United States Patent

Bixler

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[54] ELECTROCONDUCTIVE COATING

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[51] Int. Cl. **B44d 1/18,** G03g 5/00

[58] Field of Search ..... 117/215, 152, 201, 224, 138, 117/219; 96/1.8; 162/181 D

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[57] **ABSTRACT**

Paper having a surface coating of exfoliated three-layer clay exhibiting a surface conductivity of 10^8–10^{10} ohms/sq. at relative humidities from 12–15 percent may be used for making a copy sheet for electrophotography by providing an overcoating of zinc oxide. An aqueous dispersion of exfoliated three-layer clay together with water soluble electroconductive inorganic compound is described.

10 Claims, No Drawings

ELECTROCONDUCTIVE COATING

This invention relates to electrically conductive coated fibrous sheet material paper suitable for use as a base for electrostatic copy sheets and to electrostatic copy sheets made therefrom and to the method of making the same.

Sheet material for use in electrostatic or electrophotographic copying processes conventionally comprises a fibrous base sheet of paper or other fibrous material rendered electroconductive and carrying a coating of photoconductive zinc oxide held in place with a suitable binder. Such sheet material suffers from the disadvantage that electroconductive material from the base sheet tends to transfer or migrate to the overlying photoconductive layer, or to strike through the base sheet to its bottom surface whence it transfers to the photoconductive coating of the sheet next beneath it when the sheets are stacked for storage or use. The presence of electroconductive material in or on the photoconductive coating lessens the effectiveness of the latter, causing reduced contrast in the image produced.

One object of the invention is to provide a fibrous sheet having an electrically conductive coating in which the tendencies of the coating to transfer or migrate into an overlying photoconductive layer or to strike through the fibrous sheet are minimized. Other objects are to provide copy sheets for use in electrostatic copying to give improved printing characteristics including better fill-in of printed areas and deeper black printing; and to provide a base sheet having an electrically conductive coating that does not impair the quality of the base sheet and is relatively colorless, odorless and inexpensive.

Other objects, features and advantages of the invention will become apparent from the following description.

In general the invention features a fibrous sheet material having an electrically conductive coating comprising an exfoliated three-layer clay. In one preferred embodiment the coating includes a water-soluble hygroscopic inorganic electroconductive compound, particularly lithium, calcium and magnesium compounds. In another preferred embodiment lithium bentonite (lithium montmorillonite) is employed, making it possible to obtain improved conductivity, as compared to sodium or calcium bentonites. The conductive coating may be overcoated with a conventional coating of photoconductive zinc oxide to provide copy sheets suitable for use in electrostatic or electrophotographic copying.

The fibrous sheet material employed in the present invention may be any paper or unwoven fibrous web having the desired strength, including the papers commonly employed for making copy paper for use in electrostatic or electrophotographic copying.

The electroconductive coating is laid down on the fibrous sheet material from an aqueous dispersion of a an exfoliated three-layer clay by any conventional coating procedure such as drawing down, roll coating, tub sizing or the like. Among such clays which may be used are bentonite (including sodium, lithium, calcium, ferric, and chromic bentonites and montmorillonites) vermiculite, pyrophyllite, and the like, Wyoming bentonite (sodium bentonite or montmorillonite) and lithium bentonite (lithium montmorillonite) being preferred. The aqueous dispersion may be prepared by dispersing in water a previously exfoliated clay, which may contain dispersant, or a suitable dispersant may be added to the water along with the exfoliating clay to cause exfoliation to occur as the dispersion is formed. Among the well-known dispersants which may be employed are a mixture of sodium hexametaphosphate and sodium carbonate (Calgon); sodium carbonate; sodium silicate; sodium hydroxide; tetrasodium pyrophosphate; lithium hydroxide; lithium carbonate, and the like. The dispersant is preferably present in an amount sufficient to cause exfoliation to occur, an amount from 0.2 to 1.0 percent by weight of the clay, preferably about 0.5 percent by weight. The amount of clay in the aqueous dispersion may vary somewhat depending upon the particular mode of coating employed and the thickness of the coating desired but will usually be of the order of 0.5 to 10 percent by weight, preferably from 1 to 3 percent by weight.

The water-soluble inorganic electroconductive compounds may be employed in amounts up to 50 percent by weight of the clay present in the coating. Best results are usually obtained by using about 5 to 15 percent by weight, based on the weight of the clay. The compounds which are useful include such hygroscopic compounds as lithium hydroxide, lithium chloride, calcium chloride, calcium nitrate, and magnesium perchlorate.

The weight of coating for satisfactory results should be 0.5 to 5 lb. per ream, preferably 1 to 4 lb. per ream. Excellent results have been obtained with coatings in the range 1.2 to 3.2 lb. per ream.

The photoconductive zinc oxide coating applied on the surface of the clay coating may be deposited from any conventional dispersion of photoconductive zinc oxide in a solution of a suitable binder, such as polyethylene, polypropylene, styrenebutadiene copolymer, or the like, in a nonaqueous solvent such as naphtha, benzene, toluene, xylene, etc., by conventional techniques.

The following specific examples are intended to illustrate more fully the nature of the invention without acting as a limitation upon its scope.

EXAMPLE I

Volclay 625, a Wyoming bentonite or exfoliating sodium montmorillonite, mined by American Colloid Co., Skokie, Ill. is added to water at 60° C. in a Waring Blendor to produce an aqueous slurry containing 2 percent clay by weight. Calgon (sodium hexametaphosphate) is added to the slurry (0.5 percent by weight based on the clay) to act as a dispersant. The resulting dispersion is put through a Sharples Supercentrifuge operating at 23,000 r.p.m. at the rate of 100 ml./minute and a degritted dispersion of fine bentonite is recovered containing 0.8 percent total solids.

This slurry is drawn down onto Crocker Videograph paper using a No. 32 wire wound casting rod. Two or three drawdowns are required to give the desired coating with a dry weight of approximately 2 lbs./ream. The coated paper is either dried in ambient air for 1 to 2 hours or in an 80° C. forced air oven for 5 minutes. A smooth, colorless coating results.

For testing the conductivity of the coated paper it is placed in a glove box with the humidity controlled to a relative humidity in the range of 12–19 percent. The paper is conditioned overnight and then tested for surface and volume conductivity with a Keithley Instruments Co. 6105 Resistivity Adapter, and 621 Electrometer using a Sorensen High-Voltage Power Supply. The test voltages are 100 and 300 v. A coating made by the above procedure has a surface resistivity of 4×10^{9} ohms/sq. and a volume resistivity of 10^{13} ohm-cm. at 16 percent relative humidity. This surface resistivity falls within the desired range and the high-volume resistivity (approximately equal to the uncoated paper) indicates absence of strike through of coating.

For testing print quality a sheet of the above-coated paper is overcoated with 25 lbs./ream of a conventional photoconductive zinc oxide and hydrocarbon polymer binder composition, then dark adapted for several hours while conditioning at 15 percent relative humidity. This prepared sheet is then tested in an SCM copier with a standard test master. The quality of the resulting print is superior to commercially available paper having a standard quaternary polymer conductive coating. Fill-in of printed areas is better with the clay coating and deeper black printing results.

EXAMPLE II

The procedure of example I is repeated except that there is added to the clay dispersion 10 percent by weight, based on the weight of the clay, of lithium chloride. The surface resistivity of the electroconductive coating in this case is 2×10^{9}

ohms/sq., and the print quality of the finished copy sheet is noticeably improved.

An important modification of the above process is to concentrate the degritted clay slurry by heating to form a slurry containing approximately 2 percent by weight total solids. This slurry is capable of yielding 2 lbs./ream of coating with a single drawdown.

It is also possible to prepare a satisfactory slurry for coating by simply letting the large siliceous particles settle out of the 2 percent crude bentonite slurry. The supernatant dispersion may then be used for coating without supercentrifugation. Both the appearance and performance of this latter coating are satisfactory for commercial use. Lithium chloride can also be added to this dispersion to further improve performance.

EXAMPLE III

Volclay 625 is added to water at 60° C. in a Waring Blendor to produce an aqueous slurry containing 5 percent clay by weight. Lithium hydroxide (3 percent by weight based on the clay) dispersant and lithium chloride (10 percent by weight based on the clay) are added to the slurry. If desired, the pH of the dispersion can be lowered by the addition of hydrochloric acid without deleterious effect upon the coated sheet product.

The slurry is drawn down onto Crocker Videograph paper using a No. 18 wirewound rod, this rod giving a coating weight of approximately 2 lbs./ream. The coated paper is dried in ambient air for 1 to 2 hours. The surface resistivity of this coated paper is 2×10^9 ohms/sq. at 15 percent relative humidity.

EXAMPLE IV

The procedure of example III is followed except that lithium carbonate (5 percent by weight based on the clay) dispersant and lithium chloride (5 percent by weight based on the clay) are used instead of lithium hydroxide and 10 percent lithium chloride. The surface resistivity of a coating of this dispersion at 2 lbs./ream is 2×10^9 ohms./sq. at 15 percent relative humidity.

EXAMPLE V

Bentolite L, a calcium bentonite produced by Georgia Kaolin Co. is added to water at 60° C. in a Waring Blendor to produce an aqueous slurry containing 5 percent clay by weight. Sodium hexametaphosphate (0.5 percent by weight based on the clay) and sodium carbonate (1.0 percent by weight based on the weight of the clay) are added as dispersants. Lithium chloride (10 percent by weight based on the clay) is then added.

This slurry is drawn down onto Crocker Videograph paper using a No. 18 wire wound casting rod. A coating of approximately 2 lbs./ream dry weight is obtained. The coated paper is either dried in ambient air for 1 or 2 hours or in an 80° C. forced air oven for 5 minutes. A smooth, white coating results.

The coating is tested as outlined in example I. This coating has a surface resistivity of 4×10^9 ohms/sq. at 15 percent relative humidity. A print made using this formulation as the conductive coating was comparable to the print mentioned in example I.

EXAMPLE VI

Bentolite L is added to water at 60° C. in a Waring Blender to produce an aqueous slurry containing 5 percent clay by weight. Lithium carbonate (8 percent by weight based on the clay, an amount approximately equal to the one milliequivalent/gram exchange capacity of the clay) is added to the clay as a dispersant. Insoluble calcium carbonate is formed and remains in good dispersion along with the lithium bentonite which is also formed. If desired, the pH of the dispersion can be lowered by the addition of hydrochloric acid.

In this formulation the lithium ion is bound to the clay since the lithium ion is completely exchange for the calcium ion, and no ionic migration would be expected from a coating containing these insoluble lithium and calcium compounds.

The slurry is drawn down onto Crocker Videograph paper using a No. 18 wire wound rod, a 1.7 lbs./ream coating weight resulting. The coated paper is dried in ambient air for 1 to 2 hours. The surface resistivity of the coated paper is 1×10^9 ohms/sq. at 16 percent relative humidity.

EXAMPLE VII

Lithium bentonite is prepared by passing a 0.6 percent sodium bentonite (Volclay 625) aqueous dispersion (prepared as in example I) through an ion exchange column previously charged with lithium ion. The resulting lithium bentonite dispersion was coated on paper at 1.0 lbs./ream. This coating had a surface resistivity of 1×10^9 ohms./sq. at 12 percent relative humidity.

An important modification of the above process is to prepare either chromic bentonite or ferric bentonite in a similar manner. A 2 lbs./ream coating of chromic bentonite has a 4×10^9 ohms/sq. surface resistivity at 12 percent relative humidity. A 2 lbs./ream coating of ferric bentonite has a 3×10^9 ohms/sq. surface resistivity at 12 percent relative humidity.

The coated sheets of the present invention before overcoating with photoconductive zinc oxide have surface resistivities of the order of 10^8–10^{10} ohms/sq. at 12–15 percent relative humidity as contrasted with uncoated paper sheet which has a surface resistivity of the order of 10^{13}–10^{14} ohms/sq. under these conditions.

The addition of water-soluble inorganic electroconductive compounds is preferred because the pressure of such materials in the coating improves conductivity of the coating under conditions of very low relative humidity, such as may be present when the finished copy paper is stored in a warm copying machine.

While the reasons for reduced strike through and migration or transfer of the conductive coating are not fully understood, particularly when water-soluble conductive compounds are present in the coating, it is believed that the compounds become trapped within a loose gel network formed by the clay particles, this gel network serving not only to prevent migration of the water-soluble compounds but also preventing penetration of the fibrous sheet by the clay particles during the coating operation.

Other embodiments will occur to those skilled in the art and are within the following claims.

What is claimed is:

1. The process of producing paper having an electrically conductive coated surface comprising the steps of preparing an aqueous dispersion containing exfoliated three-layer sodium bentonite clay in an amount from 1 to 3 percent by weight of the dispersion, and a water-soluble inorganic electrically conductive compound selected from the class of lithium, calcium and magnesium compounds in an amount from 8 to 12 percent by weight of said sodium bentonite, coating the surface of said paper with said dispersion, and drying said coating to produce a coated paper having a surface conductivity in the approximate range of 10^8–10^{10} ohms./sq. at relative humidities from 12–15 percent.

2. The process of making copy sheet for use in electrophotography which comprises fibrous sheet material having an electrically conducted coated surface, which process comprises the steps of preparing an aqueous dispersion containing 0.5 to 10 percent by weight of exfoliated three-layer clay, coating the surface of said sheet with said dispersion, drying said coating to produce a coated sheet having a surface conductivity in the approximate range of 10^8–10^{10} ohms/sq. at relative humidities from 12–15 percent, then applying a photoconductive zinc oxide coating over said electrically conductive coating.

3. A fibrous sheet material having electrically conductive surface coating comprising exfoliated three-layer clay,

selected from the class consisting of bentonite, vermiculite and pyrophyllite, said coating also including a water-soluble electroconductive inorganic compound selected from the class of hygroscopic lithium, calcium and magnesium compounds, said compound being present in an amount from about 5 to 15 percent by weight of said clay, said coating having a surface resistivity in the approximate range of 10^8–10^{10} ohms/sq. at relative humidities from 12–15 percent.

4. A copy sheet for use in electrophotography comprising a fibrous sheet material having electrically conductive surface coating comprising exfoliated three-layer clay, said coating having a surface resistivity in the approximate range of 10^8–10^{10} ohms/sq. at relative humidities from 12–15 percent, said sheet having an overcoating comprising photoconductive zinc oxide on top of said electrically conductive coating.

5. A copy sheet for use in electrophotography as claimed in claim 4 in which the electrically conductive surface coating includes a water-soluble electroconductive inorganic compound in an amount up to 50 percent by weight of the clay.

6. A copy sheet for use in electrophotography as claimed in claim 4 in which the clay is selected from the class consisting of bentonite, vermiculite and pyrophyllite.

7. A copy sheet for use in electrophotography as claimed in claim 6 in which the weight of the electrically conductive surface coating is 0.5 to 5 lb./ream.

8. A copy sheet for use in electrophotography as claimed in claim 6 in which the electrically conductive surface coating includes a water-soluble electroconductive inorganic compound selected from the class of hygroscopic lithium, calcium and magnesium compounds, said compound being present in an amount from about 5 to 15 percent by weight of said clay.

9. A copy sheet for use in electrophotography as claimed in claim 6 in which the fibrous sheet material is paper and the electrically conductive surface coating comprises sodium bentonite in an amount from 1 to 4 lb./ream.

10. A copy sheet for use in electrophotography as claimed in claim 6 in which the fibrous sheet material is paper and the electrically conductive surface coating comprises lithium bentonite in an amount from 1 to 4 lb./ream.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,639,162 Dated February 1, 1972

Inventor(s) Harris J. Bixler

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

Column 3, line 75, "exchange" should be --exchanged--;

Column 4, line 16, "1 X 10^{9}" should be --1 X 10^{10}--;

Column 4, line 32, "pressure" should be --presence--.

Signed and sealed this 14th day of November 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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* U.S. GOVERNMENT PRINTING OFFICE : 1969 O--366-334