

[54] **ELECTROCONDUCTIVE COATING,
ELECTROSTATOGRAPHIC COPY SHEET,
AND METHODS OF MAKING AND USING
THE SAME**

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[22] Filed: **Oct. 6, 1971**

[21] Appl. No.: **187,211**

[52] **U.S. Cl.**..... **96/1.5, 96/1.8, 96/87 A,**
117/201, 117/218, 117/37 LE, 162/138,
252/500, 260/567.6 M
[51] **Int. Cl.**..... **G03g 5/10, H01b 1/06**
[58] **Field of Search**..... 96/1.5, 1.8; 117/201, 218,
117/37 LE; 162/138; 260/567.6 M; 252/500

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Primary Examiner—Charles E. Van Horn
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[57] **ABSTRACT**

An improved electroconductive coating is made by incorporating in its formulation both an organic film-forming polymer and certain low molecular weight monomeric quaternary ammonium compounds. An improved electrostatographic copy sheet is made by combining a conductive layer comprising said improved electroconductive coating and a dielectric or photoconductive printing layer.

11 Claims, No Drawings

ELECTROCONDUCTIVE COATING, ELECTROSTATOGRAPHIC COPY SHEET, AND METHODS OF MAKING AND USING THE SAME

This invention relates to an improved electroconductive coating, an improved electrostatographic copy sheet, and to methods for making and using the same. In particular, this invention relates to an improved electroconductive coating comprising in combination an organic film-forming polymer and certain low molecular weight monomeric quaternary ammonium compounds, to an improved electrostatographic copy sheet comprising in combination a conductive layer incorporating said improved electroconductive coating and a printing layer comprising a dielectric or photoconductive material, and to methods for making and using said improved electroconductive coating and said electrostatographic copy sheet.

BACKGROUND OF THE INVENTION

Electroconductive coatings have found wide application in modern technology. They are used in electrostatographic copy sheets such as electrographic and electrophotographic copy sheets, to give antistatic characteristics to fabrics, carpets, and the like, and in other applications where electrical conductivity is desired for an otherwise dielectric surface.

In electrostatographic copying an electrostatic charge pattern is generated corresponding to the desired image to be produced. The charge pattern is deposited upon an appropriate electrostatographic copy sheet capable of retaining the charge long enough to permit development of the pattern back into a visible image. This development usually comprises applying appropriately charged pigment particles to the charged surface of the copy sheet followed by permanent fixing of those particles to the sheet.

In electrographic copying the copy sheet comprises an electroconductive layer in combination with a dielectric charge-retaining layer. In use the copy sheet is charged with an electrostatic charge pattern corresponding to the desired image to be produced, followed by appropriate development. In electrophotographic copying a copy sheet is used comprising a photoconductive layer in combination with an electroconductive layer. The photoconductive layer is capable of retaining an electrostatic charge in the dark, and of subsequently permitting a portion of that charge to leak away in proportion to the amount of visible light projected on to the charged surface. In use, the photoconductive layer is uniformly electrostatically charged in the dark, the visible image to be copied is projected upon the charged surface, and finally the resulting latent electrostatic image is developed using appropriate charged pigment particles.

Both electrostatographic copying systems described, that is the electrographic and electrophotographic copying systems, require a copy sheet having an electroconductive layer. This layer must have adequate electrical conductivity, especially at low ambient relative humidity conditions. Commonly, in an electrostatographic copy sheet, a base sheet of paper is coated or impregnated with electroconductive material and comprises the conductive layer. The conductive paper is then provided with a subsequent dielectric or photoconductive coating, depending upon what type of copying the sheet is intended for. In any case, for good copying, the base paper must have adequate electrical con-

ductivity over a wide range of ambient relative humidity conditions, adequate barrier properties to prevent the contamination of one layer with the components used in other layers or with the solvents or carriers used to apply the other layers, and adequate curl characteristics both during and after processing to avoid jamming the copy machine and to provide an acceptable appearance to the final copy.

In order to satisfy these requirements, base papers have in the past been treated in a variety of ways, usually in several stages. Sizes and fillers are often added to the paper either as it is being formed by including them in the pulp furnish, on a paper machine by means of a size press, or after formation by means of a trailing blade or other type coater. Barrier and conductive additives may similarly be added during paper formation by means of a size press, or after formation by means of a trailing blade or other type coater. The electrostatographic printing layer is usually added subsequent to paper formation, commonly by means of a reverse roll or other appropriate coater.

The conductive layers have generally been of three types, those incorporating common conductors such as metal foils and carbon particles, those incorporating inorganic electrolytes such as metal salts often in combination with humectants to improve conductivity at low relative humidities, and those incorporating organic electrolytes such as conductive polymers. When conductivity is achieved by means of metal foils or carbon particles, it is expensive and inherently accompanied by problems related to the desired production of a clean, white sheet.

When conductivity is achieved through the use of inorganic salts, even with humectants, the conductivity tends to drop off sharply at very low humidities in spite of the humectant, and papers so treated tend to become limp and moist at high relative humidities. The inorganic salts must be used in combination with barrier materials to prevent them from migrating into the subsequently applied electrostatographic printing layer thereby changing its dielectric properties, and it is extremely difficult to find a satisfactory barrier material which is not precipitated from the conductive formulation by the salt.

The best approach to conductivity appears to be the use of organic polymeric electrolytes, for these materials can be designed to give good conductivities at low humidities, and to have fair to good barrier properties. The main problems encountered in the use of polymeric electrolytes have been their high cost and their tendency to permit some degree of migration of conductive material into the subsequently applied dielectric coatings during prolonged storage. Attempts to improve the barrier properties of conductive formulations incorporating these organic polymeric electrolytes by including in the formulations common organic film-forming polymer barrier materials have often met with failure due to the precipitation of the electrolyte and/or barrier material. The majority of the organic electrolytes are relatively high molecular weight polymeric quaternary ammonium compounds, e.g., see U.S. Pat. Nos. 3,011,918 and 3,288,770. It is known that monomeric quaternary ammonium compounds containing relatively long-chained radicals have conductive properties, e.g., see U.S. Pat. Nos. 3,048,539 and 3,141,905, however, in comparison with the polymeric quaternary ammonium compounds, they have been

considered of little value for use in electrostatographic copying due to relatively poorer conductivity, e.g., Vaurio and Fird, TAPPI, December 1964, Vol. 47, No. 12, pps. 163A-165A.

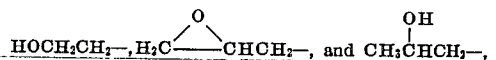
Combinations of organic film-forming polymers with ammonium compounds have been used in coating formulations, but not for the purpose of producing an improved electroconductive coating. U.S. Pat. No. 2,003,960 to Tonkin et al discloses the use of choline chloride with starch or gum to produce an improved printing paste for vat colors. U.S. Pat. No. 2,984,639 to Stamberger et al discloses the preparation of water-insoluble germicidal compositions by reacting certain monomeric quaternary ammonium compounds with a variety of synthetic polymers including styrene maleic acid copolymers. U.S. Pat. No. 3,428,485 to Bonzagni discloses the coating of paper with an ammonium salt of a particular polycarboxylic acid anhydride interpolymers, in combination with starch or proteinaceous materials, to increase the resistance of the treated paper to moisture, ink, lactic acid, and food juice.

SUMMARY OF THE INVENTION

These and other problems have been solved by the discovery of an improved electroconductive coating and formulation comprising in combination (i) an organic film-forming polymer, and (ii) a monomeric quaternary ammonium compound described by the formula:



where R^I is a radical selected from the group consisting of



R^{II} is selected from the group consisting of CH_3- and CH_3CH_2- . A is a positive integer selected from the group consisting of 1, 2, and 3, and B is an anion selected from the group consisting of chloride, fluoride and bromide. The low molecular weight monomeric quaternary ammonium salts defined above, containing radicals each having at most three carbon atoms, have been found to be compatible (cause no precipitation) with all organic film-forming polymer barrier materials tested.

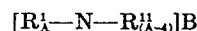
The use of quaternary ammonium compounds of the above formula, in combination with an organic film-forming polymer barrier material, has the following advantages over the prior art materials. High conductivities can be obtained even at low relative humidities. Lateral surface resistivities as low as 1×10^7 ohms, measured using a Kiethley ring apparatus, have been achieved at relative humidities of 15 percent and lower. The costs of the new coatings based on equivalent area coated are substantially lower than those of coatings providing equivalent conductivity utilizing the conventional conductive polymers. The new coatings have improved barrier properties which reduce contamination of adjacent layers by migration and penetration.

The improved electroconductive coatings can be used in the electroconductive layer of an improved electrostatographic copy sheet. In particular, these coatings are used to conductivize a base sheet which is

subsequently provided with an appropriate dielectric or photoconductive printing layer.

DETAILED DESCRIPTION OF THE INVENTION

The monomeric quaternary ammonium compounds useful in this invention can be described by the formula:



where R^I is a radical selected from the group consisting of



R^{II} is a radical selected from the group consisting of CH_3- , and CH_3CH_2- . A is a positive integer selected from the group consisting of 1, 2 and 3, and B is an anion selected from the group consisting of chloride, fluoride and bromide. Examples of suitable compounds are choline chloride, glycidyl trimethyl ammonium chloride, 2-hydroxypropyltrimethyl ammonium chloride, methyl tris (hydroxyethyl) ammonium chloride, and dimethyl dihydroxyethyl ammonium chloride. The preferred compound is choline chloride. Instead of the chloride, bromide, and fluoride anions suggested by the above formula, sulfate, carbonate, acetate, nitrate and others may be used at the loss of some conductivity. The preferred anion is chloride.

Suitable organic film-forming polymers for use in this invention are: styrene maleic acid, acid salt, and ester polymers; vinyl acetate maleic acid, acid salt, and ester polymers; polyvinyl methyl ether maleic acid, acid salt, and ester polymers; butadiene maleic acid, acid salt, and ester polymers; polyvinyl alcohols; polyvinyl acetates; starches; proteins; gums; caseins; alginates; cellulose polymers; styrene butadiene copolymers; polyamino and quaternary ammonium polymers; polyphosphate and polyphosphonium polymers; polysulfate and polysulfonium polymers; polyvinylpyrrolidones; polyethylenes; polypropylenes; polyvinylchlorides; polystyrenes; polyamides; ethylene vinyl acetate polymers; and polyacrylic polymers. A preferred organic film-forming polymer is protein.

Both hydrophilic and hydrophobic polymers can be used, though the former are preferred since most of the present conductive coating formulations are applied as aqueous systems, and further, because they retain moisture in the conductive coating thereby increasing its conductivity. Hydrophobic polymers may be used in conductive formulation emulsion systems if the polymer can be emulsified. They may also, in some cases, be milled with the quaternary ammonium compound and then extrusion coated onto a sheet of base material such as paper.

Particular examples of organic film-forming polymers suitable for use in these inventions comprise Lytron 897 and 898 (trademarks), polyvinyl acetate maleic anhydride copolymers manufactured by Monsanto Chemical Co.; Gantrez AN 139, AN 149, and AN 169 (trademarks), polyvinyl methyl ether maleic anhydride manufactured by the General Aniline Film Corp.; SMA-1000A and 3000A (trademarks), styrene maleic anhydride copolymers manufactured by Arco Chemical Co.; Maldene 631 and 286 (trademarks), butadiene maleic anhydride copolymers manufactured by Borg Warner Corp.; CMC R-75-XL (trademark), carboxy-

methyl cellulose manufactured by E. I. duPont Co.; Lemol 60-98 (trademark), manufactured by Borden Chemical Co. and Elvanol 72-60 and 73-125 (trademarks), manufactured by E. I. duPont Co., polyvinyl alcohols; delta protein (trademark), manufactured by Central Soya Co.; Prokote (trademark), manufactured by Ralston-Purina, another protein; Kofilm 80 (trademark), manufactured by National Starch Co., a starch; Kymene 557 (trademark), manufactured by Hercules Powder Co., a polyamide-epichlorohydrin resin; polyvinyl pyrrolidone; Dow Latex 630 (trademark), a styrene-butadiene copolymer; Scriptset 540 (trademark), manufactured by Monsanto Chemical Co., the half-ester of polystyrene poly maleic anhydride; Scriptset 500 (trademark), manufactured by the Monsanto Chemical Co., the di-sodium salt of polystyrene poly maleic anhydride; and K-15 (trademark), polyvinyl pyrrolidone manufactured by General Aniline and Film Co.

Other polymeric materials which may be used include: proteins such as soya protein, animal glue (gelatin), zein, and casein; gums such as carrageen, guar, jaquar, tragacanth, karaya, and locust bean gum; starches such as corn, potato, sugar beet, and tapioca, as well as the dextrins; alginates such as agar and algin; cellulose polymers such as phosphorylated cellulose, methyl cellulose, ethyl cellulose, 2-hydroxyethyl cellulose, 2-hydroxypropyl cellulose and carboxymethyl cellulose; a polyamino compound such as poly-2-(dimethylamino) ethyl methacrylate; a quaternary ammonium material such as vinyl benzyl trimethyl ammonium chloride; a polyphosphate compound such as polyvinyl phosphonic acid and/or salt; a polyphosphonium compound such as polyglycidyl tributyl phosphonium chloride; a polysulfate compound such as polysodium p-styrene sulfonate; and a polysulfonium compound such as poly (2-acryloxyethyl) dimethyl sulfonium chloride.

It is noted that, as used in this specification, "film-forming polymer" is intended to mean a polymer which is capable of being formed essentially without additives into a continuous self-supporting film. The term is not meant to indicate that such a film is, in fact, formed in the electroconductive coating of this invention, but merely that the polymer itself has the inherent capability of being formed into such a film.

Fillers, extenders, brighteners, and other materials may be added to the electroconductive coatings of this invention. Some suitable materials falling in one or another of these categories include clay, calcium carbonate, titanium dioxide, zinc oxide, silicas, and colored pigments such as chrome yellow.

The electroconductive coatings of this invention may be formulated as follows: quaternary ammonium salt, 5-95 wt. percent, 20-50 wt. percent preferred; film-forming polymer, 5-95 wt. percent, 10-50 wt. percent preferred; extender, filler, pigment, 0-60 wt. percent, 20-50 wt. percent preferred.

The inventions will be further described and illustrated by the following examples. It should be understood, however, that although these examples may describe certain preferred embodiments of the inventions, they are given primarily for the purpose of illustration and that the inventions in their broader aspects are not limited thereto.

EXAMPLE 1

A coating mix was prepared from 3.80 parts Microvelva-L Talc (International Talc, Inc.), 1.25 parts of Elvanol 72-60 polyvinyl alcohol (duPont), 6.85 parts choline chloride and 38.1 parts of water. The talc was first dispersed in a portion of water, then a 10 percent solution of the polyvinyl alcohol was blended in, followed by the choline chloride. The smooth, moderately viscous mix (Type A) was applied at 1.76 lbs. per 3,300 sq. ft. to a copy base paper rawstock (CC Base A, Weyerhaeuser Co.) by means of a laboratory trailing blade coater. The coated sheets were dried in a photographic dryer and then conditioned at 10 percent relative humidity at 25° C. At these conditions they had a lateral surface resistivity of 5×10^9 ohms.

Similar coated papers were made from a formulation of 3.80 parts talc, 1.25 parts Elvanol 72-60, 6.85 parts Dow 2611.25 polymeric vinyl benzyl quaternary ammonium conductive resin and 38.1 parts water, (Type B). These sheets and sheets of the uncoated rawstock were also conditioned as above. (The surface resistivities of all the papers were measured at 100 volts using a Keithley 610 C electrometer and 6105 resistivity electrodes.) The coated sheets had a lateral surface resistivity of 4×10^9 ohms, while the uncoated rawstock measured greater than 1×10^{14} ohms, both at 10 percent R.H.

After standing for 24 hours, both Mixes A and B were smooth and easily spreadable. An identical formulation in which the choline chloride was replaced by tetramethyl ammonium chloride became curdled and lumpy after standing for 2 hours. Thus the A and B formulations represent "compatible" mixtures, while the tetramethyl ammonium chloride formulation is "incompatible."

Subsequently another formulation was prepared similar to Type A, except that the Elvanol 72-60 (the organic film-forming polymer) was omitted, and the amount of Talc was increased to 5.05 parts. The resulting low viscosity formulation was coated at 1.65 lbs. per 3,300 sq. ft. on the paper rawstock, and conditioned at 10 percent R.H. The lateral surface resistivity was then measured to be 1.6×10^{11} ohms, a significantly higher value than that measured for the Type A formulation.

EXAMPLE 2

20 parts of protein (Prokote, Ralston-Purina) were added slowly to 72 parts water with stirring. The dispersion was then heated to 63° C, stirred for 10 minutes and 3.5 parts of triethanolamine were added followed by 28.6 parts of a 70 percent solution of choline chloride and 112 parts of water. After cooling to 43° C, the Brookfield viscosity was 200 cps at 35 percent total solids. A trailing blade coating of 1.5 lbs/3,300 ft² was applied to each side of Base A rawstock. The surface resistivities at 15 percent R.H., 25° C, measured as in Example 1, were 3×10^9 ohm-cm (wire side) and 4.4×10^9 ohm-cm (felt side). Solvent penetration was measured by placing a large drop of toluene containing a dye on the paper surface, then wiping off the excess after 10 seconds and comparing the color pattern on the opposite side against a set of standards. Penetration found was 70 percent on the wire side and 25 percent on the felt side. A coated commercial grade conductively coated CC Base A tested at the same time had

solvent penetrations of 80 percent (wire side) and 30 percent (felt side).

EXAMPLE 3

57 parts of starch (Kofilm 80, National Starch Co.), followed by 164 g of choline chloride and 18 g of 40 percent glyoxal were added to 101 g of water. The mix was stirred on a steam bath for 1 hour at 80°–87° C. 40 parts of talc (Microvelva L) were mixed with 116 g of the above mix and 17 g of water. This formulation was spread with the laboratory trailing blade coater onto Base A rawstock at 2.1 lbs. per 3,300 ft². After conditioning overnight at 15 percent relative humidity and 25° C, the surface resistivity was measured as in Example 1 to be 4×10^8 ohms-cm.

EXAMPLE 4

The coated conductive base papers prepared in Examples 1-A, 2 and 3 were coated (a) with a photoconductive coating consisting of 200 parts zinc oxide (Pho-tox 80, The New Jersey Zinc Co.), 59.6 parts of DeSoto 041 binder resin (DeSoto, Inc.), 115 parts of toluene solvent and 4.2 ml. of dye sensitized solution (100 ppm. of fluorescein sodium salt in methanol) at the rate of 18 pounds per 3,300 square feet; or (b) with a dielectric coating consisting of 200 parts of Stein Hall 1622 (Stein Hall Co.) binder resin, 100 parts of Superlith XXXN pigment (C. J. Osborn Co.) and 96 parts of toluene — these ingredients were ground in a ball mill and then applied to the base papers at a rate of 7 lbs. per 3,300 square feet.

The papers coated with the photoconductive coating give good copies when used in an SCM Copystat 44 at both 20 percent and 50 percent relative humidity. The dielectric coated papers were tested in an Electrostatic Paper Tester (Victoreen Instrument Co.) and were found to have a charge acceptance above 200 volts and satisfactory voltage decay rates, which indicate that satisfactory electrographic copies could be made using those papers.

EXAMPLE 5

5 grams of Scriptset 540, a partial ester of a polystyrene maleic acid manufactured and sold by the Monsanto Chemical Co. is slurried in 77 grams of water. Ammonium hydroxide, 28 percent, is added to bring the pH to 9.0 and to dissolve the Scriptset 540. To the resultant solution is added a 70 percent solution of choline chloride as sold by Nopco Chemical.

A 40 lbs/3,300 ft² bleached sulfite - Kraft sheet having a 100–200 density prior to size pressing was size pressed to give a pickup of total dry solids of 1.9 lbs/3300 ft².

After size pressing, the dried paper had a Mercury Densometer density of 6925 and its resistivity as measured by a Keithley electrometer using a Keithley ring after conditioning for 24 hours at 15 percent RH was 2.0×10^{12} ohms. At 50 percent RH the resistivity (surface) was 3.8×10^9 ohms.

EXAMPLE 6

Other formulations tried were as follows:

Wet Wts.	1	2	3
Scriptset 540	7	2.5	1
Choline Chloride (70%)	3	7.5	5

-Continued

Wet Wts.	1	2	3
Water	110	40.0	15.7
Ammonium Hydroxide (28%)	*	*	*

*Ammonium hydroxide added in sufficient quantity to give pH of 9.0–9.5.

A 40 lb. bleached sulfite - Kraft paper having a density of 100–200 prior to size press was size pressed to a dry solid pickup equivalent to 1.5–3.0 lbs/3,300 ft². After size pressing, the above papers had the following properties:

Density	Keithley-Surface Resistivity, ohms	
	15% RH	50% RH
4600	5.3×10^{12}	5.0×10^9
6125	5.0×10^{10}	3.0×10^8
1925	5.0×10^{10}	3.5×10^8

What is claimed is:

1. An electroconductive paper useful as a base for producing electrostatographic copy paper comprising a paper sheet coated with an electroconductive layer comprising choline chloride and an organic film-forming polymer.

2. The paper of claim 1 wherein said choline chloride comprises from 5 to 95 percent by weight of said electroconductive layer.

3. The paper of claim 1 wherein said choline chloride comprises from 20 to 50 percent by weight of said electroconductive layer.

4. In an electrostatographic copy paper, including a printing layer having a surface capable of receiving and retaining an electrostatic charge, the improvement comprising an electroconductive layer underlying said printing layer and comprising choline chloride and an organic, film-forming polymer.

5. The copy paper of claim 4 wherein said printing layer comprises a substance selected from the group consisting of dielectric and photoconductive substances.

6. The copy paper of claim 4 wherein said printing layer is comprised of photoconductive zinc oxide.

7. The paper of claim 4 wherein said choline chloride comprises from 5 to 95 percent by weight of said electroconductive layer.

8. The paper of claim 4 wherein said choline chloride comprises from 20 to 50 percent by weight of said electroconductive layer.

9. In an electrostatographic copying process wherein a liquid toner is applied to an electrostatographic copy paper including a printing layer having an electrostatic charge pattern thereon and an electroconductive layer underlying said printing layer, the improvement wherein said electroconductive layer comprises choline chloride and an organic, film-forming polymer.

10. The process of claim 9 wherein said choline chloride comprises from 5 to 95 percent by weight of said electroconductive layer.

11. The process of claim 9 wherein said choline chloride comprises from 20 to 50 percent by weight of said electroconductive layer.

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