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(54) MANUFACTURE OF MULTI-LAYER MAGNETIC RECORDING MEDIA

- (71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, 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:-
- 10 The invention relates to a process for the manufacture of multi-layer magnetic recording media.
- 15 Magnetic recording media with at least two magnetizable layers have been known for a long time. Attempts have been made to meet the special demands made on such recording media by providing the individual layers with special mechanical or magnetic properties. For example, it has been attempted to improve the abrasion resistance of the upper magnetic layer and the magnetic stability of the pigments to mechanical stress; to orient the magnetic particles in the individual layers in different recording
- 25 tions; to match the coercive forces of the individual magnetic layers to the strength of the field in front of the magnetic head; and to correlate the thicknesses and the magnetic properties of the individual layers for optimal recording at low tape speeds and/or high frequencies.
- 30 Such multi-layer recording media are usually manufactured by applying a dispersion of magnetic particles in a solution of a binder and additives in a solvent to a base, each layer being dried before the next layer is applied. However, this method is both time-consuming and expensive.
- 35 U.S. Patent 3,573,965 discloses a process for simultaneously applying a plurality of layers, specifically layers of photographic emulsion, to support. Here, the coating device is at the same distance from the support for all the layers, so that a further parameter involved in determining the
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thickness of the layers is the pressure under which the photographic emulsion issues from each of the coating dies. This device has the disadvantage that only coating compositions of relatively low viscosity can be used and that only relatively high final coating thicknesses can be produced.

The simultaneous coating of bases with at least two very viscous upper layers by means of gravity and an entraining layer of low viscosity is described in German Laid-Open Application (DOS) No. 2,309, 159 and German Published Application (DAS) No. 2,309,158. Due to the fact that the two upper layers to be applied must flow conjointly with the entraining layer onto the base under the influence of gravity only, it is not possible to attain high coating speeds without causing a break in the said upper layers. A further disadvantage is that all layers must contain the same solvent system.

British Patent 837,095 discloses a process for the manufacture of multi-layer photographic emulsions, in which the individual layers are applied successively by several coating units, without intermediate drying. Here again, a disadvantage is that high coating speeds are not achievable if the proportion of solvent in the coating composition to be applied is high.

According to the invention, there is provided a process for the manufacture of a multi-layer magnetic recording medium which process comprises coating a web of flexible tape base material with at least two layers of identical or different dispersions of finely divided magnetic pigment in a solution comprising one or more organic binders in an organic solvent, the dispersions each having a viscosity of from 100 to 700 cp, the coating being carried out by advancing the tape base material successively to each of at least two dispersion coating stations, discharging dispersion onto the tape base material at the first of said stations and forming

the so discharged dispersion into a layer of predetermined desired thickness on the tape base material by means of a doctor provided at said first station, and at the or each subsequent station discharging further dispersion onto the layer of dispersion applied at the previous station whilst said previously applied layer is unsolidified and after removal of organic solvent vapour from a region above the previously applied layer and upstream of the subsequent station, and forming the further dispersion into a further layer also of predetermined desired thickness by means of a doctor provided at the subsequent station, said manufacturing process also including the steps of magnetically orienting the magnetic particles in the applied layers, solidifying the applied layers and slitting the coated web to provide tape of desired width.

In general the removed solvent vapours are exhausted.

Conveniently, the removal of solvent vapours is effected by means of a blown stream of air. Preferably, the removal of the solvent vapour is effected by means of a blown stream of air which forms a curtain between each coating station and a subsequent coating station.

The process according to the invention is conveniently carried out in an apparatus which comprises means for advancing a tape base to be provided with said layers successively to each of at least two dispersion coating stations of the apparatus, the first of said stations comprising means to discharge dispersion and a doctor to form on said base a dispersion layer of predetermined desired thickness and the subsequent station(s) comprising means to effect removal of organic vapour in the region upstream thereof, means to discharge dispersion and a doctor to form on said base overlying the already applied layer of dispersion a further dispersion layer also of predetermined desired thickness.

The invention enables the manufacture of magnetic recording media having thin magnetic layers (e.g. of thickness in the range from 1 to 10 μ , which the uppermost layer having a thickness of from 1 to 2 μ in preference) with only one pass of the base material and without intermediate drying and without solvent condensing on the coater(s) located downstream of the first coater due to the temporary accumulation of solvent vapors. Coating faults caused by drops of condensed solvent falling on the coated web can thus be prevented even at high coating speeds of, for example, up to 250 m/minute, that is to say even if a large amount of solvent evaporates.

The invention will be described, by way of example only, with reference to the accompanying drawings, in which:-

Figure 1 is a schematic and intended to illustrate the sequence of steps of the method according to the invention, and

Figure 2 is an enlarged schematic view of part of the apparatus shown in Figure 1.

With reference to Figure 1, the base 1, which may or may not be provided with a layer of adhesion promoter, is passed over the drum 2. The drum 2 is mounted for rotation about a horizontal axis and serves as support for the base 1. Coaters 3, 3a and 3b are provided above the circumferential surface of an upper quadrant portion of the drum. Upstream of each of the coaters 2a and 3b are provided means 4 and 4a for removing organic solvent originating from the applied coatings of dispersion. Magnetic flux generating means 5 is provided to orient magnetically the magnetic particles and means 6 is provided to solidify the layers of dispersion by evaporation of solvent and chemical curing. Means 7 is provided on which to wind up the recording medium.

With reference to Figure 2, the base 1 passing over the drum 2 moves underneath the coater 3, from the cavity of which issues the magnetic dispersion which forms the first layer 8, which is entrained by the base. Upstream of the next coater encountered by the moving base 1, namely coater 3a, which applies the second layer 9 to the first layer 8 (which is still fluid) on the base 1, there is a device 4 which reduces the solvent concentration at this point.

Suitable devices of this type are, e.g. extraction devices such as vacuum slot nozzles or vacuum chests which act as extractors over the entire surface between the coaters, or air jets which pass the solvent vapors to extraction devices located elsewhere or form a curtain of air, thus preventing the solvent vapors from reaching the following coater. Where a jet of air or inert gas is used, it is necessary to ensure that the air or inert gas is free from dust particles because these particles would otherwise stick to the still fluid coating composition, causing faults in the coating.

It has proved particularly advantageous to provide a slot nozzle (gap width 0.3-1.5 mm) immediately behind each coater; this nozzle which is in the form of an air knife produces a curtain of air which prevents the solvent vapors from reaching the following coater, but does not blow away the magnetic layer. Since the slot nozzle is in close proximity to the coater, the jet of air additionally has a temperature-controlling action on the coater.

More or less the same action is achieved if the said slot nozzle is in a zone from 10 to 150 mm behind the coater.

The coaters 3 and 3a shown schematically in Figures 1 and 2, work on the conventional

knife coating principle. Such a knife coater consists essentially of a front portion with the casting lips, the distance of which from the web of tape base determines the thickness of the coating, and a rear wall. The cavity inside the coater, which is usually closed at the top, is supplied with the coating composition. A particularly advantageous embodiment of such a coater is described in German Utility Model No. 75 25 191.

The coating compositions which can be used to produce the individual layers of a multi-layer magnetic recording medium are known per se.

The magnetic pigment preferentially used is finely divided acicular gamma-iron (III) oxide having a length of from 0.1 to 2μ and in particular from 0.1 to 0.9μ , or ferromagnetic chromium dioxide of the same length. Cubic gamma-iron (III) oxide, cobalt-modified gamma-iron (III) oxide and the finely divided heavy metal alloys known for this purpose, especially alloys of iron, cobalt and/or nickel, are further examples of magnetic material.

The binder(s) may conveniently be one of the following conventionally used binders, namely a solvent-soluble copolyamide, a polyvinylformal, a polyurethane elastomer, a mixture of a polyisocyanate and a polyhydroxy compound, and a vinyl chloride polymer containing more than 60% of copolymerized vinyl chloride units, e.g. a vinyl u,r,t copolymer of chloride with one or more comonomers such as a copolymer of chloride with one or more comonomers such as a vinyl ester of a monocarboxylic acid of 2 to 9 carbon atoms, an ester of an aliphatic alcohol of 1 to 9 carbon atoms and an ethylenically unsaturated carboxylic acid of 3 to 5 carbon atoms, such as an ester of acrylic acid, methacrylic acid or maleic acid, or one of these carboxylic acids themselves; a vinyl chloride copolymer which contains hydroxyl groups and can be produced by partial hydrolysis of a vinyl chloride or vinyl ester copolymer or direct copolymerization of vinyl chloride with one or more monomers containing hydroxyl groups, such as allyl alcohol, 4-hydroxybutyl acrylate or methacrylate or 2-hydroxyethyl acrylate or methacrylate may alternatively be used as binder. Still further examples of binder materials are materials of polyurethane elastomers with polyvinylformals, phenoxy resins and vinyl chloride copolymers of the stated composition. The use of a commercial elastomer such as a polyester-urethane obtained from adipic acid, 1, 4-butanediol and 4,4-diisocyanatodiphenylmethane, has proved advantageous.

In general, 10 to 13 parts by weight of magnetic pigment are employed per 2.5 to 4.5 parts by weight of binder when produc-

ing the magnetic recording media. The optimum ratio can easily be determined in each individual case by means of a few experiments. With the process according to the invention, it is possible to apply in a particularly simple and advantageous manner magnetic dispersions which have been developed for the production of very thin layers (which are usually the uppermost layers) and have a dry thickness of only, for example, 1 to 2μ , such dispersions having high viscosities, i.e. a viscosity of from 100 to 700 cp. The use of such high viscosities has the advantage that if the optimum ratio of the viscosity of the upper layer to that of the lower layer, namely $\eta_2 : \eta_1 \sim 2:1$, is chosen, very thin upper layers can be produced. Furthermore, magnetic dispersions with such viscosities have the advantage that they give coatings exhibiting high orientation ratios.

In addition to offering the advantage of economical, simultaneous application of a plurality of coatings, the process according to the invention enables magnetic dispersions having different types of solvent system to be used. This in turn makes it possible to employ different binders in the individual layers of the multi-layer magnetic recording medium, and consequently to optimize their properties. The only point to be observed is that the less volatile solvent should be in the upper layer.

The tape base material will normally be a conventional, flexible non-magnetic tape base material, for example a web of film based on polyvinyl chloride or a polyester, such as polyethylene terephthalate films.

The application of an adhesion-promoting intermediate layer, e.g. a layer based on a vinylidene chloride copolymer, to the base before applying the magnetic layer is possible and sometimes advantageous.

As far as the electro-acoustic properties are concerned, the multi-layer magnetic recording media manufactured according to the process of the invention can, in addition to exhibiting the known improvements resulting from a multi-layer structure, exhibit the particular advantage that in the case of a recording in which essentially only the upper magnetic layer is magnetized, the playback signal level in the longitudinal direction of the tape is more uniform than in the case of prior art multi-layer magnetic recording media.

EXAMPLE

A web of polyester film 7.5μ thick is passed over a drum and is coated with a first and second fluid dispersion, by means of two conventional coaters arranged one behind the other in the direction of travel of the film, to give coatings having a thickness of 4.5μ and 2.0μ respectively. The first

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dispersion consists of acicular gamma-iron (III) oxide having a length of 0.1 to 0.9 μm in a solution of polyurethane, as the binder, in a mixture of tetrahydrofuran and dioxane as the solvent, and the second dispersion consists of acicular chromium dioxide having a length of 0.1 to 0.9 μm in a solution of the same composition. The distance between the coaters is 300 mm. Upstream of the second coater, at a distance of 20 mm therefrom, there is located a slot nozzle of the same width as the web of film and having a gap width of 1 mm. Air under a pressure of 2000 mm water column is blown via this slot nozzle onto the layer which has just been applied, thus producing a curtain of air which prevents solvent vapors from reaching the second coater and condensing on the metal parts thereof. After the two layers have been applied, the magnetizable particles are magnetically oriented by a conventional method and the composite layer is solidified by removing the solvent. The resulting web is subsequently slit into magnetic tapes of the desired width in a conventional manner.

WHAT WE CLAIM IS:-

1. A process for the manufacture of a multi layer magnetic recording medium which process comprises coating a web of flexible tape base material with at least two layers of identical or different dispersions of finely divided magnetic pigment in a solution comprising one or more organic binders in an organic solvent, the dispersions each having a viscosity of from 100 to 700 cp, the coating being carried out by advancing the tape base material successively to each of at least two dispersion coating stations, discharging dispersion onto the tape base material at the first of said stations and forming the so discharged dispersion into a layer of predetermined desired thickness on the tape base material by means of a doctor provided at said first station, and at the or each subsequent station discharging further dispersion onto the layer of dispersion applied at the previous station whilst said previously applied layer is unsolidified and after removal of organic solvent vapour from a region above the previously applied layer and upstream of the subsequent station, and forming the further dispersion into a further layer also of predetermined desired thickness by means of a doctor provided at the subsequent station, said manufacturing process also including the steps of magnetically orienting the magnetic particles in the applied layers, solidifying the applied layers and slitting the coated web to provide tape of desired width.

2. A process as claimed in claim 1, wherein the removed solvent vapours are exhausted.

3. A process as claimed in claim 1 or

claim 2, wherein the removal of solvent vapours is effected by means of a blown stream of air.

4. A process as claimed in claim 3 wherein removal of the solvent vapour is effected by means of a blown stream of air which forms a curtain between each coating station and a subsequent coating station.

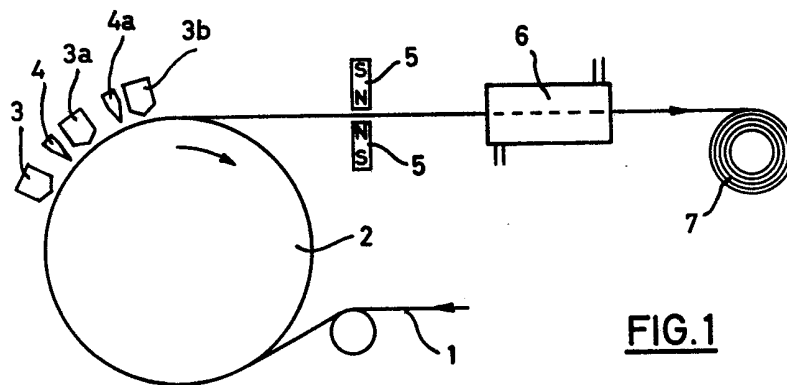
5. A process as claimed in any of claims 1 to 4 when carried out using an apparatus comprising means for advancing a tape base to be provided with said layers successively to each of at least two dispersion coating stations of the apparatus, the first of said stations comprising means to discharge dispersion and a doctor to form on said base a dispersion layer of predetermined desired thickness and the subsequent station(s) comprising means to effect removal of organic vapour in the region upstream thereof, means to discharge dispersion and a doctor to form on said base overlying the already applied layer of dispersion a further dispersion layer also of predetermined desired thickness.

6. A process as claimed in claim 1 when carried out using an apparatus substantially as hereinbefore described with reference to, and as illustrated in, the accompanying drawings.

7. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

8. A multi-layer magnetic recording medium whenever obtained by a process as claimed in any preceding claim.

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**FIG.1**

