ELECTROSTATIC CONDUCTIVE PAPER AND PROCESS OF MANUFACTURE THEREOF

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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 recorded 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 dielectric 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.

A primary object of my invention is 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\(^4\) to 10\(^5\) 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\(^4\) to 10\(^5\) 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 quaternary ammonium compounds which contain at least one benzyl or a substituted benzyl group as a substituent of the nitrogen atom will impart electric conductivity to paper and will function adequately in the transfer of an electrostatic charge to a dielectric coating thereon and the formation of latent image patterns.

The quaternary ammonium compounds suitable for incorporation in the paper base of the present invention are those having the general formula:

\[ R_1 \]  
\[ R_1-N-R_1 \]  
\[ R_1-X \]

wherein \( R_1 \) and \( R_2 \) are low molecular alkyl groups, particularly methyl and ethyl groups, \( R_3 \) is a long chain aliphatic hydrocarbon containing from 8 to 18 carbon atoms, \( R_4 \) is a benzyl or substituted benzyl group and \( X \) is chlorine or bromine.

Other useful quaternary ammonium compounds are the following:

- Alkyl polyethoxyethanol benzyl ammonium chloride, available as Katapone VV 328
- N-alkyl (C\(_x\)-C\(_y\)) di-methyl benzyl ammonium chloride, the Bional RO-50 of General Dyestuff
- N-alkyl (C\(_x\) H\(_8\)-C\(_x\) H\(_7\)) di-methyl benzyl ammonium chloride sold under the trade name Bional A-50
- Alkyl dimethyl 3,4 dichloro benzyl ammonium chloride, Tetrosan 3,4D
- Para di-hydroxy phenoxo ethoxy ethyl di-methyl benzyl ammonium chloride, the Hyman 1622 of Rohm & Haas
- N-alkyl dimethyl methylbenzyl ammonium chloride, sold under the trade name Btc-471

A paper sheet, approximately 250 mills caliper contains a quaternary ammonium salt in sufficient quantity to impart the desired specific electric conductivity to the paper sheet and carries on one side a film 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 quaternary ammonium salt. Alternatively, the base sheet may be impregnated with the quaternary ammonium salt 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**

To dry mixture of 980 parts by weight of alkali soluble polyvinylacetate and 980 parts by weight of barium sulfate added 5600 parts by weight of water and the mixture stirred for 5 minutes, a suitable defoamer being added to facilitate formation of the solution. To this mixture was added 250 parts by weight of 28% aqueous ammonium hydroxide and stirring continued for 30 minutes at room temperature. The resultant solution was filtered to remove any residual solids therefrom and applied as a coating to one side of a sheet of 48 pound/3000 square feet surface area bleached southern kraft paper in a trailing blade type coater. The coating equipment was adjusted so that the paper sheet moved at a rate of approximately 10 feet per minute through the treating bath with one side of the sheet tightly pressed against the feed roll to restrict material pickup to the exposed side. The doctor blade was adjusted to restrict the pickup of coating mixture to approximately 7 pounds per 3000 square feet of surface area. After emergence from the treating bath the coated sheet was dried at a temperature of from 300 to 350° F., cooled and reeled.

To complete the composite paper an aqueous solution containing 65% by weight of Tetrosan 3,4D, an alkyl dimethyl 3,4 dichloro benzyl ammonium chloride, was sprayed over the uncoated side of the polyvinylacetate coated paper previously prepared, using a Pasche automatic spray gun delivering 4 pounds of solution per reel of paper with the sheet traveling at 10 feet per minute through the spray. The sprayed sheet was passed between a pressure nip formed by opposed rolls of 40 durometer rubber of the Shore scale under 80 pounds per square inch pressure after which the sheet was again dried. The final composite sheet had a specific surface
The value of the finished sheet as an electrostatic image recording medium was evidenced 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, there occurred through the sheet a current of 1000 volts. When the latter side of the sheet was made to carry a current of 108 ohms obtained by placing on the sheet two point electrodes one inch apart.

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 containing:

| Parts by weight | 
|-----------------|------------------|
| Alkali soluble vinyl acetate | 15.5 |
| Barium sulfate | 15.5 |
| Ammonium hydroxide (28%) | 5 |
| Water | 65 |

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 300 f.p.m., and 9.6 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 an aqueous solution containing 50% by weight of alkyl-dimethyl, 3,4-dichloro benzyl ammonium chloride was applied by spraying to the uncoated side of this paper in an amount such that there was retained in the paper at least 1/2 pound of the quaternary ammonium salt per 3000 square feet of paper. The final paper recorded satisfactorily electrostatically induced images.

Example III

A bleached Kraft having a basis weight of 35 pounds per 3000 square feet (ream) was impregnated with an aqueous solution containing 35% by weight of N-alkyl dimethyl methyl benzyl ammonium chloride in sufficient amount that there was retained in the sheet in excess of 1/2 pound of the quaternary ammonium salt 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 II, modified by the substitution of rutile titanium dioxide for one half of the barium sulfate content thereof, and the coated paper containing about 10 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 II, also recorded satisfactorily electrostatically induced images.

It has been determined that the concentrations of quaternary ammonium compound impregnates are not critical to the success of the present invention. For example, amounts in the range of from 0.5 to 10 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 quaternary salt employed and the specific conductivity which is desired in the final product. While the specific conductivity is of minor significance, it is preferred, however, that the basic sheet exhibits an approximate specific conductivity between 106 and 108 ohms and the composite to have a specific conductivity of from 1012 to 1014 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 bleached 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 polyvinylacetate constitutes 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 3 and 11 pounds per 3000 square feet of paper surface, and it is preferably applied on the dielectric coating of the polyvinylacetate type in the range of from 7 to 10 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. An electrostatic image recording medium, consisting of a haphazardly arranged cellulose fiber containing web, having dispersed therein a water soluble quaternary ammonium salt of the formula

\[ R_1 R_2 N R_3 R_4 \]

wherein \( R_1 \) and \( R_2 \) are lower alkyl groups, \( R_3 \) is a long chain aliphatic hydrocarbon containing from 8 to 18 carbon atoms, \( R_4 \) is a halogen substituted benzyl, and \( X \) is at least one member of the group consisting of chlorine and bromine, and carrying on at least one surface of said web a discrete layer of a synthetic resin dielectric material, said cellulose web having a specific conductivity of from 106 to 108 ohms and the resin surfaced web a specific conductivity therethrough of from 1012 to 1014 ohms.

2. An electrostatic image recording medium consisting of a haphazardly arranged cellulose fiber web, having dispersed therein a water soluble quaternary ammonium salt of the formula

\[ R_1 R_2 N R_3 R_4 \]

wherein \( R_1 \) and \( R_4 \) are lower alkyl groups, \( R_3 \) is a long chain aliphatic compound containing from 8 to 18 carbon atoms, \( R_4 \) is a lower alkyl substituted benzyl group, and \( X \) is at least one member of the group consisting of chlorine and bromine, and carrying on at least one surface of said web a discrete layer of synthetic resin dielectric material, said cellulose web having a specific conductivity of from 106 to 108 ohms and the resin surfaced web a specific conductivity therethrough of from 1012 to 1014 ohms.

3. An electrostatic image recording medium consisting of a haphazardly arranged cellulose fiber paper web having dispersed therein a water soluble quaternary ammonium salt of the formula

\[ R_1 R_2 N R_3 R_4 \]

wherein \( R_1 \) and \( R_3 \) are lower alkyl groups, \( R_4 \) is an alkyl substituted phenoxy alkoxyl alkyl group, \( R_4 \) is a benzyl group and \( X \) is at least onemember of the group consisting of chlorine and bromine, and carrying on at least one surface of said web a discrete layer of a synthetic resin dielectric material, said cellulose web having a specific conductivity of from 106 to 108 ohms and the resin surfaced web a specific conductivity therethrough of from 1012 to 1014 ohms.
4. An electrostatic image recording medium consisting of a haphazardly arranged cellulose fiber comprising web, having dispersed therein a water soluble quaternary ammonium salt of the formula

\[ R_1-X \]

wherein \( R_1 \) and \( R_2 \) are lower alkyl groups, \( R_3 \) is a polyalkylether alkyl hydroxy substituent, \( R_4 \) is a benzyl group, and \( X \) is at least one member of the group consisting of chlorine and bromine, and carrying on at least one surface of said web a discrete layer of a synthetic resin dielectric material, said cellulose web having a specific conductivity of from \( 10^2 \) to \( 10^9 \) ohms and the resin surfaced web a specific conductivity thereethrough of from \( 10^{12} \) to \( 10^{14} \) ohms.

5. An electrostatic image recording medium consisting of a haphazardly arranged cellulose fiber comprising web of from 2 to 5 mils caliper having dispersed therein a water soluble quaternary ammonium salt of the formula

\[ R_4 \]

\[ R_1-N-R_3 \]

\[ R_2 \]

wherein \( R_1 \) and \( R_2 \) are lower alkyl groups, \( R_3 \) is a long chain aliphatic compound containing from 8 to 18 carbon atoms and \( R_4 \) is a substituted benzyl group wherein the substituents are selected from the group consisting of halogen and lower alkyl and \( X \) is at least one member of the group consisting of chlorine and bromine and carrying on at least one surface a discrete layer of about 0.5 mils caliper of polyvinylacetate in admixture with barium sulfate, said cellulose web having a specific conductivity of about \( 10^9 \) ohms and the resin surfaced web a specific conductivity thereethrough of from \( 10^{12} \) to \( 10^{14} \) ohms.

6. A process of producing an electrostatic image recording medium which comprises impregnating a haphazardly arranged cellulose fiber comprising web with from 1 to 20% of its weight of a water soluble quaternary ammonium salt of the formula

\[ R_4 \]

\[ R_1-N-R_3 \]

\[ R_2 \]

\[ X \]

wherein \( R_1 \) and \( R_2 \) are lower alkyl groups, \( R_3 \) is a long chain aliphatic substituent containing from 8 to 18 carbon atoms and \( R_4 \) is a benzyl group, and \( X \) is at least one member of the group consisting of chlorine and bromine, and applying to at least one surface of said web a discrete layer of a synthetic resin dielectric material.

7. A process of producing an electrostatic image recording medium according to claim 6 wherein the discrete layer is polyvinylacetate.

8. A process of producing an electrostatic image recording medium according to claim 6 wherein the discrete layer is polyvinylacetate in admixture with barium sulphate.

9. An electrostatic image recording medium according to claim 8 wherein the water soluble quaternary ammonium compound is alkyl dimethyl 3,4 dichlorobenzyl ammonium chloride wherein the alkyl is of from 8 to 18 carbon atoms.

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