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3,808,136

MAGNETIC COMPOSITION FOR DEPOSIT ON SOUND RECORDING TAPE OR MOTION PICTURE FILM

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No Drawing. Original application May 1, 1970, Ser. No. 33,969, now Patent No. 3,713,887. Divided and this application Apr. 20, 1972, Ser. No. 246,012
Int. Cl. H01j 1/26
U.S. Cl. 252—62.54 9 Claims

ABSTRACT OF THE DISCLOSURE

A composition adapted for producing a magnetic recording member such as tape or striped motion picture film wherein a layer of ferromagnetic particles is bound on a synthetic resin web by a binder. The composition comprises ferromagnetic particles and a resinous binder phase consisting essentially of, in percent by weight, 20% to 80% of cellulose nitrate in intimate mixture with 80% to 20% of a polymeric composition consisting essentially of, by weight, 50–80% vinylidene chloride, 2–30% acrylonitrile, and 0–60% of a lower alkyl unsubstituted or hydroxy substituted acrylic ester or methacrylic ester such as methyl methacrylate or acrylate or hydroxy propyl methacrylate. This binder is especially good for poly(ethylene terephthalate) webs. Best adherence to a web is secured when the ferromagnetic particles and the above binder are deposited from an organic solvent wherein at least 8% of the solvent is a lower N,N-dialkylamide of a lower aliphatic acid such as N,N-dimethyl formamide or acetamide.

This is a division of application Ser. No. 33,969 filed May 1, 1970, now Pat. No. 3,713,887.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to applying a tightly adherent coating to a web of synthetic resin, particularly to a polymeric linear terephthalate ester film such as poly (ethylene terephthalate). More particularly, the invention is concerned with applying a tightly adherent coating of a magnetic recording composition to such a web in the form of photographic motion picture film or magnetic recording tape, and with the resulting product. Additionally, the invention relates to novel compositions that can be used for binding a magnetic material to such a web; and to a novel composition that can be used successfully for binding a magnetic material to both poly(ethylene terephthalate) webs and to cellulose ester webs.

Prior Art

Magnetic stripes have been successfully applied to photographic film having a cellulose ester base by employing the compositions described in U.S. Pat. 3,220,843. These compositions are particularly advantageous because they will strike through the antihalation layer normally present on photographic film and will adhere directly to the cellulose ester web rather than to the antihalation layer itself. This is essential because the antihalation layer is normally dissolved off the web during the developing of the photographic film in alkaline solutions.

When the web is poly(ethylene terephthalate), with or without an antihalation layer or an antistatic layer on the back of the film, I have found that the compositions of Pat. No. 3,220,843 do not adhere tightly, apparently because poly(ethylene terephthalate) is much more inert than cellulose esters.

The removable antihalation and antistatic layer to which the magnetic stripping is applied are those customarily used on polyester photographic films, which are removed from the film during processing in alkaline solutions. Such layers are disclosed in U.S. Pat. 2,976,168. Some polyester films carry a non-removable antistatic layer such as that disclosed in U.S. Pat. 3,437,484. The magnetic striping composition must strike through either of these layers to the base to obtain good adhersion. Sometimes the magnetic stripes are applied to the emulsion side of the film.

SUMMARY OF THE INVENTION

In accordance with the present invention the tight adherence of a magnetic recording composition to a poly(ethylene terephthalate) base, such as photographic film or a magnetic tape, is accomplished by applying the magnetic composition as a dispersion of ferromagnetic particles in a solvent-binder composition comprising in percents by weight:

(A) a resinous binder phase which consists essentially of 20 to 80% of low or high viscosity cellulose nitrate, in intimate mixture with 80 to 20% of a polymeric composition consisting essentially of 50 to 80% of vinylidene chloride, 2 to 30% of acrylonitrile, and 0 to 60% of a lower alkyl unsubstituted or hydroxy substituted acrylic or methacrylic ester, and

(B) a solvent phase comprising one or more vaporizable organic solvents, at least 8% of which is a lower N,N-dialkylamide of a lower aliphatic acid such as N,N-dimethyl formamide or N,N-dimethyl acetamide.

When none of the acrylic or methacrylic ester is used, the polymeric composition is known as a copolymer; and when acrylic or methacrylic ester is used, the polymeric composition is known as a terpolymer.

Advantageously, the resinous binder phase (A) constitutes 5 to 40%; and the solvent phase (B) constitutes 60 to 95% of the solvent-binder composition.

Preferred ranges within the broad operable ranges set forth above for the resinous binder phase ar 50 to 70% of cellulose nitrate and 50 to 30% of the polymeric composition. In general the best results are secured when using a 1:1 ratio of cellulose nitrate to the polymeric composition in the resin phase; and when using at least about 30% of N,N-dimethyl formamide in the solvent phase.

I have found that magnetic stripes or layers adhere with remarkable strength to a poly(ethylene terephthalate) web when my novel binder compositions are employed. I have found it particularly advantageous, when depositing one or more magnetic stripes on a poly(ethylene terephthalate) film base having an antihalation layer, for the binder materials and ferromagnetic particles to be dispersed in an easily vaporizable organic solvent or mixture of solvents which cause the composition to strike through the antihalation layer and adhere tightly to the poly(ethylene terephthalate) base material. Suitable essential organic solvents are a lower N,N-dialkyl amide of a lower aliphatic acid, for example, N,N-dimethyl formamide with or without N,N-dimethyl acetamide, which can be combined with other solvents such as 2-ethoxy ethanol, 2-butoxyethanol, methyl ethyl ketone, n-butanol or amyl acetate. The small quantities of n-butanol in the examples accompany the cellulose nitrate as purchased, but this solvent is not essential to operability.

Other materials can be used in the compositions to provide some desirable effects, without modifying the essential activity of the principal ingredients. For example, surfactants and plasticizers can be included without materially affecting adherence of the stripes.

After deposition of the magnetic compositions described above, the web of poly(ethylene terephthalate) is passed through a drying zone wherein the solvents evaporate,

leaving on the web a layer of ferromagnetic particles embedded in a resinous binder mixture consisting essentially of cellulose nitrate (advantageously 20 to 80%), and the polymeric composition (advantageously 80 to 20%) consisting essentially of 50 to 80% of vinylidene chloride, 2 to 30% of acrylonitrile, and 0 to 60% of lower alkyl unsubstituted or hydroxy substituted acrylic or methacrylic ester, all percents being by weight.

On striped motion picture film the finished stripes generally are about 0.4 mil thick and may be 12, 30, or 100 mils wide, whereas the film is much wider, e.g. 8 or 16 mm.

The aforementioned acrylic ester-containing terpolymers may be prepared by known methods such as emulsion polymerization or the like. Especially useful terpolymers are those comprising vinylidene chloride, acrylonitrile, and unsubstituted or hydroxy substituted lower alkyl acrylic esters. Particularly useful terpolymers have from about 50–80% vinylidene chloride, about 2–30% acrylonitrile and about 1–60% unsubstituted lower alkyl acrylic ester, especially wherein the lower alkyl acrylic ester may be a lower alkyl acrylate residue wherein the lower alkyl has 1–4 carbon atoms, e.g. methyl acrylate, ethyl acrylate, etc. or a lower alkyl alkacrylate, wherein the lower alkyl has 1–4 carbon atoms, and where the alk-prefix in alkacrylate represents an alkyl group of 1–4 carbon atoms, e.g. methyl methacrylate, ethyl methacrylate, butyl methacrylate.

Other especially useful terpolymers are those containing an hydroxy substituted lower alkyl acrylic ester. Examples of these hydroxy substituted lower alkyl acrylic esters are hydroxypropyl acrylate and hydroxypropyl methacrylate. A particularly useful range is from about 50–80% vinylidene chloride, about 2–30% acrylonitrile and about 1–60% hydroxy substituted lower alkyl acrylic ester.

With respect to the above-described substituted and unsubstituted acrylic ester-containing terpolymers it will be appreciated that other ratios of the monomeric substituents may be used providing the products are sufficiently soluble in the solvent stage. The molecular weight of the resulting polymer may also be varied, but an especially useful molecular weight range is characterized by an inherent viscosity of from about 0.10 to 0.65, particularly from about 0.15 to 0.25 deciliter/gram in N,N-dimethyl formamide.

When using a copolymer instead of the terpolymer, the same technique is followed but the acrylic ester is omitted.

The magnetic materials of the striping composition can vary in magnetic properties, such as permeability and coercivity. Ferromagnetic materials of well known types such as acicular magnetic iron oxide (gamma ferric oxide) can be used. Desirable properties can be obtained by varying the ingredients of magnetic compositions. Thus magnetizable alloys are useful, for instance, alloys with iron or copper, aluminum, nickel, cobalt, and carbon, one component thereof being non-magnetic in most cases. The magnetic materials may be prepared as finely divided particles by various methods including the thermal decomposition of the corresponding metal carbonyls. Iron prepared from iron carbonyl may be employed, but iron alloys prepared from mixtures of metal carbonyls may also be used as, for example, iron alloys with nickel, cobalt, chromium, tungsten, or molybdenum. The methods of U.S. Pat. 2,694,656 may, for example, be used for preparing suitable ferromagnetic materials. The IRN magnetic iron oxides manufactured by the C. K. Willliams Co., 640 N. Street, Easton, Pa., are very useful, e.g., MO–4030 magnetic iron oxide or MO–2035 magnetic iron oxide having higher coercivity.

The proportions of binder to magnetic oxide or its equivalent in the final dried coating may vary from about 1:1 to 1:5 by weight.

THE PREFERRED EMBODIMENTS

The following examples illustrate the principles of the invention in greater detail. In all of the examples the dispersions are ball-milled for 6 or 7 days or until the particle size of the magnetic iron oxide (γ ferric oxide in every example) is judged to be satisfactory. The dispersions are then coated on the antihalation coating of poly(ethylene terephthalate) motion picture film to form a narrow stripe adjacent to each edge of the film, the solvents are allowed to evaporate, and the adhesion of the stripes is tested by (a) dry stripping wherein a sticky tape such as Scotch brand tape of the 3M Company is applied to the stripe and then pulled off; and (b) a caustic dip adhesion test wherein sample lengths of striped film are placed in aqueous NaOH solutions (.1 N and 2.5 N) and subjected to 1 minute of ultrasonic vibration. The samples are then washed and dried, and then subjected to the dry stripping test described in (a) above.

EXAMPLE 1

Dispersion:
31.5% gamma ferric oxide
6.7% terpolymer [1] (IV=.20, .54 and .68)
6.7% ¼ sec. SS cellulose nitrate (30% wet with alcohol)
21.0% 2-ethoxyethanol
34.1% N,N-dimethylformamide

Final coating	Binder of final coating
15.6% terpolymer. 10.9% cellulose nitrate. 73.5% gamma ferric oxide.	59% terpolymer. 41% cellulose nitrate.

[1] Methyl methacrylate 20%, vinylidene chloride 60%, acrylonitrile 20%.

Good adherence to poly(ethylene terephthalate) web having a resin base antihalation layer.

EXAMPLE 2

Dispersion:
24.0% gamma ferric oxide
2.9% 40–60 sec. SS cellulose nitrate
2.9% terpolymer [1] (IV=.20)
5.8% maleic alkyl polyester plasticizer
2.4% sorbitan tristearate
24.1% 2-ethoxyethanol
4.0% N,N-dimethylacetamide
33.9% N,N-dimethylformamide

Final coating	Binder of final coating
9.7% cellulose nitrate. 9.7% terpolymer. 80.6% gamma ferric oxide.	50% cellulose nitrate. 50% terpolymer.

[1] Same as Example 1.

Good adherence to poly(ethylene terephthalate) web having a resin base antihalation layer.

EXAMPLE 3

Dispersion:
31.0% gamma ferric oxide
9.9% terpolymer [1] (IV=.20)
4.8% ¼ sec. SS cellulose nitrate (30% wet with alcohol)
20.6% 2-ethoxyethanol
33.7% N,N-dimethylformamide

Final coating	Binder of final coating
7.7% cellulose nitrate. 22.3% terpolymer. 70.7% gamma ferric oxide.	25% cellulose nitrate. 75% terpolymer.

[1] Same as Example 1.

Good adherence to poly(ethylene terephthalate) web having a resin base antihalation layer.

Good adherence to unsubbed poly(ethylene terephthalate) web.

EXAMPLE 4

Dispersion:
31.3% gamma ferric oxide
3.4% terpolymer [1] (IV=.20)
14.3% ¼ sec. SS cellulose nitrate (30% wet with alcohol)
16.8% 2-ethoxyethanol
34.2% N,N-dimethylformamide

Final coating	Binder of final coating
22.4% cellulose nitrate. 7.6% terpolymer. 70.0% gamma ferric oxide.	75% cellulose nitrate. 25% terpolymer.

[1] Same as Example 1.

Good adherence to poly(ethylene terephthalate) web having resin base antihalation layer.

EXAMPLE 5

Dispersion:
30.5% gamma ferric oxide
6.5% terpolymer [1]
9.3% ¼ sec SS cellulose nitrate (30% set with alcohol)
8.9% methyl ethyl ketone
15.4% 2-ethoxyethanol
29.4% N,N-dimethylformamide

Final coating	Binder of final coating
15.0% cellulose nitrate. 15.0% terpolymer. 70.0% gamma ferric oxide.	50% cellulose nitrate. 50% terpolymer.

[1] 30% methyl acrylate, 66.5% vinylidene chloride, 3.5% acrylonitrile.

Good adherence to poly(ethylene terephthalate) web having resin base antihalation layer, to unsubbed poly (ethylene terephthalate) web.

EXAMPLE 6

Dispersion:
30.5% gamma ferric oxide
6.5% copolymer [1]
9.3% ¼ sec. SS cellulose nitrate (30% wet with alcohol)
20.4% 2-ethoxyethanol
33.3% N,N-dimethylformamide

Final coating	Binder of final coating
15.0% cellulose nitrate. 15.0% copolymer. 70.0% gamma ferric oxide.	50% cellulose nitrate. 50% copolymer.

[1] 75% vinylidene chloride, 25% acrylonitrile.

Adherence same as in Example 5.

EXAMPLE 7

Dispersion:
26.1% gamma ferric oxide
5.7% terpolymer [1] (IV=.20)
5.7% 40-60 sec. SS cellulose nitrate
20.0% 2-ethoxyethanol
33.9% N,N-dimethylformamide
6.9% N,N-dimethylacetamide
1.7% n-butyl alcohol

Final coating	Binder of final coating
15.2% cellulose nitrate. 15.2% terpolymer. 69.9% gamma ferric oxide.	50% cellulose nitrate. 50% terpolymer.

[1] Same as in Example 1.

Adherence same as in Example 5.

EXAMPLE 8

Dispersion:
24.0% gamma ferric oxide
6.0% terpolymer [1] (IV=.68)
6.0% 40-60 sec. SS cellulose nitrate
12.0% 2-ethoxyethanol
12.0% methyl ethyl ketone
30.8% N,N-dimethylformamide
7.3% N,N-dimethylacetamide
1.9% n-butyl alcohol

Final coating	Binder of final coating
16.7% cellulose nitrate. 16.7% terpolymer. 66.6% gamma ferric oxide.	50% cellulose nitrate. 50% terpolymer.

[1] Same as in Example 1.

Good adherence to poly(ethylene terephthalate) web having resin base antihalation layer or an antistatic layer.

EXAMPLE 9

Dispersion:
26.5% gamma ferric oxide
5.8% terpolymer [1]
5.8% 40-60 sec. SS cellulose nitrate
19.9% amyl acetzte
27.8% 2-butoxyethanol
12.0% N,N-dimethylformamide
2.2% n-butyl alcohol

Final coating	Binder of final coating
15.5% cellulose nitrate. 15.5% terpolymer. 69.0% gamma ferric oxide.	50% cellulose nitrate. 50% terpolymer.

[1] Same as in Example 1.

Good adherence to poly(ethylene terephthalate) web having a resin base antihalation layer.

Good adherence to emulsion side of poly(ethylene terephthalate) web.

Good adherence also would be expected on cellulose triacetate film without excessive curl occurring, whereas more than 14% of N,N-dimethylformamide causes too much curl.

This dispersion would be useful for striping motion picture film subsequent to development; and would provide exceptional operating flexibility because it can be applied to both acetate and polyester films without requiring that the film types be sequestered before striping.

EXAMPLE 10

Dispersion:
23.6% gamma ferric oxide
5.2% terpolymer [1]
2.6% 40-60 sec SS cellulose nitrate
2.6% 300-500 sec. SS cellulose nitrate
2.4% sorbitan tristearate
12.8% 2-butoxyethanol
12.8% methyl ethyl ketone
27.0% N,N-dimethylformamide
9.0% N,N-dimethylacetamide
2.0% n-butyl alcohol

Final coating	Binder of final coating
76.% 40-60 sec. SS cellulose nitrate. 7.6% 300-500 sec. SS cellulose nitrate. 15.3% terpolymer. 69.5% gamma ferric oxide.	25% 40-60 celluose nitrate. 25% 300-500 sec. SS cellulose nitrate. 50% terpolymer.

[1] Same as in Example 1.

Good adherence to unsubbed, resin jet backed, and antistatic backed poly(ethylene terephthalate).

Good adherence to emulsion side of poly(ethylene terephthalate) web.

EXAMPLE 11

Dispersion:
23.7% gamma ferric oxide
4.1% terpolymer [1]
6.2% 300-500 sec. SS cellulose nitrate
2.4% sorbitan tristearate
9.2% 2-butoxyethanol
9.2% methyl ethyl ketone
28.6% N,N-dimethylformamide
14.0% N,N-dimethylacetamide
2.6% n-butyl alcohol

Final coating	Binder of final coating
18.4% cellulose nitrate. 12.1% terpolymer. 69.5% gamma ferric oxide.	60% cellulose nitrate. 40% terpolymer.

[1] Same as in Example 1.

Good adherence to unsubbed, resin jet, and antistatic backed poly(ethylene terephthalate) web.

Good adherence to emulsion side of poly(ethylene terephthalate) web.

EXAMPLE 12

Dispersion:
25.1% gamma ferric oxide
5.4% terpolymer [1]
5.4% 40-60 sec. cellulose nitrate
2.5% sorbitan tristearate
11.9% methyl ethyl ketone
11.9% 2-butoxyethanol
29.4% N,N-dimethylformamide
6.6% N,N-dimethylacetamide
1.8% n-butyl alcohol

Final coating	Binder of final coating
15% terpolymer. 15% cellulose nitrate. 70% gamma ferric oxide.	50% terpolymer. 50% cellulose nitrate.

[1] Hydroxy propyl methacrylate 10%, vinylidene chloride 67.5%, acrylonitrile 22.5%.

Good adherence to unsubbed, resin jet backed, and antistatic backed poly(ethylene terephthalate). Good adherence to emulsion side of poly(ethylene terephthalate) web.

To summarize, the adherence of the magnetic stripes to poly(ethylene terephthalate) motion picture film having a synthetic resin based antihalation layer is good in every instance.

In addition, the magnetic stripes applied to unsubbed poly(ethylene terephthalate) motion picture film are judged to have good adherence in the case of Examples 3, 5, 6, 7, 10, 11 and 12, but the test was not run on unsubbed film base for the other examples.

Adherence is also good on poly(ethylene terephthalate) film base having an antistatic layer with the compositions of Examples 5, 6, 7, 8, 10, 11 and 12. Adherence is fair with the compositions of Examples 1, 2 and 4; and was not tested for Examples 3 and 9.

In contrast, when using similar copolymer and terpolymer compositions without cellulose nitrate, adherence to polyester film is not satisfactory.

On the other hand, dispersions wherein 40–60 second SS cellulose nitrate alone is the binder do not adhere to unsubbed polyester, or polyester having antihalation or antistatic coatings; and ¼ second SS cellulose nitrate alone provides poor adherence to unsubbed polyester, and polyester having an antistatic coating.

Thus, it is evident that the compositions of the present invention are the only ones which provide good adherence to all three types of polyester webs so that one dispersion formulation suffices for striping all of the commonly produced types of polyester motion picture films.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A composition adapted for producing a magnetic recording member, said composition comprising ferromagnetic particles; and a solvent-binder composition comprising a resinous binder phase consisting essentially of, in percent by weight, 20 to 80% of cellulose nitrate, 80 to 20% of a polymeric composition consisting essentially of 50 to 80% of vinylidene chloride, 2 to 30% of acrylonitrile, and 0 to 60% of a lower alkyl unsubstituted or hydroxy substituted acrylic ester or methacrylic ester, and an organic solvent phase at least 8% of which is a lower N,N-dialkylamide of a lower aliphatic acid.

2. A composition in accordance with claim **1**, wherein said resinous binder phase constitutes 5 to 40%, and said solvent phase constitutes 60 to 95% of said solvent-binder composition.

3. A composition in accordance with claim **1** wherein said dialkylamide is at least one member of the group consisting of lower N,N-dialkyl formamides and lower N,N-dialkylacetamides.

4. A composition in accordance with claim **3**, wherein said dialkylamide comprises between 8 and 14% of said organic solvent phase.

5. A composition in accordance with claim **3** wherein said dialkylamide comprises more than 25% of said organic solvent phase.

6. A composition in accordance with claim **1** wherein said acrylic ester or methacrylic ester is present in an amount between 1 and 60%.

7. A composition in accordance with claim **1** wherein said cellulose nitrate is present in an amount between 50 and 70% and said polymeric composition is present in an amount between 30 and 50% in said resinous binder phase.

8. A composition in accordance with claim **1** wherein said lower N,N-dialkylamide of a lower aliphatic acid is at least one member of the group consisting of N,N-dimethyl formamide and N,N-dimethyl acetamide.

9. A composition in accordance with claim **1** wherein said lower alkyl unsubstituted or hydroxy substituted acrylic ester or methacrylic ester is present in an amount of at least 1% of said polymeric composition by weight.

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96—84 R, 87 R; 117—138.8 F, 161 C, 235

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,808,136 Dated April 30, 1974

Inventor(s) Ronald M. Stimson

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 57, "70.7%" should read --70.0%--.

Column 5, line 4, "set" should read --wet--.

Column 5, line 37, "69.9%" should read --69.6%--.

Column 5, line 60, "acetzte" should read --acetate--.

Column 6, line 16, "76.%" should read --7.6%--.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
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