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[54] **ELECTROCONDUCTIVE PAPER, ELECTROGRAPHIC RECORDING PAPER, AND METHOD OF MAKING SAME**

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[52] **U.S. Cl.** ....**96/1.7,** 96/1.5, 117/155 U, 117/201, 117/218, 162/138

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[58] **Field of Search** ....96/1, 1 PC, 1.5, 1.7; 117/156, 117/201, 218, 215, 155 U; 162/138, 181, 162

[56] **References Cited**

UNITED STATES PATENTS

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FOREIGN PATENTS OR APPLICATIONS

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[57] **ABSTRACT**

Electroconductive paper utilizing montmorillonite clay in a binder as the conductive agent is disclosed. The electroconductive paper can be overcoated with a dielectric film or a coating of a photoconductor in a non-conductive or dielectric binder for an electrostatic printing purpose. When the montmorillonite clay is in a non-water-sensitive binder such as a latex binder, an aqueous coating of photoconductive material can be used.

20 Claims, No Drawings

ELECTROCONDUCTIVE PAPER, ELECTROGRAPHIC RECORDING PAPER, AND METHOD OF MAKING SAME

This application is a continuation-in-part of applications Ser. No. 565,685 and 565,686 both filed on July 18, 1966, and both now being abandoned. The disclosures of said applications are incorporated herein by reference.

This invention relates to the manufacture of paper which is adapted for the electrophotographic reproduction of images. It relates more particularly to paper having unique electroconductive properties.

In the preparation of paper and other cellulosic webbed base materials adapted for electrographic printing, it has previously been difficult to find satisfactory electroconductive substances which are favorably adapted for the critical needs of good electroconductivity, especially at low relative humidities, and which can be readily applied from aqueous media to paper in usual ways.

The moisture content of paper and, hence, its electrical conductivity is determined by the relative humidity of its environment. Thus, it has been shown that ordinary paper has a resistivity of about 10^{14} ohm/sq. at 5 percent relative humidity and about 10^{7} ohm/sq. at 95 percent relative humidity. It has also been shown, and is well known by those skilled in the art, that paper carrying a photoconductive surface, i.e., zinc oxide in an insulating binder, will not readily dissipate a negative charge from its surface to ground on exposure to light if the paper base has a resistivity much greater than about 10^{9} ohm/sq. Hence, while an ordinary paper base carrying a photoconductive surface may perform satisfactorily with the type of copy machines in which the papers are more or less automatically processed at high relative humidity, the product may be absolutely useless under dry conditions. It is for this reason that conductive agents are added to electrophotographic base papers.

In the prior art, several methods of obtaining conductivity have been used. One method consists of adding a humectant such as glycerine or glycol. At the low range of humidities satisfactory conductivity is obtained; however, at the high range of humidities the conductivity is generally much higher than needed and tends to cause problems in this respect and furthermore, at the high humidities the sheet tends to become wet and extremely limp. Hydroscopic salts such as lithium chloride have been proposed and while they give somewhat better results than the humectants, they are still subject to similar disadvantages. Water soluble conductive polymers have been proposed such as polymerized vinylbenzyl trimethyl ammonium chloride. While these materials show some advantages over the former substances, they suffer from the disadvantage of relatively high cost. None of the above mentioned conductive agents are suitable if the zinc oxide or other photoconductor is applied from an aqueous media using water soluble or water dispersible insulating binder materials since the water soluble conductive agent would migrate into the zinc oxide layer and so reduce its resistance that electrostatic charging and, hence, formation of an electrostatic latent image would be impossible to attain.

It has been discovered in accordance with the present invention that particulate montmorillonite clays in an aqueous synthetic resin latex system when applied as a coating on a conventional kraft or sulfite sheet of paper or other cellulosic webbed base sheet produce an electroconductive paper that possesses good electroconductivity at low relative humidities. It has further been found that a paper web so treated is equally well suited for application of zinc oxide or other photoconductors from the conventional hydrocarbon solvent systems or photoconductive formulations applied from aqueous dispersions to give useful products for electrostatic printing. The clay coatings of the instant invention are further characterized by their very low cost.

Furthermore, the montmorillonite clay can be bound by conventional paper pigment binders such as gelatins, cellulose ethers and esters, casein and starch in conventional clay to binder proportions, although these binders tend to be water sensitive and therefore are not preferred when the photoconductor is to be applied from an aqueous system. It has also been observed that base paper containing montmorillonite clay bound with gelatins, cellulose esters and ethers, casein, and starch are somewhat less conductive than comparable base sheets prepared with latex binders, but nevertheless, the papers using montmorillonite/conventional binders are much more conductive than similar papers which do not contain montmorillonite.

In addition to latex binders and conventional binders mentioned above, other film-forming resinous binders such as thermosetting and thermoplastic coating materials can be used as a binder for the montmorillonite.

The montmorillonite clay minerals are complex hydrated aluminum silicates containing traces of alkali and alkaline earth metals such as sodium, magnesium and calcium along with other associated impurities such as iron and silica. Some common designations for minerals in the montmorillonite group are bentonite and fuller's earth. It is not clearly understood why the montmorillonite clays function to give the superior results in conjunction with the photoconductors; however, it is thought that possibly they may function as solid proton doners. We do not, however, wish to limit the function of the specific clay to any special theory.

Kaolin type clays and other pigments such as titanium dioxide, calcium carbonate, barium sulfate and the like are commonly utilized as paper coating pigments in combination with various adhesives, dispersing agents and stabilizing agents. These materials do not enhance the conductivity of the paper base although they can be present in the base sheet if they are required for color, strength, appearance or some other reason. These conventional materials merely function as "inerts" with respect to conductivity. Conductivity can be obtained through the use of montmorillonite clay even in the presence of such conventional materials, although these materials may function as "diluents" and detract somewhat from the conductivity. For attaining conductivities suitable for commercial electrostatic printing applications the montmorillonite content should be at least about 20 percent by weight of the total content of clays and inorganic fillers and pigments. Usually, the content of such other clays and fillers is minimized. Preferably, montmorillonite clay is used in the substantial absence of other clays and fillers. This will be further explained in the examples. Similarly, it is well known to those skilled in the art that montmorillonite clays are not considered suitable for conventional pigmented printing paper coatings for many reasons such as poor rheological characteristics, difficulty of obtaining sufficient coating weight, etc. Hence, no commercial utilization of these clays in the huge coated printing paper industry exists.

The binding vehicle for the montmorillonite clay is not particularly critical as long as the binding material is compatible with the montmorillonite and capable of curing to a uniform coating film containing dispersed montmorillonite on the paper base. Curing as used herein means that the binding vehicle forms a film on drying, heating, calendering or otherwise processing. Curing does not necessarily infer crosslinking exclusively but can include coalescence as upon drying a latex. The film-forming binding material, of course, must be substantially unaffected by any overcoating composition (i.e., photoconductive insulating coating or merely a dielectric coating not containing a photoconductor as disclosed in Canadian Pat. No. 643,783, the teaching of which is incorporated by reference) that may be subsequently applied.

For instance, when a photoconductive insulating coating is applied from an aqueous coating composition the film-forming binder for the montmorillonite should not be water soluble or otherwise water sensitive so as to prevent migration of the conductive montmorillonite into the insulating top coating. Similarly, the film-forming montmorillonite binder should not be organic solvent sensitive when an insulating top coating is applied from an organic solvent.

Suitable film-forming binder vehicles include the natural or conventional paper pigment binders such as casein; glues, gelatin; starch; polyvinyl alcohol; gums and cellulose esters and ethers (e.g., carboxyl methyl cellulose, sodium carboxylmethyl cellulose, cellulose acetate and hydroxy ethyl cellulose). Some of these binders tend to be water sensitive or water soluble and, therefore, are not usually used when the conductive paper base is to be overcoated with an aqueous coating composition.

Other suitable film-forming binders include the conventional thermoplastic and thermosetting resinous polymers (including homopolymers, copolymers, terpolymers, etc.), resinous coatings such as polyolefins (e.g., polyethylene, oxidized or emulsifiable polyethylene, and polypropylene); natural or synthetic waxes such as carnauba wax and petroleum wax; modified or unmodified polyesters (e.g., the ethylene glycol/maleic/phthalate styrene type and glycerol phthalate type including those known as alkyds); shellac; petroleum resins; natural resins; epoxide resins (e.g., diglycidyl ethers of bisphenol A and its homologs); silicone resins; urea-formaldehyde resins; melamine-formaldehyde resins; phenol formaldehyde resins; allyl resins; polystyrene resins; polyamides such as nylon; vinyl resins such as polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl-chloride-polyvinyl acetate resins, vinyl chloride-styrene resins, vinyl chloride-butadiene resins, vinyl chloride-acrylonitrile resins; acrylic acid and acrylic ester polymers such as polymethyl methacrylate, methyl methacrylate-styrene; acetal polymers and copolymers; chlorinated rubber; acrylonitrile-butadiene-styrene polymers; isoprene polymers; butadiene-styrene copolymers; polyvinyl butyral resin; styrene-ethylene copolymers; polyfluoroethylene resins, polyvinylidene fluoride resins and polyurethane resins. These resins can be in the form of solvent solution (e.g., in aromatic hydrocarbons such as toluene and xylene; aliphatics such as hexane, octane or even cycloaliphatics such as cyclohexane; or even in solution in a vinyl monomer polymerizable with ethylenic unsaturation present in the film-forming resins), water solution or aqueous latex depending on chemical and physical properties of the particular resins and the particular application for the electroconductive paper prepared therefrom.

For application to the paper base, a slurry or dispersion of montmorillonite clay in the resin solution, suspension or latex is prepared according to conventional techniques for preparing clay in binder dispersions such as disclosed in U.S. Pat. No. 3,028,258 the teaching of which is incorporated by reference. The montmorillonite clay to binder ratio is not particularly critical as long as there is sufficient montmorillonite to provide a resistivity of less than about 10^9 ohm/sq. in the deposited coating. If the montmorillonite to binder ratio is too high the clay will not be securely held in place and the paper will tend to be chalky. When the montmorillonite to binder ratio is too low, the conductivity will suffer as a result of an excess of insulating binder. Satisfactory results are obtained when the binder is present in the proportion of about 5 percent to about 200 percent by weight based on the montmorillonite clay. For efficiency and economy the binder is present in the proportion of about 25 percent to about 100 percent by weight based on clay. When other clays or fillers are present in addition to the montmorillonite the binder is present in the proportion of 5 to 200 percent (and preferably 25 to 100 percent) by weight based on the total clay and filler content. Preferably other clays and inorganic fillers are substantially absent and montmorillonite clay is the only clay present.

The montmorillonite/binder coating composition can be applied to the paper base by conventional coating means, such as spray coating, roller coating, dip coating, air doctoring and the like in dry coating weights of from about 5 lb./ream and lower to 20 lb./ream and higher (based on 500 sheets 25 × 38 inches per ream). Also, the coating can be provided in the form of a film if resinous material containing montmorillonite clay is laminated onto the surface of the base sheet, as represented by the lamination of a film of polyethylene containing dispersed montmorillonite onto the paper base sheets.

Film-forming latex binders for montmorillonite clays are mentioned above in conjunction with a preferred practice of the invention. Latex or latices are colloidal suspensions of synthetic polymers as prepared by emulsion or suspension polymerization. These latices are preferred montmorillonite binders for use in conjunction with aqueous photoconductive top coating for economy and efficiency because the cured latex binder is not sensitive to the aqueous photoconductor coating and there is no migration of montmorillonite from the conductive base coat to the insulating photoconductive top coat. Furthermore, the latices are not burdened with the cost disadvantages and safety hazards associated with organic solvent coating systems. Occasionally, montmorillonite clay will destabilize certain latices prior to application of the paper coating. This problem can be remedied by the addition of conventional latex stabilizer as discussed below.

Several latices suitable for use in the present invention are available commercially. These include butadiene-styrene latices (Latex 512R, Dow Chemical) containing 35–55 percent total solids; vinyl chloride latices containing 50–55 percent total solids; vinylidene chloride-acrylonitrile copolymers (Saran F122-A15, Dow Chemical); polystyrene latices containing 35–45 percent solids; vinyl ester latices such as polyvinyl acetate containing 40–55 percent total solids (Gelva S-55, Shawinigan); latices of polyvinyl acetate-polyvinyl chloride (Resyn 2507, National Starch) containing 40–50 percent total solids; butadiene-acrylonitrile copolymers (Hycar 1577, Goodrich); styrene-acrylonitrile latices, polymethy methacrylate latices and butadiene-acrylic ester latices. The latices usually have an average molecular weight in the range of about 25,000 to about 100,000.

In most synthetic latices, surface active materials are used in the emulsion polymerization to prevent the agglomeration of particles by maintaining a hydrophilic surface. There is a minimum protection requirement for storage latex stability and additional protection is required in the case when the latex is to be blended with montmorillonite clays. Stability can be varied by changing the amount of surface active material in a given latex. The stabilizer requirement for a specific application depends primarily on the particle size and the application, type of polymer, type of stabilizer, pH and compounding ingredients. Control of latex stability and coagulability can be controlled by additional stabilizers when formulating the montmorillonite coating composition.

There are four types of surface active stabilizers used for this purpose: fatty acid soaps, rosin soaps, alkyl aryl sulfonates, alkyl sulfates and other anionics with broad pH range and non-ionic agents stable to a wide range of chemical compounds. These surface active stabilizers can be supplemented with a small amount, i.e., less than 1 percent of the coating composition, of protective colloid materials such as polyvinyl alcohols, casein, soya protein, cellulose ethers and esters (i.e., carboxyl methyl cellulose, hydroxyl ethyl cellulose), gums and starches. Other common suspension stabilizers include finely divided inorganic precipitates such as magnesium phosphate and potassium pyrophosphate. In general, these suspension stabilizers serve the purpose of lowering the interfacial tension between the dispersed and continuous phases. Additionally, antifloccuating agents such as Tamol-N which is a sodium salt of a condensation product of formaldehyde and β-naphthalene sulfonic acid sold by Rohm and Haas Company can be used for additional stability.

Electroconductive base paper containing montmorillonite in a binder as discussed above provide excellent substrates for receiving photoconductive insulating top coatings as disclosed in U.S. Pat. Nos. 2,959,481; 3,052,539 and 3,431,106 the teachings of which are incorporated by reference.

For use in the instant invention, we have found that the binder that gives superior results for binding the montmorillonite clay to the paper substrate is an aqueous dispersion of a styrene-butadiene copolymer latex containing from about 15 to 85 percent butadiene and is advantageously employed as a base paper for "Electrofax" printing at relative humidities of 25 percent or lower. Other preferred synthetic resin lattices which are operable in place of the styrene-butadiene copolymer are polyvinyl acetate and polyvinylidene chloride latices.

Suitable styrene-butadiene latices can be obtained under various brand names such as:

Latex 3820 and Latex 630 produced by Dow Chemical Co.

Ucar Latex 110 produced by Union Carbide Chemicals Corp.

Dylex Latex produced by Koppers Co., Inc.

Montmorillonite clays in particulate form can be obtained under various brand names such as:

Wyo-Jel produced by Archer-Daniels Midland Co.

Volclay produced by American Colloids Co.

Bentolite produced by Georgia Kaolin Co.

Albertabond produced by National Lead Co.

As mentioned above, electrophotographic recording sheets have been made by coating an electroconductive substrate, usually paper, with a solution of an insulating resin such as silicone or polyvinyl acetate in an aromatic hydrocarbon solvent such as toluene. The finely divided photoconductor is suspended in this solution. Satisfactory results are obtained when the ratio of photoconductor to binder resin solids is within the range of 1:1 8:1 with a coating thickness in the range of 0.2 to 1 mil. A preferred photoconductor is zinc oxide for economy and efficiency. Other photoconductors such as the oxides of aluminum, antimony, bismuth, cadmium, lead, mercury, molybdenum, the iodides, selenides, sulfides or tellurides of these metals; sulfur, anthracene, selenium, polyvinyl carbazole and the like are also suitable for the present invention.

Apparatus required for the application of such organic solvent systems are usually costly, are subject to fire and health hazards. While the organic solvent coating procedures result in electrophotographic recording sheets that give excellent reproduction of images, they suffer generally from poor adhesion of the photoconductive layer to the electroconductive substrate, high cost and the problems of applying the coating as mentioned above.

Attempts heretofore made to apply the photoconductor to a paper substrate from an aqueous medium resulted in generally unsatisfactory performance. A major problem in former aqueous zinc oxide photoconductive coatings has been drastically diminished electrical insulating properties with consequent high dark decay. General overall print quality was also not comparable to the commercially available "Electrofax" papers produced with the solvent systems.

According to another aspect of the present invention electroconductive base papers containing montmorillonite in a coalesced latex binder are overcoated with a dispersion of photoconductive materials such as sulfur, selenium, cadmium sulfide, polyvinyl carbazole, but preferably zinc oxide in an aqueous solution of acrylic resin. The acrylic resin contains sufficient carboxylic acid functionality to be "water solubilized" (i.e., stably dispersed in water) by neutralization with a base. The base used is a volatile or fugitive base such as ammonia or other amino base (i.e., a primary, secondary or tertiary amine, rather than a fixed alkali metal or alkaline earth metal hydroxide) so that no appreciable ionic residues result from the decomposition of the base during the curing of the photoconductive insulating coating. A substantial proportion of ionic residues in the photoconductive coating would, of course, have a detrimental effect on performance.

The photoconductor can be any conventional photoconductor such as those mentioned above that is compatible with the acrylic resin solution. Photoconductive zinc oxide is preferred for efficiency and economy. Suitable photoconductive zinc oxides are commercially available under the names Photox 80 and Photox 801 (sold by New Jersey Zinc Co.); PC 321, PC 331, and PC 340 (sold by St. Joseph Lead Co.), and ZZZ-66-1 (sold by American Zinc Smelting Co.).

The acrylic resins suitable for the present purposes are those resinous film-forming polymers (the term "polymers" as used herein includes homopolymers, copolymers, terpolymers, etc.) containing carboxylic acid functionality in an amount sufficient to provide the polymer with an acid number in the range of about 25 to about 150. At acid numbers below 25 "water solubility" is not readily achieved upon neutralization with a base. At acid numbers above 150 there is the possibility of an undesirable interaction with the zinc oxide.

Compositionally, the acrylic acid resins can be an addition polymer of acrylic acid and any vinyl monomer or monomers copolymerizable therewith. Suitable vinyl monomers for polymerization with acrylic acid to form the acrylic polymers include acylic esters such as methyl acrylate, butyl acrylate, methyl methacrylate, 2 ethyl hexyl acrylate, hydroxypropyl methacrylate, ethyl acrylate and the like; aromatic monomers such as styrene and vinyl toluene; vinyl chloride; ethylene; vinylidene chloride; lower alkyl (C_1–C_4) substituted acrylic monomers (i.e., those having carboxyl groups contributed by α, β-unsaturated carboxylic acids or residues thereof, etc.) and so on. Also included are the acrylic interpolymers disclosed in U.S. Pat. No. 2,767,153 such as the interpolymers of 2-ethyl-hexyl acrylate-styrene-acrylonitrile and methacrylic acid.

These resinous, film-forming, acrylic polymers are water solubilized by neutralization or partial neutralization with a water soluble, volatile, amino base such as ammonia, hydroxyl amines, polyamines and monoamines such as monoethanolamine. Typical amino bases include hydroxy amines, polyamines and monoamines such as: monoethanolamine, diethanolamine, triethanolamine, N-methyl ethanolamine, N-aminoethylethanolamine, N-methyl diethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine, "polyglycol amines" such as $HO(C_2H_4O)_2C_3H_6NH_2$, hydroxylamine, butanolamine, hexanolamine, methyldiethanolamine, octanolamine, and alkylene oxide reaction products of mono- and polyamines such as the reaction product of ethylene diamine with ethylene oxide or propylene oxide, laurylamine with ethylene oxide, etc.; ethylene diamine, diethylene triamine, triethylene tetramine, hexamethylene tetramine, tetraethylene pentamine, propylene diamine, 1,3 diaminopropane, imino-bis-propyl amine, and the like; and mono-,di- and tri-lower alkyl (C_{1-8}) amines such as mono-, di- and triethyl amine.

In addition to the photoconductor and acrylic binder the aqueous coating composition contains sensitizing dyes such as Bromphenol Blue, Rose Bengal and Fluorscein and adjunct materials such as Aluminum Oxide, e.g., Hydral 710 made by Alcoa and a dispersing agent for the pigment, e.g., Tamol 850 made by Rohm and Haas (a sodium salt of polymeric carboxylic acid).

For optimum results, the photoconductive coating contains from 5 to 30 percent of the acrylic binder solids, 0.005 to 0.01 percent of sensitizing dye, and 5 to 25 percent of aluminum oxide, all percentages being by weight and based upon the zinc oxide.

The preferred electroconductive base, as described above consists of paper coated with a montmorillonite clay dispersed in a latex binder, the quantity of binder ranging from 5 to 200 percent by weight of clay.

The bromphenol dye is the only essential dye required for panchromatic sensitization of the zinc oxide photoconductor. The other dyestuffs are optional and add only small improvement to the image quality. This is contrary to the prior art and not readily understood. It appears that the bromphenol blue has also a synergistic effect in the instant invention system, enhancing its quality.

The aluminum oxide gives considerable improved image smoothness and eliminates pinholes in the solid black areas as well as giving good smoothness in the gray areas. In this respect it is essential. Incorporation of the dispersing agent for the pigment is optional.

The following examples illustrate ways in which the principle of the invention has been applied but are not to be construed as limiting its scope. All parts are parts by weight and all percentages are weight percentages unless otherwise indicated.

EXAMPLE 1

Part A—Preparation of the Electroconductive Paper Base

A sheet of 40 pounds per ream of a bleached kraft paper was coated in a conventional roll coater with the following composition:

Ingredients	Parts by Weight
Bentonite Clay (Volclay)	100
Latex 3820 (50% solids) butadiene-styrene copolymer	200
Water	1,000

The paper picked up approximately 10 pounds per ream of coating material. The coated paper was dried to coalesce the latex binder to form a water resistant coating containing uniformly dispersed montmorillonite clay particles. The coating paper had a resistivity value well below 10^9 ohm/sq.

Similar results are obtained using a butadiene-styrene acrylonitrile latex (40 percent solids) or a butyl methacrylate latex or polyvinyl chloride latex (50 percent solids), polyvinyl butyral latex (35–45 percent solids), polyvinyl acetate latex (40–50 percent solids) or polyvinylidene chloride latex in place of butadiene-styrene latex 3820 used above.

Similar results are also obtained by depositing the montmorillonite on the paper from a toluene solution of polystyrene resin; or a methanol solution of shellac; or an acetone solution of vinyl chloride-vinyl acetate copolymer, or an ethyl acetate-toluene solution of nitrocellulose.

Part B—Deposition of a Photoconductive Coating From a Solvent System on the Conductive Paper of Part A

A conventional solvent base zinc oxide "Electrofax" coating similar to that described by C. J. Young and H. G. Greig in "Electrofax Direct Electrographic Printing on Paper," "RCA Review," Vol. XV, No. 4, pages 469, 484 (Dec. 1954) was applied to the paper with a pickup of about 20 pounds per ream. After drying, the paper was conditioned in the dark at 25 percent relative humidity and then processed in an SCM Electrostatic Copy Machine Model 33 to produce a copy of a typewritten document. A print of excellent contrast and density resulted with no appreciable background.

Similar results are obtained using selenium, sulfur or cadmium sulfide in place of zinc oxide as the photoconductor.

EXAMPLE 2

An electroconductive base paper of 50 pounds weight per ream (25 × 38 inches—500) made in accordance with part A of example 1 was coated with the following composition on a conventional air knife coater and dried.

Ingredients	Parts by Weight
Film-forming acrylic polymer solution *	60
Photox 801 Zinc Oxide	90
Hydral 710 Aluminum Oxide	10
Bromphenol Blue	0.006
Water	30

* Film-forming acrylic polymer solution comprising an aqueous solution containing about 30% of an ammonia neutralized, low molecular weight, ethyl acrylate-methyl methacrylate-acrylic acid terpolymer having the aforementioned monomeric components present in the respective ratio of 65/27/8. The polymer also contains hydroxyl functionality in the proportion of 1% to 2% of the polymer. The polymer had an Acid Number of about 50–55. The polymer had a weight average extended chain length (in Angstrom units) of about 895.4 and a number average extended chain length (in Angstrom units) of about 343.4. The polydispersity index (wt. average extended chain length divided by no. average extended chain length) was about 2.6.

The above composition when applied to give a coating weight of 20 to 40 pounds per ream produced a photoconductive copy sheet which gave copy quality as to image density, gray scale, and speed equal to conventional commercially available solvent coated products. Prints of excellent quality were obtained at 25 percent relative humidity. The copies were prepared using the commercial papers and those of the invention on commercial electrostatic copy machines, including

SCM machines, Models 33, 44, or 55
Charles Bruning "Copytron" 2000, 2001
APECO "Electrostat"

Similar results can be obtained using Carboset 514 acrylic resin solution sold by B. F. Goodrich Company as the film-forming acrylic binder.

EXAMPLE 3

PART A

A sheet of 40 pounds per ream of a bleached kraft paper was coated with a rod coater with the following composition:

Ingredients	Parts by Weight
Bentonite	100
Latex 630 (50% solids) butadiene-styrene copolymer	50
Water	1,000

The paper picked up approximately 10 pounds per ream of coating material. The coated paper was dried to coalesce the latex binder to form a water resistant coating containing uniformly dispersed montmorillonite clay particles. The coated paper had a resistivity value well below 10^9 ohm/sq.

PART B

When coated with either the solvent base photoconductive zinc oxide coating as described in part B of example 1 or the aqueous zinc oxide coating as described in example 2 and a copy made on a Charles Bruning Company Model No. 2000 Copytron Electrostatic printing machine, copies of excellent density and contrast resulted at 25 percent relative humidity.

EXAMPLE 4

The electroconductive paper prepared in part A of example 3 was coated with a photoconductive coating composition similar to the composition of example 2 except that the film-forming acrylic polymer solution was an aqueous solution containing about 35 percent solids of an ammonia neutralized polymer of methyl methacrylate/n-butyl acrylate/styrene/acrylic acid having an acid number of about 75–80 and having the aforementioned monomeric components present in the respective ratio of 40/35/15/10. The polymer had a weight average extended chain length (in Angstrom units) of about 941.5, and a number average extended chain length (in angstrom units) of about 335.4. The polydispersity index (wt. average extended chain length divided by no. average extended chain length) was about 2.8.

The coating method was similar to that employed in example 2. Photocopies of original documents were prepared on this paper prepared in this example by the method of example 2 and excellent quality photoreproductions resulted.

When the adhesive binders such as starch or casein are used to bind the montmorillonite clay in the paper base, and this conductive paper base is overcoated with a photoconductor in an insulating binder from a non-aqueous coating composition, copies can be made on a conventional electrostatic machine using papers coated therewith; although the base papers are not as conductive as those base papers utilizing the latex binders.

EXAMPLE 5

To demonstrate the use of conventional paper coating clays and fillers with montmorillonite clay in producing electroconductive paper, the following tests were conducted.

Coating A—Volclay brand bentonite clay (a type of montmorillonite clay) was dispersed at 11.5 percent solids concentration in water with 1 percent of a sodium hexametaphosphate dispersing agent, (Calgon, sold by Calgon Company) based on bentonite together with 20 percent of a butadiene-styrene latex, Dow 630 (20 percent latex solids based on bentonite).

Coating B—A conventional kaolin paper coating clay was dispersed at 65 percent solids in water with 0.5 percent sodium hexametaphosphate together with 20 percent butadiene-styrene latex, Dow 630 (20 percent latex solids content based on clay).

Coating A and coating B were blended in various proportions to provide various ratios of montmorillonite to kaolin as reported below. Coating A, coating B and the various blends were individually coated on ordinary bleached kraft papers having no special previous treatment with a No. 32 rod coater. The coatings were dried, calendered and conditioned for 2 hours at 50 percent relative humidity and then conditioned overnight at 20 percent relative humidity. The log of the resistivities of the coated surfaces at 20 percent humidity were then determined and the results are reported below:

Ratio of Montmorillonite Clay to Kaolin Clay		Log of the Resistivity in ohm/sq. of the Coated Surface
∞	(coating A)	8.70
4:1		8.73
2:1		8.76
1:1		8.60
1:2		8.83
1:4		9.41
1:8		10.46
0	(coating B)	12.39

The above data indicates that the log of the surface resistivity of the coated surface decreases from 12.39 to 8.70 in going from 100 percent kaolin clay to 100 percent bentonite clay in the paper coating. This data demonstrates that conventional pigments and fillers can be used in conjunction with the montmorillonite clay in electroconductive paper when these pigments and fillers are required to obtain some property other than conductivity in the paper. This data indicates that the montmorillonite content should be at least about 20 percent by weight of the total clay and filler content in order to achieve a resistivity of about 10^9 ohm/sq.

If conductive agents of the type described and utilized in the prior art were applied in place of the montmorillonite pigment, no copy would result if the aqueous zinc oxide type of coating were used as the photoconductive layer because of migration of the agent into the zinc oxide layer which would result, as described earlier.

The quantities of film-forming binder based on the clay are in the range of 25–100 percent by weight of solids with maximum practical limits of 5–200 percent. Coating weights of the electroconductive clay coating can vary from 5–20 pounds per ream (25 × 38 inches—500).

While the use of the electroconductive composition of the present invention is emphasized for use in the range of relative humidities of 25 percent and less, good results are obtained also at relative humidities above 25 percent.

To produce an aqueous coated paper for electrographic printing, sometimes called "direct electrostatic printing," as described in Canadian Pat. No. 643,783 issued June 26, 1962, to the A. B. Dick Co., only a simple modification in the composition of our zinc oxide coating is required. Since direct electrostatic printing, as described in the above patent, requires a dielectric surface coating on an electroconductive base, it was found that a coating of a water soluble acrylic resin of the type described herein (without zinc oxide) when coated on the electroconductive base as described in part A of example 1 produces a product well suited to the purpose. The electroconductive base is coated on a conventional air knife coater from a 25 percent water solution of the special acrylic resin to give a coat weight of 3 to 6 pounds per ream (25 × 38 inches—500). The prior art teaches that the dielectric coatings must be applied from solvent systems, but we have found that good results are obtained from this aqueous solution thus eliminating all the disadvantages of working with an organic solvent.

Having thus described the invention, what is claimed is:

1. In an electroconductive paper base sheet comprising a cellulosic web containing a conductive agent and an insulating binder for said conductive agent, said binder comprising a film-forming thermoplastic or thermosetting resinous binder, the improvement wherein said conductive agent comprises montmorillonite clay in a proportion sufficient for imparting a resistivity of about 10^9 ohm/sq. or less to said base sheet, said montmorillonite clay comprising at least about 20 percent by weight of the total content of clays and inorganic fillers.

2. The electroconductive paper base sheet of claim 1 wherein said binder is present in the proportion of about 5 percent to about 200 percent by weight based on the total clay and filler content.

3. The electroconductive paper base sheet of claim 1 further including a dielectric coating thereon whereby said paper is adapted for electrographic printing.

4. The electroconductive paper base sheet of claim 1 wherein said film-forming resinous binder is the coalesced residue of an aqueous latex of said resinous polymer.

5. The electroconductive paper base sheet of claim 2 wherein said montmorillonite clay is bentonite or fuller's earth.

6. The electroconductive paper base sheet of claim 2 wherein said montmorillonite clay is present in the substantial absence of other clays and other fillers.

7. The electroconductive paper base sheet of claim 3 wherein said dielectric coating further contains a photoconductive material dispersed therethrough.

8. The electroconductive paper of claim 7 wherein said photoconductive material is zinc oxide.

9. In the method for forming an electroconductive paper base sheet wherein a paper base sheet is coated with a conductive agent and an insulating binder for said conductive agent, the improvement which comprises;

coating said paper base sheet with a film-forming thermosetting or thermoplastic resinous binder containing dispersed particles of montmorillonite clay in a proportion sufficient for imparting a resistivity of about 10^9 ohm/sq. or less to said paper base, and

curing the film-forming binder to form a binder film.

10. The method of claim 9 wherein said binder is present in the proportion of about 5 percent to about 200 percent by weight based on said montmorillonite clay.

11. The method of claim 10 wherein said binder is an aqueous latex of a film-forming polymer.

12. The method of claim 11 further including the steps of applying a coating mixture comprising a resin dispersion stabilized with a fugitive base, said resin being a film-forming, acrylic acid resin having an acid number in the range of about 25 to about 150, and particulate photoconductive zinc oxide, and curing said resin to form an insulating coating film containing photoconductive zinc oxide dispersed therethrough.

13. An electroconductive paper for electrographic printing characterized by good electrical conductivity over a wide range of relative humidity comprising a paper base sheet having a continuous coating of a clay of the montmorillonite type in admixture with a styrene-butadiene copolymer or polyvinyl acetate or polyvinylidene chloride latex binder, said binder being present in an amount of 5 to 200 percent by weight based on said clay.

14. An electroconductive paper for electrographic printing characterized by good electrical conductivity over a wide range of relative humidity comprising a paper base sheet having a continuous coating of clay of the montmorillonite type in admixture with a styrene-butadiene copolymer binder, said binder being present in an amount of 5 to 200 percent by weight based on said clay.

15. The paper of claim 13 in which said clay is bentonite and said binder is a copolymer of styrene and butadiene containing over 5 percent by weight of butadiene.

16. The paper of claim 14 in which binder is present in the amount of 25 to 100 percent by weight based on said clay.

17. An electrostatic recording sheet for printing copies by electrostatic reproduction which comprises an electroconductive cellulosic base sheet having a coating of an admixture of montmorillonite clay and styrene-butadiene copolymer binder, and an electrostatic surface coating consisting essentially of photoconductive zinc oxide and a panchromatic sensitive dye dispersed in a polymeric binder film of an acrylic acid resin said resin having an acid number in the range of about 25 to about 150.

18. The sheet of claim 17 in which said surface coating also contains aluminum oxide.

19. The sheet of claim 18 in which said surface coating contains from 5 to 30 percent of acrylic resin solids, 0.005 to 0.01 percent dye and 5 to 25 percent of aluminum oxide, all percentages having been based by weight upon the zinc oxide.

20. The sheet of claim 17 in which said dye is bromphenol blue.

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