

1

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METHOD OF MANUFACTURING BASES FOR ELECTROSTATIC RECORDING MATERIAL OR ELECTROPHOTOGRAPHIC MATERIAL

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ABSTRACT OF THE DISCLOSURE

A method for manufacturing a base for an electrostatic recording material or electrophotographic sensitive material, which comprises forming an electroconductive layer on at least one surface of a base consisting of a non-metallic substance by treating said surface with a treating mixture containing colloidal alumina of more than 70% by weight of the non-volatile components of the mixture.

This invention relates to a method for the manufacture of a base to be used for electrostatic recording material or electrophotographic material.

Generally, the electrophotographic sensitive material or electrostatic recording material has a base such as is described below.

On a base which has been treated specially so as to have a high electric conductivity in a particularly wide range of relative humidity, there is formed an insulating recording layer by coating or other suitable method.

The methods which are employed for rendering the base electroconductive as mentioned above are generally classified into the following two types.

In one type of the methods, hygroscopic materials such as inorganic salt, hygroscopic polyhydroxy compound, cationic surface active agent, or quaternary ammonium salt polymer is impregnated in the fibrous structure of raw paper stock in the entire thickness thereof. The various compounds mentioned above may be used independently or in combination.

In the other type of the methods, a continuous film having low resistance is provided at least on the surface of the base on which the recording layer is subsequently formed. In the latter case, the layer of low resistance may also be formed on the rear side thereof. This continuous film of low resistance is ordinarily prepared by using a water-soluble polymer as the principal component. Typical examples of such polymer are quaternary ammonium salt polymer and polyvinyl benzenesulfonate.

Such polymers are difficult to be modified (or converted) water insoluble, so that they remain water-soluble after coating. The presence of such water-soluble sub-coating under the recording layer gives rise to the following shortcomings. An aqueous coating mixture is difficult to apply on the water-soluble sub-coating since the conductive or low resistant material thereof will diffuse into the mixture. Such contamination will fatally deteriorate the insulating property of the recording layer. In the case of the electrophotographic material, it is important for the purpose of lowering possible residual electric potential after the step of light attenuation of electric charge on the insulative layer. Thus, it is altogether undesirable for the low-resistant layer to undergo such dissolution.

Heretofore, several kinds of low-resistant layers sparingly soluble or totally insoluble in water have been proposed. Of course, vacuum deposited films of metal are ideal as such low-resistance layer but, on many occasions,

2

they prove to be undesirable as for dark colored appearance and mechanical properties.

A water-insoluble conductive coating comprising carbon black dispersed in a water-insoluble resinous binder has also as ideal electrical property but is not suited for the present purpose due to its deep color. In case where resins such as of gelatin and casein are cured to form a subcoating their behaviors at low humidities involve problems yet to be solved.

An object of the present invention resides in providing a method for the manufacture of a base for electrostatic recording material or electrophotographic material of sufficient conductivity, which is free from the aforementioned shortcomings.

Another object of the present invention is to provide a simple and improved method of converting highly electroconductive the surface and, if needed, the interior of non-metallic support material.

Still another object of the present invention is to provide a manufacturing method for a base for electrostatic recording material or electrophotographic sensitive material suitable for forming an insulative recording layer through application of an aqueous coating mixture.

The aforementioned objects of the present invention have been accomplished by the discovery of a method for the manufacture of a base for use in the electrostatic recording material or electrophotographic material, which method is characterized in that at least one surface of the base made of a non-metallic substance is treated with a mixture containing colloidal alumina as the principal non-volatile component thereof.

Non-metallic base materials for use in the present invention include paper, unwoven fabrics, wood, plastic films, and cloth.

The aforementioned colloidal alumina is usually marketed in the form of aqueous dispersion. Examples are "Aluminasol 100" and "Aluminasol 200" made by Nissan Chemical and "Baymal" made by Du Pont.

A method of preparing colloidal alumina and the characteristics thereof are, for example, described in "Inorganic Colloid Chemistry" volume II (1935) written by H. B. Weiser.

Colloidal alumina is an amorphous colloidal powder of aluminum oxide with the surface comprising hydroxide.

In general, colloidal alumina in the form of aqueous dispersion exhibits pH 3 to 5 and has a positive charge. As a pair ion to the positive charge, inorganic and organic acid ions are both proper, in particular, chlorine ion is preferable, because in the case of under the same condition except the kind of the pair ion, a layer containing a chlorine ion as the pair ion has a lower electric resistance comparing with layers containing the other acid ions as the pair ion.

When the aforementioned non-metallic base is treated with a liquid containing colloidal alumina as the principal component, there is formed a low-resistant layer on the surface of the non-metallic base. This low-resistant layer is water resistant, tough, and exhibits an excellent solvent hold out.

Therefore, the coating mixture used for forming an insulative layer on the low-resistant layer mainly comprising colloidal alumina may be of both organic solvent types and aqueous types.

However, a coating mixture which extremely easily penetrates of a porous structure sometimes partially penetrates into the low-resistance layer comprising colloidal alumina. Accordingly, it is necessary to elaborate composition of the mixture to be spread on the said low-resistant layer or to suitably increase the viscosity of the mixture. To be more specific, the speed at which a porous structure is permeated differs from solvent to solvent;

nonpolar aliphatic hydrocarbons and aromatic hydrocarbons quickly permeate while esters and ketones have a slower permeation speed. In case where the said coating mixture of insulative recording layer contains therein a finely-divided photoconductor and a binder, the permeation of the coating mixture into the low-resistant layer is retarded for the combination of a high affinity between the photoconductor powder and the binders and for a binder of a high molecular weight. The permeation can be controlled to a negligible extent if the coating mixture is provided in as high a concentration as possible and the coating method is so devised as to permit the coated mixture to dry quickly. Where the said coating liquid is an aqueous mixture the permeation of the liquid into the low-resistance layer is negligible in general. So the cares which are taken in the case of the organic solvent coating mixture becomes less important.

Among a variety of non-metallic base materials, one such as art, machine-coated, or baryta paper.

Having a water resistant pigment coating thereon is especially desirable. Although clay baryta coatings have somewhat unsuitable electrical properties for the purpose of electrophotography or electrostatic recording, they exhibit a considerable degree of solvent holdout. Thus by further treating such coatings with a treating mixture mainly comprising colloidal alumina an ideal base paper can be produced having perfect electrical and solvent hold-out properties.

In the treating solution to be used for the invention, colloidal alumina should occupy an amount exceeding 70% by weight of the total non-volatile ingredient, with the remainders consisting of a water resistant binder, a moisture absorbing agent, an active agent, and the like. In most uses, however, satisfactory results can be derived from using a treating solution of such type that the insoluble ingredient thereof consists solely of colloidal alumina.

The dry amount of colloidal alumina to be applied may be in the range of from 0.1 g. to 3 g. preferably in the range of from 0.2 g. to 1.5 g., per square meter of the surface of the base.

When colloidal alumina is spread on the coated surface of a machine-coated paper to a thickness of about 1 g./m.² and then allowed to dry, there is obtained a surface resistance of about 5×10^7 to 10^8 /square in the atmosphere having about 40% of relative humidity.

It is permissible to have moisture-absorbing inorganic salt or moisture-absorbing polyhydric compound incorporated into the low-resistance layer component. However, the electric properties are satisfactory without addition of such compounds.

Since the low-resistance layer is required to be resistant to water, special consideration must be paid to the selection of other ingredients, such as resin and pigment, to be blended with colloidal alumina so that the layer to be formed eventually becomes resistant to water. As such other substance, it is desirable to use a water-soluble polymer capable of forming a water insoluble cured film or an aqueous emulsion of resin capable of forming a water-insoluble film. Desirable examples are styrene/butadiene copolymer latex and butadiene/methylmethacrylate copolymer latex.

The low-resistant surface which has been obtained in this manner is strongly hydrophilic. Showing least tendency to repel an aqueous coating mixture which is sometimes repelled from the untreated machine-coated surface.

The electrostatic recording layer is obtained by spreading on the colloidal alumina layer and drying an aqueous emulsion of polyvinyl acetate, polyacrylic ester, polymethacrylic ester, or alkyd resin or an organic solvent solution of various insulative, water-insoluble resin.

As regards electrostatic recording layers, detailed descriptions are found, for example, in the specifications of U.S. Pat. No. 3,216,853, Japan patent publication No. SHO 38/24,345, Japan patent publication No. SHO 38/

25,938, Japan patent publication No. SHO 38/24,344, Japan patent publication No. SHO 38/24,343, and Japan patent publication No. SHO 38/14,345.

An electrophotographic sensitive layer to be formed on said low-resistance layer may be obtained by spreading and drying a mixture of a photoconductive inorganic powder with a water-soluble resin like melamine-formaldehyde resin, urea-formaldehyde resin, or a resin soluble in alkaline aqueous solution, such as acetic acid/vinylcrotonic acid copolymer or acrylic ester/acrylic acid copolymer, or a water emulsion of various resin. Alternatively, it may be obtained by coating a mixture of a solution of insulative resin in an organic solvent with a photoconductive inorganic powder.

Besides, an electrophotographic sensitive layer can be obtained by spreading a solution of an organic photoconductive substance in an organic solvent, a mixture having an organic photoconductive substance and an insulative resin dissolved in an organic solvent, or a mixture having a finely divided powder of an organic photoconductive substance dispersed in an insulative resin solution.

In case where the base of a non-metallic material to be used for the present invention is a plastic film instead of paper, formation of a colloidal alumina low-resistant layer proves quite advantageous. When a colloidal alumina layer is formed on a cellulose triacetate film under coated with gelatin, for example, a slightly opaque base results. This base behaves as a desirable base for electrophotographic sensitive material or electrostatic recording material except in extremely large sizes.

In case of paper support formation of a colloidal alumina layer on the rear surface of the paper not carrying the recording layer is valuable in the sense of lowering the contact resistance with an external conductor and desirable from the standpoint of decreasing curl. In case where the liquid developing process is combined with the recording material having the colloidal alumina layer provided also on the side of the base carrying no recording layer (as the rear-side layer), the rear-surface of colloidal alumina has an insufficient hold-out property to prevent the carrier liquid of the liquid developing agent from permeating into the paper interior. However, it has been found that in some kinds of uses, the weak resistance permits ready drying and therefore is more desirable.

It is frequently practiced to provide on the rear side a layer comprising carbon black as the principal component and having high electroconductivity. As concerns this practice, a detailed description is found in the specification of Japan patent application No. SHO 43/84,771.

In the present invention, when the non-volatile ingredient having colloidal alumina as the principal component is prepared in the form of water dispersion and, as such, spread on the base made of non-metallic material, the layer containing colloidal alumina remains on the surface of the material to give rise to a layer which is continuous in the lateral direction. When such porous base material as paper is treated by using, as the treating solution, a dispersion containing organic solvents such as methanol or ethanol or of mixture of such organic solvent with water, the greater part of colloidal alumina is allowed to permeate into the porous structure so that there is obtained a base having extremely low resistance in the longitudinal direction. This is extremely advantageous from the viewpoint of practical utilization. The impregnation of colloidal alumina throughout the entire thickness of the paper can be accomplished in the stage of paper manufacturing by on machine processing.

In a high-quality paper of 100 to 150 g./m.², the resistance in the longitudinal direction generally falls in the range of from 10^8 to 10^9 Ω /cm.² (resistance exhibited per unit area) or even exceeds this range in the neighborhood of 40% RH. By contrast, incorporation of 1.0 to 4.1 g./m.² of colloidal alumina gives the paper having a resistance of the order of 10^6 Ω /cm.². Thus, it is desirable to have colloidal alumina incorporated in an amount of

5

0.5 to 5%, preferably 0.5 to 3%, based on the weight of the base stock.

Utilization of the aforementioned technique of the present invention for the treatment of a paper base carrying thereon a clay layer such as art paper, machine-coated paper, and baryta paper is particularly desirable, because there can be obtained inexpensively a base for electrostatic recording material or electrophotographic sensitive material having excellent smoothness and exhibiting desirable behaviors in a wide range of humidity.

The recording material prepared by the treatment of the present invention so as to have an insulative recording layer provided on the base has no undercoated layer susceptible to water. Therefore, even when the print is immersed in water while in use or in storage, there is no fear of the recording layer being separated.

A more specific description is made of the present invention by referring to preferred embodiments of the invention.

EXAMPLE 1

A milky white dispersion comprising 10 parts by weight of Aluminasol 100 made by Nissan Chemical and 30 parts by weight of water was spread to a dry thickness of 1.2 g./m.² on both sides of a single art paper (90 μ in thickness). On the treated art surface, the surface resistance was $4 \times 10^8 \Omega$ /square at 40% of RH. When an electrophotographic sensitive layer consisting of 100 parts of photoconductive zinc oxide and 30 parts by vinyl chloride/vinyl acetate copolymer was applied with butyl acetate as the solvent thereon, a recording sheet extremely satisfactory properties resulted.

EXAMPLE 2

On the coated surface of a single machine-coat paper (70 μ in thickness), a milky white dispersion prepared by diluting 8 parts by weight of Aluminasol 100 made by Nissan Chemical and 2 parts by weight of Snow-tex O (water dispersion of colloidal silica) similarly made by Nissan Chemical with 30 parts by weight of water was spread to a dry weight of 1.0 g./m.². On the rear side, there was spread a black electro-conductive paint consisting of a water emulsion of polyvinyl acetate and carbon black.

On the coated surface which had undergone the preceding treatment, there was applied and dried a coating mixture which comprised photoconductive zinc oxide dispersed in an aqueous solution of ammonium salt of vinyl acetate/crotonic acid copolymer.

Thus, there was obtained an electrophotographic sensitive paper having excellent properties over a wide range of relative humidity.

EXAMPLE 3

On both surfaces of PHO paper (having a thickness of about 150 μ) made by Fuji Photo Film Co., there was applied and dried a water type coating dispersion comprising 400 parts by weight of Aluminasol 100, 18 parts by weight of polyvinyl alcohol, and 2 parts by weight of Edoran, an organic chromic complex made by Edogawa Chemical. The dry weight of the coat was 2 g./m.². Edoran converts polyvinyl alcohol water insoluble.

When an insulative recording layer composed of photoconductive zinc oxide and an epoxy ester of dehydrated castor oil fatty acid was spread on this layer and allowed to dry, there was obtained an electrophotographic sensitive paper having satisfactory properties.

EXAMPLE 4

On the treated paper of Example 3 having a low-resistance layer formed thereon, there was provided an electrostatic recording layer composed of 100 parts by weight polybutyl methacrylate and 20 parts by weight of finely divided colloidal silica. As the solvent for coating, there was used a mixture of ethyl acetate and butyl ace-

6

tate. Thus, there was obtained an electrostatic recording material having excellent properties.

EXAMPLE 5

An excellent electrophotographic sensitive material could be prepared by applying a coating liquid having polyvinyl carbazole in benzene to the base treated by the procedure of Example 1.

EXAMPLE 6

An excellent electrostatic recording paper could be obtained by applying to the paper treated by the procedure of Example 2 a water emulsion of vinyl acetate/ethylacrylate copolymer to a dry weight of 8 g./m.²

EXAMPLE 7

On both surfaces of a single machine-coat paper (thickness 70 μ), the low-resistance layer coating liquid prepared as described in Example 3 was applied and allowed to dry. An excellent electrophotographic recording material was obtained by applying to the front surface machine (coated side) a coating mixture comprising 100 parts by weight of photoconductive zinc oxide, 50 parts of styrene/butadiene copolymer latex (50% of solid component), and 5 parts of ammoniacal shellac solution (20%).

EXAMPLE 8

To the rear surface of a single art paper (100 μ in thickness), a mixture of carbon black with styrene/butadiene copolymer latex was applied. On the art surface thereof, a mixture of Aluminasol 100 (non-volatile content about 20%) and butadiene/methylmethacrylate copolymer latex (non-volatile content 50%) was applied. Since mixing of these two dispersions in their undiluted state caused coagulation, each was diluted prior to mixing. That is, 10 parts of Aluminasol was diluted with 30 parts of water, and 10 parts of the latex with 90 parts of water respectively. Then, the two diluted solutions were combined. The coating weight was 2 g./m.².

When any one of the coating mixtures described in the preceding examples were applied to this layer, there were produced recording materials having excellent properties.

EXAMPLE 9

To the subbed surface of a polyethylene terephthalate film having a thickness of 120 μ and subbed with gelatin, for the photographic use 10% water dispersion of colloidal alumina (containing a small quantity of nionic active agent) was applied to a dry weight of 1.2 g./m.². On the resultant coat, there was spread a coating liquid having 10 parts of polyvinyl carbazol and 5 parts of diphenyl chloride so as to give rise to a dry film of 10 μ in thickness. The resultant recording material was substantially transparent and exhibited excellent electrophotographic properties.

EXAMPLE 10

One surface of an ordinary document paper was subjected to the treatment as employed in Example 1, while the other surface was coated with 5% methanol solution of maleic anhydride/vinyl acetate copolymer. On the surface coated with the copolymer, there was formed the same electrophotographic sensitive layer as described in Example 1. That is to say, this practice corresponds to a case in which the undercoating on the recording layer side of the base was accomplished by the conventionally known method, while the rear surface of the base was subjected to the treatment of the present invention to improve the electroconductivity.

EXAMPLE 11

On the non-art surface of the single art paper (130

7

g./m.²), there was applied the dispersion of the following composition:

	Parts
Aluminasol 100 (made by Nissan Chemical) -----	10
Methanol -----	90

Although Aluminasol 100 was a water dispersion, it could be diluted with methanol. The dry weight was 2 g./m.².

Prior to the coating, the said art paper showed a resistance of $8 \times 10^8 \Omega/\text{cm}^2$ in the longitudinal direction (in the direction of thickness) at 40% RH and 20° C. After the treatment, the resistance was $3 \times 10^5 \Omega/\text{cm}^2$. A sensitive paper of excellent properties could be obtained by directly applying the coating mixture for recording layer of Example 2 to the front surface of the thus treated single art paper.

Similarly, a sensitive paper of excellent properties was obtained by spreading the coating mixture of Example 4 directly to the said art surface.

What is claimed is:

1. A method for manufacturing a base for an electrostatic recording material or electrophotographic sensitive material, which comprises forming an electroconductive layer on at least one surface of a base consisting of a non-metallic substance by treating said surface with a treating mixture containing colloidal alumina of more than 70% by weight of the non-volatile components of the mixture.

2. The method for manufacturing a base for electrostatic recording material or electrophotographic sensitive material as claimed in claim 1, wherein the dry amount of said colloidal alumina to be applied is in the range of from 0.2 g. to 3 g. per square meter of the surface of the base.

3. The method for manufacturing a base for electrostatic recording material or electrophotographic sensitive material as claimed in claim 1, wherein said base consists of paper.

4. The method for manufacturing a base for electrostatic recording material or electrophotographic sensitive material as claimed in claim 1, wherein at least one surface of said base consists of a water-resistant layer containing clay or pigment.

5. The method for manufacturing a base for electrostatic recording material or electrophotographic sensitive material as claimed in claim 4, wherein said water-resistant surface of said base is treated with a treating mixture con-

8

taining said colloidal alumina as the principal non-volatile component.

6. The method for manufacturing a base for electrostatic recording material or electrophotographic sensitive material as claimed in claim 1, wherein said base consists of a plastic film.

7. A method for manufacturing a base for an electrostatic recording material or electrophotographic sensitive material, which comprises treating at least one surface of a base consisting of a non-metallic substance with a treating mixture, the non-volatile component of said treating mixture consisting of colloidal alumina of more than 70% by weight thereof and a water-insoluble resin.

8. A method for manufacturing an electrostatic recording material or electrophotographic sensitive material which comprises forming an electroconductive layer on at least one surface of a base on a non-metallic substance by treating said surface with a treating mixture containing colloidal alumina of more than 70% by weight of the non-volatile components of the treating mixture, and applying an electrostatic recording layer or an electrophotographic sensitive layer to said electroconductive layer.

9. A method as in claim 1 where said non-volatile components consist solely of colloidal alumina.

10. A method as in claim 8 wherein said non-volatile components consist solely of colloidal alumina.

11. A method as in claim 8 where said electrostatic recording layer or electrophotographic sensitive layer is applied by applying a solution of photoconductive particles and binder therefor to said electroconductive layer for a length of time sufficient to dry the solvent.

12. A method as in claim 11 where said solvent is water.

13. A method as in claim 12 where said solvent is organic and where there is an affinity between said photoconductive powders and said binder.

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WILLIAM L. JARVIS, Primary Examiner

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