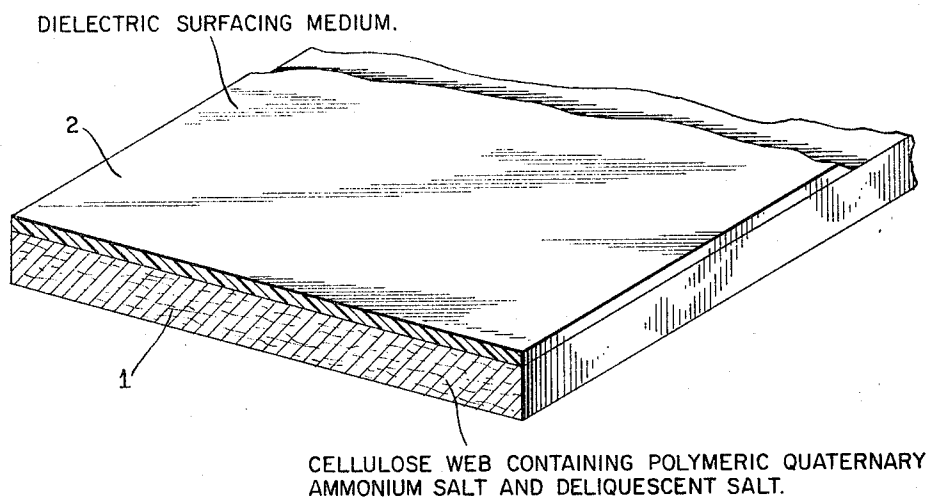


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ELECTROSTATIC CONDUCTIVE PAPER AND PROCESS
OF MANUFACTURE THEREOF
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ELECTROSTATIC CONDUCTIVE PAPER AND PROCESS OF MANUFACTURE THEREOF

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6 Claims. (Cl. 117—201)

The present invention relates to a novel recording medium and more particularly to an electrically conducting paper useful in the electrostatic printing art.

The basic principles of electrostatic printing are quite simple. An electrostatic charge is imparted to paper or other dielectric material in a predetermined pattern which is subsequently made visible by dusting with a powder carrying an opposite charge. The powder is attracted to the charged areas of the paper to make the latent charge image visible. The powder can be permanently fused to the paper by heat, pressure or other means.

Where in the electrostatic printing the electrically recording paper is subjected to a modulated voltage to create the latent image in accordance with the intensity of the voltage, the recording paper includes a base sheet coated upon opposite sides with dielectrical and conductive layers with a sealing media interposed therebetween to prevent migration of the conductive material into the dielectric. Manifestly, the inclusion of additional lamina in a composite sheet adds to the cost of production thereof and also creates a source of potential product deterioration.

However, the preparation of an electrostatic image recording paper in which the dielectric layer is directly superposed upon the conductive paper base has necessitated the development of a specialized combination of chemical additives which will impart to the paper, good electroconductivity over a relatively wide range of relative humidities, which will readily be incorporated in said base paper and which will be resistant to migration therefrom.

It is, therefore, a primary object of my invention to provide an electrostatic image recording medium composed of a dielectric coating applied directly to an electrically conducting paper sheet.

Another object of my invention is to provide an electrically conductive paper having a specific conductivity of from 10^7 to 10^{10} ohms in which the sensitizing agent of the paper exhibits exceptional stability against migrating forces.

A still further object of the present invention is to provide an improved electrostatic image recording medium, composed of an electrically conducting paper surfaced with a dielectric, the composite having a specific electrical conductivity in the range of from 10^{11} to 10^{14} ohms.

Other objects and advantages of my invention will be readily apparent from the following detailed description of certain preferred embodiments thereof when taken in conjunction with the accompanying drawing wherein the single figure represents a fragmentary perspective view of a recording sheet as contemplated by the invention.

I have discovered that the water soluble polymeric quaternary ammonium compounds when supplemented by the admixture therewith of relatively lesser amounts of one or more deliquescent salts. Quaternary ammonium compounds having the acrylate functions are derived from either the unsaturated ester quaternary ammonium monomers which are obtained from Rohn & Haas Company, Philadelphia, Pa., or are prepared in their entirety by a method which is also applicable to quaternary ammonium esters and illustrated in Melamed U.S. Patent 2,980,657, April 18, 1961. The first and the last of the above listed compounds are prepared by polymerizing in the conventional manner the vinylbenzyl quaternary ammonium monomers which are available from sources such as Dow

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Chemical Company, Midland, Mich. such as for example lithium chloride will impart electric conductivity to paper and will function adequately over a wide range of relative humidities in the transfer of an electrostatic charge to a dielectric coating thereon and the formation of latent image patterns.

The polymeric quaternary ammonium salts suitable for incorporation in the paper base of the present invention are those obtained through polymerization of compounds which have the general formula:



wherein R_1 , R_2 and R_3 are low molecular alkyl radicals, one or more of which will include the polymerizable



grouping, R_4 is a long chain aliphatic hydrocarbon or mixed alkyl, aryl, and aralkyl hydrocarbon radical from 6 to 20 carbon atoms and a polymerizable



grouping and X is a chloride, bromide, nitrate or hydroxyl anion.

Among the quaternary ammonium salts which are represented in their essential by the foregoing formulas are the following:

- 30 Polyvinyl benzyl trimethyl ammonium chloride
- Poly (N,N dimethyl-N-benzylamino ethyl acrylate chloride)
- Poly (N,N diethyl-N-benzylamino ethyl acrylate chloride)
- 35 Poly (N-benzyl-ethyl pyridyl ethyl acrylate chloride)
- Polyvinyl benzyl dimethyl ethyl ammonium chloride

The deliquescent salts suitable for admixture with the polymeric quaternary ammonium salts and incorporation in the base stratum of an electroconducting paper include lithium chloride, lithium bromide, zinc chloride, calcium chloride, and magnesium chloride. The presence of these salts in the impregnating solution permits a reduction in the amount of quaternary amine necessary to impart the desired level of conductivity to the paper base and accordingly enables a material reduction in the cost of manufacture of the ultimate image recording medium.

A paper sheet 1, approximately $2\frac{1}{2}$ mils caliper contains a mixture of a polymeric quaternary ammonium salt and a deliquescent salt in sufficient quantity to impart the desired specific electric conductivity to the paper sheet and carries on one side a film 2 of a dielectric material such as for example an alkali soluble polyvinylacetate resin.

The sequence of steps entailed in fabrication of the composite recording sheet is not critical. For example, the layer of dielectric material may be applied to one side of a web of paper from a coating bath or by air knife, coating or doctor blading and thereafter the opposite side of the coated sheet may be impregnated by spraying with a concentrated aqueous solution of the polymeric quaternary ammonium salt-deliquescent salt mixture. Alternatively, the base sheet may be impregnated with the salt solution prior to the application thereto of the dielectric coating material.

My invention is illustrated more specifically in the following examples which, however, are not to be construed as imposing any particular limitation thereon.

Example 1

An aqueous suspension composed of 934 grams of an alkali soluble polyvinyl acetate, 498 grams of clay and 125 grams of barium sulfate in 5000 cc. of water containing 200 cc. of 28% NH_4OH was applied as a coating to one side of a sheet of 48 pounds/3000 square feet surface

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area bleached southern kraft paper by an air knife coater. The coating equipment was adjusted so that the paper sheet was advanced at a rate of approximately 20 feet per minute with the application of coating mixture controlled to approximately 5 pounds (solids basis) per 3000 square feet of surface area. After emergence from the coater, the sheet was dried at a temperature of from 300 to 350° F., cooled and reeled.

To complete the composite paper an aqueous solution containing 6% by weight of polymerized vinyl benzyl trimethyl ammonium chloride and 4% by weight of lithium chloride was sprayed over the uncoated side of the dielectric surfaced paper previously prepared, using an air knife adjusted to deposit 1.25 pounds of solution (solids basis) per ream of paper with the sheet traveling at 35 feet per minute, and the sheet was again dried. The final composite sheet had a surface conductivity of 10^9 ohms.

The value of the finished sheet as an electrostatic image recording medium was evinced by the following test. A piece of letterpress type was superposed on the dielectric (resin coated) side of the sheet. The other side of the sheet contacted a metal platen. Upon connecting the piece of type to the negative pole of a constant voltage source and the metal platen to the positive pole thereof and passing a current of 1000 volts through the sheet there was created a latent electrostatic image in the paper. A developing powder dusted over the sheet was attracted to the charged portion of the paper to produce thereon a patterned image of the letterpress type and upon heating the developing powder was fused to form a permanent image.

Example II

A coating formulation prepared as in Example I was applied to 35 pounds/3000 square feet surface area paper by means of an air knife coater. The coater was run at 25 f.p.m. and 6 pounds dry weight of coating was applied per 3000 square feet surface area. The coating was dried by passing through a hot air oven at 300° F. and reeled. Subsequently a solution containing 6% by weight of poly(N,N-dimethyl-N-benzylamino ethyl acrylate chloride) and 4% by weight of calcium chloride in 40% by weight of isopropyl alcohol and 50% by weight of water was applied by an air knife to the uncoated side of this paper in an amount such that there was retained in the paper at least 1.35 pounds of the salt mixture per 3000 square feet of paper. The final paper recorded satisfactorily electrostatically induced images, under 1000 volts and 50% relative humidity.

Example III

A bleached kraft having a basis weight of 35 pounds per 3000 square foot ream was impregnated with an aqueous solution containing 9% by weight of poly(N-benzyl-ethyl pyridyl ethyl acrylate chloride) and 6% by weight of lithium chloride so that there was retained in the sheet approximately 2.0 pounds of the mixed salts per 3000 square feet. The impregnated paper was passed between a roll nip, dried at 300° F. and reeled.

This impregnated paper was subsequently coated with the coating formulation of Example I, modified by the substitution of rutile titanium dioxide for one-half of the barium sulfate, and the coated paper containing about 12 pounds (dry weight) of the dielectric material per 3000 square feet of surface area was dried at 300° F. This final paper, which was considerably more opaque than the paper of Example I, also recorded satisfactorily electrostatically induced images.

It has been determined that the concentrations of mixed amine-deliquescent salt impregnates are not critical to the success of the present invention. For example, amounts in the range of from 0.5 to 5 pounds per 3000 square feet of paper have been employed in source concentrations of from 25 to 85% by weight and will vary within these limits depending upon the specific salts employed and the specific conductivity which is desired in the final product.

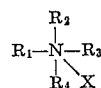
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Nor is the ratio between the polymeric quaternary amine and deliquescent salt in the salt mixture critical for successful results have been obtained with ratios varying from 2:1 to as high as 5:1. While the specific conductivity is of minor significance, it is preferred, however, that the basic sheet exhibits an approximate specific conductivity between 10^7 and 10^9 ohms and the composite to have a specific conductivity of from 10^{12} and 10^{14} ohms measured by placing one electrode on the dielectric side and the second electrode on the conductive side of the sheet.

Papers varying in caliper within the range of 2 to 5 mils have been successfully employed in the formation of image recording sheets while the preferred range of caliper is from 2.5 to 3 mils. Although a bleach kraft composite of 65% pine and 35% gum will possess greater inherent strength because of the larger proportions of long fibers therein, my invention is not limited to such paper and other types and weights of sheeting are equally serviceable. As to the material forming the dielectric coating of the sheet, the alkali soluble polyvinylacetates constitute a well recognized class of synthetic resin suitable for such application. I do not wish to be limited to the particular resin, however, for other resins, such as ethyl cellulose, will serve equally as well. The dielectric coating may vary between 2.5 and 10 pounds per 3000 square feet of paper surface, and it is preferred to apply the dielectric in the case of the polyvinylacetate type in the range of from 4 to 8 pounds per 3000 square feet. Generally, as the percentage of dielectric surfacing is decreased, the capacity of the composite sheet to accept and retain a given electrostatic charge is impaired. Heavier coatings of dielectric are possible although these will merely increase production costs without the realization of corresponding improvement in reproduction characteristics.

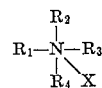
What I claim is:

1. As an electrostatic image-recording medium: a cellulose web having a dispersed polymeric quaternary ammonium salt at least one precursor of which has the formula



wherein R_1 and R_2 are lower alkyls, R_3 is a benzyl radical, R_4 is an alkyl ester of an unsaturated acid and X is an anion; a deliquescent salt in admixture with said polymeric salt, and on one surface of said cellulose web a layer of a dielectric material said quaternary ammonium and deliquescent salt containing cellulose web having a specific conductivity of from 10^7 to 10^{10} ohms.

2. As an electrostatic image-recording medium: a cellulose web having a dispersed polymeric quaternary ammonium salt, at least one precursor of which has the formula



wherein R_1 and R_2 are lower alkyl, R_3 is a benzyl radical, R_4 is an alkyl ester of acrylic acid and X is an anion selected from at least one member of the group consisting of chloride, bromide, nitrate and hydroxyl; in admixture with said polymeric salt, a deliquescent salt selected from at least one member of the class consisting of lithium chloride, zinc chloride, magnesium chloride and calcium chloride; and on one surface of said cellulose web a layer of a dielectric material said quaternary ammonium and deliquescent salt having a specific conductivity of from 10^7 to 10^{10} ohms.

3. The image-recording medium according to claim 2 wherein the polymeric salt precursor is N, N-dimethyl-N-benzylammonium ethyl acrylate chloride.

4. The image-recording medium of claim 2 wherein the dielectric surface material is pigmented polyvinylacetate.

5. As an electrostatic image-recording medium; a cellu-

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lose web having a dispersed polymeric quaternary ammonium salt at least one precursor of which has the formula



wherein R_1 and R_2 are lower alkyl, R_3 is benzyl, R_4 is an alkyl ester of acrylic acid and X is chloride; lithium chloride deliquescent salt in admixture with said polymeric salt, and on one surface of said cellulosic web a layer of a dielectric material said quaternary ammonium and deliquescent salt containing cellulose web having a specific conductivity of from 10^7 to 10^{10} ohms.

6. As an electrostatic image-recording medium; a cellulose web having dispersed therein a polymeric quaternary ammonium salt the precursor of which is N-benzylethyl

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pyridinium ethyl acrylate chloride; a deliquescent salt in admixture with said polymeric salt, and on one surface of said cellulose web a layer of a dielectric material said quaternary ammonium and deliquescent salt containing cellulose web having a specific conductivity of from 10^7 to 10^{10} ohms..

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