pellicule mince métallique.

8. Matériel d'enregistrement mangétique suivant la revendication 1, caractérisé en outre en ce que la couche mangétisable comporte des particules magnétisables dans un liant organique.

9. Matériel d'enregistrement mangétique suivant la revendication 1, caractérisé en outre en ce que le monomère de perfluoropolyéther a une fonctionnalité de 1,5 à 20,0 groupes polymérisables éthyliquement insaturés, et en ce que la quantite du monomère aromatique ou héterocyclique utilisé pour la couche interne constitue de 1 à 40 parties en poids par partie en poids du monomère de perfluoropolyéther utilisé dans la couche externe.

10. Matériel d'enregistrement mangétique suivant la revendication 1, caractérisé en outre en ce que le polymère insoluble susdit de la couche interne est formé de 80 à 95 parties en poids de 1,3-bis 3-[2,2,2-(tri-acryloyloxyméthyl)éthoxy]-2-hydroxypropyl-5,5-diméthyl-2,4-imidazolidinedione ou du diméthacrylate de bisphénol A hydroxypropoxylé, et de 20 à 5 parties en poids d'alpha-méthylstyrène, et en ce que le polymère insoluble susdit de la couche externe est formé d'un monomère comportant un segment de perfluoropolyéther qui est:

$$—CF_2O—(CF_2CF_2O)_m—(CF_2O)_n—CF_2—$$

ou *m* et *n* désignent des chaînons répartis de façon désordonnée, le rapport m/n étant de l'ordre de 0,2/1 à 5/1, le poids moléculaire numérique moyen du segment susdit est de l'ordre de 800 à 10.000, et au moins 75% de la couche externe étant formés par ces segments.

11. Procédé de fabrication du matériel d'enregistrement magnétique suivant la revendication 1, caractérisé en ce qu'il comprend les phases suivantes:

(a) l'application, sur la surface de la couche magnétisable du matériel susdit, d'une première solution de 80 à 95 parties du monomère polymérisable, aromatique ou hétérocyclique, filmogène susdit, et, de façon correspondante, de 20 à 5 parties en poids du monomère aromatique vinylique précité pour former une couche interne,

(b) l'application, sur la couche interne, d'une seconde solution du monomère de perfluoropolyéther susdit, le segment de perfluoropolyéther comportant une série de chaînons de $—C_aF_{2a}O—$, où la lettre *a* désigne indépendamment, dans chaque chaînon, un nombre entier de 1 à 4, pour former une couche externe, et

(c) le séchage des couches susdites et la polymérisation des monomères.

12. Procédé suivant la revendication 11, caractérisé en outre en ce que la phase d'enrobage (a) est suivie par un séchage pour former une couche interne sèche avant la phase d'enrobage (b).

13. Procédé suivant l'une ou l'autre des revendications 11 et 12, caractérisé en outre en ce que la phase (c) suppose l'exposition des deux couches à un rayonnement ultraviolet.

14. Procédé suivant la revendication 13, caractérisé en outre en ce que le rayonnement est réalisé dans une atmosphère inerte.

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15. Procédé suivant la revendication 11, caractérisé en outre en ce que le monomère aromatique vinylique susdit est un styrène.

16. Procédé suivant la revendication 11, caractérisé en outre en ce que le styrène est de l'alpha-méthystyrène.

17. Procédé suivant la revendication 12, caractérisé en outre en ce que le monomère susdit de perfluoropolyéther répond à la formule:

$$Q—(C_aF_{2a}O)_kC_aF_{2a}—Z$$

dans laquelle Q représente un groupe éthyléniquement insaturé, polymérisable, attaché à une chaîne de chaînons de $—C_aF_{2a}O—$ répartis de façon désordonnée où la lettre *a* représente indépendamment, dans chaque chaîon de ce genre, un nombre entier de 1 à 4, et *k* est un nombre de 1 à 300, tandis que Z est choisi parmi Q, $—OCF_3$, $—OCF_2CF_3$ et $—OCF(CF_3)CF_3$.

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