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(54) **Recording material**

(57) The present invention provides a recording material in which a resin layer containing both of a large particle size sponge silica having a particle size 8 to 18 μ m and a small particle size sponge silica having a particle size 1 to 7 μ m is provided as a record reception layer on at least one face of a base material. The sponge

silica means silica of a sponge-like structure having many pores in silica particles. It is preferable that a pore volume of silica used for the present invention is 0.7 to 7ml/g, and 0.8 to 4ml/g is particularly preferable. If the pore volume of sponge silica is too small, there is a tendency that the record reception property of the reception layer is lowered.

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DescriptionBACKGROUND OF THE INVENTION5 1. Field of the Invention

[0001] The present invention relates to a recording material for use in recording by a visual recording method by means of printing, writing, or the like.

10 2. Description of the Related Art

[0002] Conventionally, in case of performing various existing recording such as printing on a plastic sheet, etc. by an oil-based ink, a water-based ink, and an UV curable ink, toner printing (a copy by a copy machine), thermal transfer printing, ink-jet printing, writing by a water-based pen, writing by an oil-based pen, writing by a pencil, stamp sealing, vermilion inktpad sealing or the like, it was difficult to perform all the records efficiently on a species of recording material, in particular a recording material in which a plastic sheet is a base material.

[0003] In consequence, a reception layer corresponding to a record method in each record method is provided on a surface such as the plastic sheet, and then each record is generally performed.

[0004] According to such the method, however, the record reception layer corresponding to the record method in each record method must be provided, and intricacy is apt to occur inevitably.

SUMMARY OF THE INVENTION

[0005] Therefore, it is an object of the present invention to provide a recording material provided with a multifunctional record reception layer which is capable of coping with various species of record method as described.

[0006] Furthermore, it is another object of the present invention to provide a recording material in which, in the case where recording is performed with drawings, characters or the like by the aforesaid various existing record methods, the drawings or the characters are clearly recorded without smears and stains, and furthermore the recorded drawings or characters have excellent strength, for example excellent water-resistance, rub-resistance, or the like.

[0007] In order to resolve the aforesaid problems, the present invention provides a recording material in which a resin layer containing both of a large particle size silica having a particle size 8 to 18 μ m and a small particle size silica having a particle size 1 to 7 μ m is provided as a record reception layer on at least one face of a base material.

[0008] The base material used for the present invention is not in particular restricted if the base material is a material on which a record reception layer can be provided, but in a material in which the base material per se does not also contain a plurality of species of record reception property, effects of the present invention are especially great. As such the base materials, a film, a sheet, a plate, a spin-coated CD disc or the like composed of polyethylene, polypropylene, polyester, polycarbonate, polymetaacrylate, a metal or the like are illustrated. Furthermore, as the base material of the present invention, a paper, a synthetic paper or the like can also be illustrated.

[0009] It is preferable that a pore volume of silica used for the present invention is 0.7 to 7ml/g, and 0.8 to 4ml/g is particularly preferable. If the pore volume of silica is too small, there is a tendency that the record reception property of the reception layer is lowered. Furthermore, if the pore volume of silica is too large, the viscosity of the resin liquid substance constituting the reception layer is conspicuously high, and there is a tendency that a coat operation is conspicuously difficult in a manufacture of the recording material (according to a tenth aspect of the present invention).

[0010] As the resin liquid substance, a resin solution, a resin emulsion, a melted hot melt resin, a two-part curing type uncured resin, an ultraviolet rays curing type uncured resin, or the like can be illustrated. As operations of curing after these resin agents are coated or printed on the base material, evaporation, cooling, or heating of a solvent or a dispersing medium, or ultraviolet rays irradiation or the like is adopted in response to each substance. According to the present invention, use of a non-water-soluble resin is preferable in order to attain excellent water-resistance.

[0011] The large particle size silica and the small particle size silica are both used in the record reception layer in the present invention. The large particle size silica has a particle size of 8 to 18 μ m. And if only the large particle size silica is used, there occurs drawbacks that sedimentation of silica occurs in the resin agent and it is easy to cause quality variations in the reception layer, and further rub-resistance of the reception layer is lowered, etc.

[0012] Furthermore, if only the small particle size silica of a particle size 1 to 7 μ m is used, a reduction in reception performance is caused, and objects of the present invention cannot be attained.

[0013] Furthermore, concerning a ratio of an amount of large particle size silica used to an amount of small particle size silica, it is preferable that a weight ration of the small particle size silica to the large particle size silica is about 0.1 to 5. By using at this ratio or so, it becomes easy to eliminate both drawbacks and maintain merits by synergism.

[0014] Furthermore, the record reception layer in the present invention contains silica and a resin. In the relationship

of the silica amount and the resin amount, if the former is too much, a reduction in the rub-resistance of the record reception layer is caused, and if the latter is too much, a reduction in reception performance is caused. Accordingly, it is preferable that a resin of 15 to 150 pts.wt. per 100 pts.wt. of silica is used.

[0015] Furthermore, it is preferable that the pore volume of silica is about 0.8 to 4ml/g as described above. If the pore volume is too small, a reduction in the reception performance is caused, and there is a tendency that the rub-resistance is also lowered. If the pore volume rate is too large, it becomes easy to cause a reduction in strength such as the rub-resistance of the record reception layer. Furthermore, it is not necessarily necessary that the pore volumes of the large particle size silica and small particle size silica are the same.

[0016] Furthermore, in the reception layer of the present invention, in addition to silica and a binder resin, additives such as silica of a particle size 7 to 8 μm, a surfactant, a leveling agent, a dye fixing agent, various pigments, various fillers or the like can from time to time be used as an object demands.

[0017] Sponge silica which is a structural element according to the present invention will be described, and the sponge silica means silica of a sponge-like structure having many pores in silica particles. As a manufacture of silica, a sedimenting method and a gelling method exist, and it is possible to obtain silica which has a sufficient pore volume in case of using the gelling method. Thus, it is preferable that the sponge silica which is a structural element according to the present invention is manufactured by the gelling method.

[0018] Furthermore, the present invention provides the recording material in which the reception layer is provided on one face of the plastic sheet and the adhesives layer is provided on the other one face. This adhesives layer is freely peeled off and re-adhered, preferably. This adhesives layer which is freely peeled off is formed by applying or drying an adhesives solution or an emulsion containing an adhesive minute sphere of a particle size 2 to 100μm on the base material, or formed by applying a radioactive rays curing ink on the base material, and next irradiating radioactive rays.

[0019] As for an applying method, any one of screen printing, offset printing, photogravure printing, flexographic printing, letter press printing, roll coating, spray coating and the like may be used, and the screen printing in which a film thickness of the adhesive layer can be increased is the most suitable. A pattern of printing or coating when the adhesive layer is formed may be set solid all over, set linear, set dotted, or set designed, and the printing or coating may be performed in an area of 10% or more of a sheet-like base material, preferably 20% or more thereof. The film thickness of the adhesive layer is preferably 4μm or more, and it is particularly desirable that the film thickness is 10μm or more from a viewpoint of re-exfoliation and adhesive stability.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0020] After a coat agent composed of 50 pts.wt. of silica of a pore volume 1.9ml/g and a particle size 11μm, 50 pts.wt. of sponge silica of a pore volume 1.7ml/g and a particle size 5μm, and 500 pts.wt. of acrylate emulsion of resin concentration 10% is coated on a polyester sheet, water is heated and evaporated, to form a recording material A in which a reception layer is provided on one face of a polyester sheet. Furthermore, recording materials B, C, D, E, F, G are made according to the similar step. A composition of the reception layer of these recording material is designated on Table 1.

(Table 1)

Recording Material	Silica of Large Particle Size	Silica of Small Particle Size	Resin
A	50 pts.wt. of pore capacity 1.9ml/g and particle size 11μm	50 pts.wt. of pore capacity 1.7ml/g and particle size 5μm	50 pts.wt. of acrylate
B	80 pts.wt. of the ditto silica	20 pts.wt. of the ditto silica	50 pts.wt. of the ditto resin
C	20 pts.wt. of the ditto silica	80 pts.wt. of the ditto silica	50 pts.wt. of the ditto resin
D	50 pts.wt. of the ditto silica	50 pts.wt. of the ditto silica	100 pts.wt. of the ditto resin
E	50 pts.wt. of pore capacity 1.0ml/g and particle size 12μm	50 pts.wt. of pore capacity 3.0ml/g and particle size 5μm	50 pts.wt. of the ditto resin
F	-	100 pts.wt. of pore capacity 1.7ml/g and particle size 5μm	50 pts.wt. of the ditto resin

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(Table 1) (continued)

Recording Material	Silica of Large Particle Size	Silica of Small Particle Size	Resin
G	50 pts.wt. of pore capacity 0.1ml/g or less and particle size 11 μ m of non-sponge silica	50 pts.wt. of pore capacity 0.1ml/g or less and particle size 5 μ m of non-sponge silica	50 pts.wt. of the ditto resin

[0021] Next, the same characters and drawings are recorded on the reception layer face of these recording materials A to G by oil ink printing, toner printing (a copy by a copy machine), thermal transfer printing, ink-jet printing, recording by a water pen, recording by a pencil, stamp sealing, or vermilion inkpad sealing, and the resultants are shown in Table 2. As shown in Table 2, Embodiments 1 to 5 use each of the recording materials A to E shown in Table 1, and Comparative Examples 1, 2 use the recording materials F, G.

(Table 2)

Embodiments and Comparative Examples	Recording Material	Recording Method and Evaluation		
		Oil Ink Printing	Toner Printing (a copy by a copy machine)	Thermal Transfer Printing
Embodiment 1	A	○	○	○
Embodiment 2	B	○	○	○
Embodiment 3	C	○	○	○
Embodiment 4	D	○	○	○
Embodiment 5	E	○	○	○
Comparative Example 1	F	○	○	○
Comparative Example 2	G	○	○	×

Embodiments and Comparative Examples	Recording Material	Recording Method and Evaluation		
		Ink-Jet Printing	Water Pen Recording	Oil pen Recording
Embodiment 1	A	○	○	○
Embodiment 2	B	○	○	○
Embodiment 3	C	○	○	○
Embodiment 4	D	○	○	○
Embodiment 5	E	○	○	○
Comparative Example 1	F	×	×	○
Comparative Example 2	G	×	×	○

Embodiments and Comparative Examples	Recording Material	Recording Method and Evaluation		
		Pencil Recording	Stamp Sealing	Vermilion Inkpad Sealing
Embodiment 1	A	○	○	○
Embodiment 2	B	○	○	○

(continued)

Embodiments and Comparative Examples	Recording Material	Recording Method and Evaluation		
		Pencil Recording	Stamp Sealing	Vermilion Inkpads Sealing
Embodiment 3	C	○	○	○
Embodiment 4	D	○	○	○
Embodiment 5	E	○	○	○
Comparative Example 1	F	○	×	×
Comparative Example 2	G	○	×	×

[0022] However, mark ○ in Table 2 indicates that both definition and rub-resistance of records are excellent, and mark × indicates that one or both of them is inferior. Incidentally, in the definition of the records, the decision was made by visual observation. Furthermore, in the rub-resistance, the decision was made according to whether or not characters and drawings were blurred by rubbing the characters and drawings which were printed, written and sealed by a finger.

[0023] As can be seen from Table 2, the embodiments 1 to 5 were excellent in the definition and rub-resistance of records in any one of the various present record methods (the oil ink printing, the toner printing (a copy by a copy machine), the thermal transfer printing, the ink-jet printing, the entering by a water pen, the entering by an oil pen, the entering by a pencil, the stamp sealing, and the vermilion inkpads sealing).

[0024] Incidentally, the adhesives layer or the adhesives layer which can be freely peeled off is provided on a back face of the sheet of these embodiments 1 to 5, so that the sheet which is excellent in the definition and the rub-resistance of the records and can be held to a glass face, a desk face, or the like by the adhesives layer can be attained.

[0025] As described above, according to the present invention, in the case where recording is performed with drawings, characters or the like by the various present record methods, the drawings or characters are clearly recorded without being ink-stained, and furthermore it is possible to provide the recording material in which the recorded drawings or characters display excellent strength, for example excellent rub-resistance, or the like. Furthermore, it is possible to also provide the recording material which is excellent in the vivid record and rub-resistance, and can be adhered or re-exfoliated.

Claims

1. A recording material, wherein
a resin layer which contains both of a large particle size silica having a particle size 8 to 18 μ m and a small particle size silica having a particle size 1 to 7 μ m is provided as a record reception layer on at least one face of a base material.
2. A recording material according to claim 1, wherein
a weight ratio of the small particle size silica to the large particle size silica is 0.1 to 5.
3. A recording material according to claim 1 or 2, wherein
a pore volume of the large particle size silica and small particle size silica is 0.8 to 4ml/g.
4. A recording material according to claim 1, 2, or 3, wherein
the resin layer contains 15 to 150 pts.wt. of a resin per 100 pts.wt. of all weight of silica.
5. A recording material according to claim any one of claims 1 to 4, wherein
the silica is a sponge silica.
6. A recording material according to any one of claims 1 to 5, wherein
the silica is manufactured by a gelling method.
7. A recording material according to any one of claims 1 to 6, wherein
the base material is a plastic sheet.

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8. A recording material according to claim 7, wherein
the record reception layer is provided on one face of the plastic sheet and an adhesives layer is provided on
the other face.

5 9. A recording material according to claim 8, wherein
the adhesives layer is made of adhesives which can freely be peeled off and stick again.

10 10. A method of manufacturing a recording material according to any one of claims 1 to 7, wherein
after a liquid substance in which silica is scattered in a resin liquid substance is coated or printed on the base
material, a resin is cured.

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 9175

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ANNEX TO THE EUROPEAN SEARCH REPORT
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