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3,743,537

METHOD OF MAKING AN ELECTROPHOTOGRAPHIC RECORDING MEMBER

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No Drawing, Filed Oct. 14, 1970, Ser. No. 80,805
Claims priority, application Japan, Apr. 13, 1970, 45/8,716

Int. Cl. B44d 1/18

U.S. Cl. 117—215

16 Claims

ABSTRACT OF THE DISCLOSURE

A method of manufacturing an electrophotographic paper comprising the steps of forming a smooth, electrically conductive barrier subcoating on a water-resistant layer provided on a paper base by applying to the water-resistant layer a treating mixture containing colloidal alumina, calendering the subcoating to improve the surface smoothness and uniformity, the colloidal alumina forming the subcoating being not less than 70% by weight of the dried subcoating; and then providing an electrophotographic light-sensitive layer on the smoothed subcoating.

This invention relates to a manufacturing method of base paper for use in the electrophotographic recording sheet, and especially to such method including special treatments of base paper.

An electrophotographic paper generally comprises a base paper comprising cellulose fiber, a conductive resinous coating provided on the surface of the base paper, and an electrophotographic light sensitive layer formed on said coating. The electrically conductive coating is necessary to prevent the penetration of organic solvents into the porous structure of the paper at the coating procedure of the electrophotographic layer, and to maintain a certain level of conductivity of the support under low relative humidity conditions. Therefore such conductive coatings are often referred to as conductive barrier coatings. (Barrier against permeation of organic solvents.)

Moreover, treatments of the back surface of recording papers are sometimes practiced for the purpose of curl-balancing. Back coatings, in most cases, also serve to increase the conductivity of the paper ones. When the resulting electrophotographic paper is assumed to be subjected to liquid development, developer pick-up from the back surface should also be prevented in order to promote drying after processing. Employment of treating process such as size press enables a simultaneous formation of the conductive and back coatings.

Coating mixtures for providing electrophotographic layers are applied on the conductive barrier coatings prepared in the above-described manner. Electrophotographic layers are normally produced by utilizing coating mixtures comprising finely-divided photoconductors such as zinc oxide dispersed in organic solvent solutions containing resinous materials; recently water-dilutable mixtures are also employed.

Now electrophotography has obtained a great success in copying documents, for which purpose almost all the requirement for the base paper as for the smoothness of the surface, the surface conductivity, solvent barrier property, etc. are satisfied with the use of technological means already known to those skilled in the art.

Far more severe requirements arise, however, for the electrophotographic paper which is expected to reproduce a high-quality, continuous tone image which appears substantially equal to or better than those made on photographic papers which utilize silver halide emulsions as light sensitive material.

A better smoothness and uniformity exceeding the conventionally accepted levels is required of the surface of the base paper on which the electrophotographic layer is to be formed. An electrophotographic paper made with a commercially available are paper, which has a smoothness of 400 (sec) as measured by "Oken smoothness measuring instrument" (by Asahi Seikosha, Japan), cannot provide prints equivalent to those on the conventional silver halide glossy photographic papers. This may be mainly attributed to lowering of the original smoothness or uniformity of the art paper during coating and drying operations for providing the conductive barrier coating with the use of aqueous coating solutions, which brings about expansion followed by shrinkage of the paper base. For example, the original smoothness of 400 (secs) of an art paper 120 to 140 micron thick reduces to about 250 in the same measurement with Oken smoothness measuring instrument after treatment with an aqueous solution. On the paper coated with a conductive barrier coating are often observed irregularities having relatively large intervals, which adversely affect the quality of an image finally obtained. Calendering of the paper following the subcoating formation seems promising to overcome such disadvantages. However, most of conventional conductive barrier coatings are made of thermoplastic resins which become noticeably tacky upon heating, thus rejecting such processing. Polyvinylbenzyltrimethyl-ammonium chloride, water-soluble salts of polyvinylbenzene sulfonic acid, Calgon Conductive Polymer 261 are among suitable materials for conductive barrier coatings. All of them are strongly hydrophilic and of polar nature, and thus retain moisture therein even at low relative humidity conditions exhibiting low electrical resistance. Attempts have been made to render these materials insoluble in water after coating, resulting, however, in a remarkable rise of production cost.

Accordingly, the object of the present invention is to provide a manufacturing method of base paper for use in the electrophotographic recording sheet overcoming these difficulties.

The present object has been achieved by providing a method comprising (I) forming a thin subcoating substantially comprising colloidal alumina on a water-resistant layer formed on a paper support of cellulosic fiber, said water-resistant layer mainly consisting of clay or other inorganic pigments, and then calendering the surface of the subcoated paper with calender rolls; or (II) cast coating a colloidal alumina dispersion to such support to improve the uniformity of the paper surface, and (III) finally providing an electrophotographic light-sensitive layer on said calendered surface.

Colloidal alumina used in the present invention is normally synthesized from water-soluble aluminum salts, depending on which various sorts of negative ion are adsorbed on the surface of the colloid particles, including chloride anion or organic carboxylic acid radicals such as acetate. For the present purpose, colloidal alumina containing chloride anion is especially suited as regards the electrical conductivity of the resulting coating. Aqueous dispersions of colloidal alumina are available under the trade name "Alumina Sol 100," "Alumina Sol 200" and "Alumina Sol 300" marketed by Nissan Kagaku Ltd., among which "Alumina Sol 100" is most suited. By diluting this product with water a coating dispersion is readily prepared. It may be applied on the coated surface of paper having at least one side of them coated with water-resistant layers such as art paper, machine coated paper, and baryta paper. Desirable coating weights of the colloidal alumina lie between 0.1 to 3 g./m.² on dry base, and more preferably 0.2 to 1.5 g./m.². The dried coating is water-resistant and works well as a barrier layer against solvent permeation in conjunction with the underlying

clay or pigment coatings. In case of baryta paper for photographic paper, the baryta layer which contains the binding material in a lower ratio to the pigment than other clay coatings, permits the colloidal alumina dispersion to diffuse into its structure, thus leaving a subcoated paper which still allows solvent permeation to some extent. But because of its extremely fine structure with a high uniformity, the permeation occurs quite uniformly to provide an electrophotographic paper with satisfactory properties.

In the conductive barrier coatings of the present invention, the colloidal alumina should occupy not less than 70% of the total dried coating weight. Ingredients to be incorporated in the coatings are rather few mainly due to the sensitivity of the dispersion stability of this colloid. Since the colloidal particles are charged positive in the dispersion, only cationic polymeric electrolytes are permitted as long as polymeric materials are concerned. In fact, the colloidal alumina dispersion is compatible with cationic polymers such as polyvinylbenzyltrimethylammonium chloride.

Electrically neutral polymers such as polyvinylalcohol are compatible with the colloid; such materials may preferably be used with suitable curing agents to make the resulting coatings water resistant. Cationic polymer emulsions may also be used. The same restriction as for electrical polarity holds to other inorganic pigment dispersions. Surface resistivities increase with the use of more resistant materials incorporated in the colloidal alumina coatings. Desirable coating weight ranges for mixed type barrier coatings can be found by maintaining the coated weight of the alumina in the range mentioned above, and at the same time by keeping the alumina concentration in the dried coatings not lower than 70%.

Back surface treatment, which is not necessary for very thin papers, is advantageously carried out for most purposes. Compositions for the back coating are generally common to the conductive barrier coatings, mainly comprising electrically conductive resinous materials. No further descriptions will be given here since the back treatment does not construct the essential feature of the present invention.

Anyway prior to smoothing operation all the treatments for the base paper with aqueous treating agents should be preferably finished. Treatment with solutions comprising organic solvent which will not substantially affect on the smoothness and uniformity of the paper may be carried out after the smoothing operation. For example, an electrically insulating layer which controls the carrier injection from the underlying layer into the photoconductive layer may be formed on the conductive barrier coating after calendering operation provided the coating mixture comprises organic solvents.

The smoothing operation may be accomplished with any of known techniques known to those skilled in the art. The colloidal alumina coating in accordance with the present invention would not melt or soften by heating, without showing any tendency to adhere to the calender rolls.

Then one can readily produce an electrophotographic paper by applying a coating mixture comprising an organic solvent and drying said coated mixture under a relatively mild condition. The improvement of smoothness by calendering or cast coating is so remarkable that the resulting paper exhibits extremely high qualities never realized by previous methods.

The surface resistance of the coating primarily comprising colloidal alumina is sufficiently low under dry conditions, being slightly higher than the coating of polyvinylbenzyltrimethylammonium chloride with the same coating weight by the factor of 5 to 10 near 30 to 40% R.H. This value can meet the requirement for most uses. It should be noted that the colloidal alumina is far less expensive than quaternary ammonium polymers, making

the present invention a very profitable method for industrial applications.

In the manufacture of coated paper such as art, or baryta paper, calendering is normally carried out after the formation of the clay or pigment coating. Such calendering of the clay or pigment coating which is normally accomplished prior to the coating of colloidal alumina coating may be omitted in practicing the present invention, since the final smoothness of the paper is chiefly determined by the calendering after the coating of colloidal alumina sub-layer. Calendering may be carried out by using ordinary calender rolls, or super calender rolls, immediately after the subcoating is dried, and prior to winding of the paper, or it may be accomplished on a calendering machine as an independent setup.

In cast-coating, as is well known to those skilled in the art, the conductive barrier coating is brought into contact with a mirror-polished surface of metal roller or of a metallic belt while it is still wet until the coating dries to form a very smooth surface.

EXAMPLE I

A milky dispersion comprising 10 parts by weight of colloidal alumina available from Nissan Kagaku Ind. Ltd., under the trade name "Alumina Sol 100" and 30 parts by weight of water was applied on both surfaces of a one-side coated art paper (90 micron thick) to give a dried coating weight of 1.2 g./m.² on each surface. The surface resistivity of the front surface was 4×10^8 ohms/square at 40% R.H. On the alumina coated art surface was formed an electrophotographic layer comprising 100 parts of photoconductive zinc oxide, and 20 parts of a copolymer comprising ethyl acrylate, methyl methacrylate, and acrylic acid with the use of a mixed solvent or xylol and toluol as the coating solvent.

This product exhibited desirable properties when used to reproduce documents. When a continuous tone image was reproduced on this product, however, from a photographic positive print, unevenness of toner deposition appeared throughout the reproduced image corresponding to the ruggedness of the paper which had been formed during the coating and drying of the subcoating. Such ruggedness was easily observed even after the fixation of the toner image with application of a clear lacquer solution.

To overcome such defects in the final print, the subcoated base paper was subjected to super calendering. The paper was passed through a seven-stage calender with a nip pressure of 200 kg./cm. at 80° C. This calendering operation raised the surface smoothness from 250 (sec) before treatment to 20 (sec) by the measurements with Oken smoothness measuring instrument (Asahi Seiko). The testing procedure followed the descriptions shown in P197 of "Pulp and Paper; Their Testing Methods" edited by Paper and Pulp Technological Institute (Japan).

The electrophotographic coating of the same composition as above was formed on this smoothed surface. Similar procedures gave a very high quality image having an appearance equivalent to those of photographic prints with far less ruggedness, mottles, and irregularities.

EXAMPLE II

On the coated side of a one-side machine coated paper (70 micron thick) was applied a subcoating mixture comprising 8 parts by weight of colloidal alumina, "Alumina Sol 100" (Nissan Kagaku Ltd.), 2 parts by weight of colloidal silica aqueous dispersion made by Nissan Kagaku under the trade name "Snowtex O," and 30 parts by weight of water so as to give a dried coating weight of 1.0 g./m.². On the rear surface was coated a black conductive paint comprising carbon black dispersed in an aqueous emulsion of polyvinylacetate. After the rear coating was dried and prior to winding, the paper was subjected to calendering operation by means of five stage machine calender with 90 kg./cm. nip pressure.

An electrophotographic coating comprising 100 parts of photoconductive zinc oxide, 20 parts of vinyl chloride/vinyl acetate copolymer, and 5 parts of ethylphthalylethylglycolate was formed on the subcoating by using butylacetate as coating solvent. A recording sheet having a desirable quality resulted.

EXAMPLE III

On the non-coated side of one-side coated art paper (130 micron thick) was coated an electrically conductive resin ECR-134 marketed by Dow Chemical Co. diluted with water and methanol to give a dried coating weight of 1.5 g./m.². Then on the art surface was applied a mixture of "Alumina Sol 100" and a latex of butadiene/methylmethacrylate copolymer by cast coating. It has been proved that the addition of the alumina sol to the latex in a concentrated dispersion deteriorated the stability of the latex. Therefore, the addition was performed after 100 parts of the alumina sol was diluted with 300 parts of water to 10 parts of the latex diluted with 90 parts of water. The coated weight was 2 g./m.². As for the composition of the subcoating, Alumina Sol 100 contains about 20% non-volatile while the latex contains 50% solid content, before dilution; therefore, the dried subcoating was composed of 80% of the colloidal alumina and 20% of the copolymer. On the subcoating, an organic photoconductive coating comprising 10 parts of polyvinylcarbazol and 5 parts of chlorinated diphenyl was formed by using benzene as coating solvent to give a dried thickness of about 10 microns.

An electrophotographic paper resulted to give similar satisfactory properties as those in the preceding examples to.

EXAMPLE IV

The rear surface of photographic baryta paper (120 micron thick with a baryta coating weight of 20 g./m.²) was treated with an aqueous solution of a cationic polymer "Conductive Resin 261" from Calgon corporation to give a dried coating weight of 1.2 g./m.².

The baryta coated front surface was then treated with a colloidal alumina dispersion comprising 20 parts of "Alumina Sol 100" and 80 parts of water. The coated weight was 1.2 g./m.². This treated surface was calendered in the same manner as in Example I. Then a photoconductive coating comprising 100 parts by weight of zinc oxide, 12 parts by weight of styrenated alkyd and 8 parts by weight of polyisocyanated compound (Desmodur L of Bayer AG., West Germany) was formed with the use of a mixed solvent of toluol and butyl acetate. The dried thickness of the photoconductive layer was about 8 microns. The electrophotographic paper thus prepared exhibited quite acceptable qualities.

EXAMPLE V

On the calendered base paper described in Example I was provided an electrophotographic coating of Example IV. A similarly satisfactory result was obtained.

EXAMPLE VI

The rear surface of photographic baryta paper as described in Example IV was treated with an aqueous solution of potassium polyvinylbenzene sulfonate to give a dried coating weight of 0.1 g./m.².

The baryta coated front surface was then treated mixture comprising 8 parts of Alumina Sol 300 (20% non-volatile) and 4 parts of 10% aqueous methanol (1:1) solution of ECR-34 to give a dried coating weight of 1.5 g./m.². On this an electrophotographic coating of Example IV was provided. A recording sheet having a superior quality was obtained. Alumina Sol 300 made by

Nissan Kagaku Ltd., contains organic carboxylic acid anion.

What is claimed is:

1. A method of manufacturing an electrophotographic paper comprising the steps of forming a smooth, electrically conductive barrier subcoating on a water-resistant layer provided on a paper base by applying to said water-resistant layer a treating mixture containing colloidal alumina; calendering said subcoating to improve the surface smoothness and uniformity, the colloidal alumina forming the subcoating being not less than 70% by weight of the dried subcoating; and then providing an electrophotographic light-sensitive layer on the smoothed subcoating.
2. The method of claim 1 wherein said paper base is selected from the group consisting of paper machine coated with said water-resistant layer and baryta paper.
3. The method of claim 1 wherein said colloidal alumina contains chloride anion.
4. The method of claim 1 wherein said colloidal alumina contains acetate anion.
5. The method as in claim 1 where said paper base comprises cellulosic fibers.
6. The method of claim 1 where said water-resistant layer is selected from the group consisting of clay and inorganic pigments.
7. The method of claim 1 wherein said electrically conductive barrier subcoating comprises more than 70% by weight of colloidal alumina and the balance of a quaternary ammonium polymer.
8. The method of claim 7 wherein the range of dried coating weight of said colloidal alumina is 0.1-3 g./m.².
9. A method of manufacturing an electrophotographic paper comprising the steps of forming a smooth, electrically conductive barrier subcoating on a water-resistant layer provided on a paper base by cast coating a treating mixture containing colloidal alumina on said water-resistant layer, the colloidal alumina forming the subcoating being not less than 70% by weight of the dried subcoating; and then providing an electrophotographic light-sensitive layer on the smooth subcoating.
10. The method of claim 9 wherein said paper base is selected from the group consisting of paper coated with said water-resistant layer and baryta paper.
11. The method of claim 9 wherein said colloidal alumina contains chloride anion.
12. The method of claim 9 wherein said colloidal alumina contains acetate anion.
13. The method as in claim 9 where said paper base comprises cellulosic fibers.
14. The method of claim 9 where said water-resistant layer is selected from the group consisting of clay and inorganic pigments.
15. The method of claim 9 wherein said electrically conductive barrier subcoating comprises more than 70% by weight of colloidal alumina and the balance of a quaternary ammonium polymer.
16. The method of claim 15 wherein the range of dried coating weight of said colloidal alumina is 0.1-3 g./m.².

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CAMERON K. WEIFFENBACH, Primary Examiner

U.S. Cl. X.R.

96-1.5, 1.8, 85, 67; 117-219; 346-135

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,743,537 Dated July 3, 1973

Inventor(s) Satoru Honjo et al.

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

Column 1, line 8, "Apr. 13, 1970" should read
--- October 15, 1969 ---.

Column 1, line 9, "45/8,716" should read --- 82337/69 ---.

Signed and Sealed this

First Day of February 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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