Dec. 5, 1961 L. H. SILVERNAIL ET AL 3,011,918

ELECTROCONDUCTIVE COATED PAPER AND METHOD OF MAKING THE SAME

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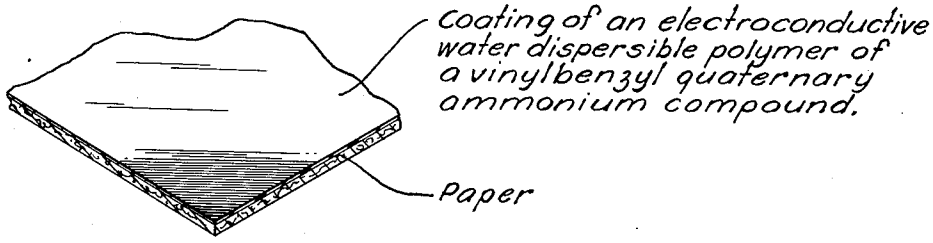

Fig. 1

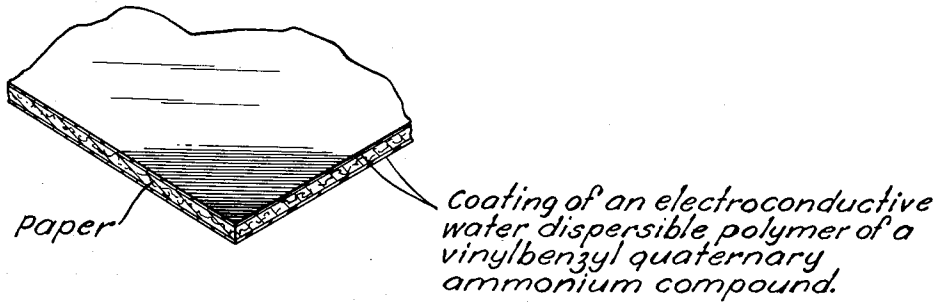

Fig. 2

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ELECTROCONDUCTIVE COATED PAPER AND METHOD OF MAKING THE SAME

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11 Claims. (Cl. 117—201)

This invention relates to the manufacture of paper having a printing surface containing an electroconductive material consisting of a polymer of a predominant amount of a vinylbenzyl quaternary ammonium compound and adapted to electrographic printing. It relates more particularly to paper having a printing surface adapted for electrographic printing and containing a polymer comprised of a polymerized vinylbenzyl quaternary ammonium compound, e.g. vinylbenzyl trimethyl ammonium chloride.

In the preparation of a coated paper it is common practice to prepare a mixture of water and a pigment such as clay or the like, together with other materials such as for example a soluble pyrophosphate which may act as a dispersing and stabilizing agent, and blend the mixture with an adhesive material to produce a composition useful in the art for coating a cellulose web and produce a finished paper having a high degree of brightness, smoothness and gloss and a good finish and hand after calendering.

In the preparation of paper having a printing surface adapted for electrographic printing it has previously been difficult to find a satisfactory electroconductive substance which is favorably adapted for the critical needs of good electroconductivity at low relative humidity and which is soluble or at least dispersible in aqueous media to form a coating composition that can readily be applied to paper or a cellulose web in usual ways.

Among the requirements of a paper adapted for electrographic printing, it is necessary that the paper have a conductivity corresponding to a volume resistivity within the range of from 0.25×10^6 to 50×10^6 ohms at ordinary temperatures and pressures, e.g. at room temperature and atmospheric pressure. The volume resistivity of paper is determined in usual ways, e.g. by measuring the surface resistivity of a sheet of the paper between electrodes spaced 0.25 inch apart and extending 0.5 inch onto the surface from one edge of the paper. Since the surface of the paper between the electrodes is relatively large compared to the volume of the paper between the electrodes, and is substantially equal to the volume, the determining of the surface resistivity can conveniently be carried out and is a measure of the volume resistivity of the paper. The conductivity of the paper is the reciprocal of the resistivity. In other words, a paper adapted for electrographic printing and having a conductivity corresponding to a volume conductivity of from 4×10^{-6} to 0.02×10^{-6} mho humidities of from 10 to 75 percent has correspondingly a volume conductivity of from 4×10^{-6} to 0.02×10^{-6} mho at said relative humidities.

It has now been discovered in accordance with the present invention that polymers of vinylbenzyl quaternary ammonium compounds can readily be incorporated with or applied as a coating to a cellulose web or paper to produce a paper having an electroconductive surface adapted for electrographic printing and possessing good electroconductivity at low relative humidity. It has further been found that a cellulose web or paper containing polymers of vinylbenzyl quaternary ammonium compounds is adapted for electrographic printing at relative humidities between about 5 and 100 percent and is advantageously

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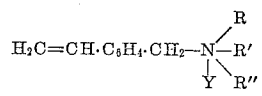
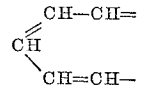
employed for such printing at relative humidities of 25 percent or lower.

The polymers of vinylbenzyl quaternary ammonium compounds to be employed in practice of the invention can be any water-soluble or water-dispersible homopolymer or copolymer of one or more vinylbenzyl quaternary ammonium compounds, or copolymers of a predominant amount of a vinylbenzyl quaternary ammonium compound and a minor amount of a nonacidic copolymerizable compound such as acrylamide, or copolymers containing in the polymer molecules residues corresponding to from 95.0 to 99.99 percent by weight of one or more vinylbenzyl quaternary ammonium compounds and from 5.0 to 0.01 percent by weight of divinylbenzene.

More specifically, the electroconductive substance can be a homopolymer or a copolymer of any two or more vinylbenzyl quaternary ammonium compounds having the general formula:



wherein R, R′ and R″ each represents individually a monovalent radical selected from the group consisting of CH_2OHCH_2—, $CH_3CHOHCH_2$—, $CH_2OHCHOHCH_2$— and alkyl, aryl cycloalkyl and aralkyl hydrocarbon radicals, and R, R′ and R″ collectively represent the trivalent radical of the formula:



wherein the three valences are attached to the nitrogen atom, the said R groups containing a total of not more than 12 carbon atoms in the sum of the constituent radicals, or a copolymer of at least 65 percent by weight of any one or more of such vinylbenzyl quaternary ammonium compounds with not more than 35 percent by weight of acrylamide, or a copolymer containing in the polymer molecules residues corresponding to from 95.0 to 99.99, preferably from 99.0 to 99.99, percent by weight of any one or more of such vinylbenzyl quaternary ammonium compounds and from 5.0 to 0.01, preferably from 1.0 to 0.01, percent by weight of divinylbenzene. Mixtures of any two or more of the homopolymers or copolymers can also be used.

The polymers are of relatively high molecular weight and are characterized by a viscosity of at least 2 centipoises for a 0.5 percent by weight solution of the polymer in an aqueous 2 percent by weight solution of sodium chloride at 25° C. as determined with an Ostwald viscosimeter. The term "viscosity" as herein employed refers to the viscosity of the aforesaid polymer solutions or dispersions under the above conditions.

In a preferred embodiment of the invention the electroconductive substance is a homopolymer or copolymer of one or more vinylbenzyl quaternary ammonium compounds having the aforementioned general formula wherein R represents an alkyl radical containing from 1 to 4 carbon atoms, R′ and R″ each represents a radical of the group consisting of CH_2OHCH_2—, $CH_3CHOHCH_2$—, $CH_2OHCHOHCH_2$— and lower alkyl radicals containing from 1 to 4 carbon atoms and Y is an anion, e.g. a sulfate, a chloride, a nitrate, or a hydroxyl ion, copolymers of at least 65 percent by weight of any two or more of such vinylbenzyl quaternary ammonium compounds and not more than 35 percent by weight of acrylamide, or copolymers of from 99.0 to 99.99 percent by weight of at least one such vinylbenzyl quaternary ammonium compound and from 1.0 to 0.01 percent by weight of divinylbenzene.

The vinylbenzyl quaternary ammonium compounds to

be employed in preparing the polymers for use in the invention can readily be prepared by reaction of vinylbenzyl chloride or bromide, (chloromethyl)styrene, or (bromomethyl)styrene, with a tertiary amine such as trimethylamine, triethylamine, tripropylamine, tributylamine, dimethylethanolamine, methyldiisopropanolamine, dimethylbenzylamine, dimethylaniline, dimethylcyclohexylamine, N,N - dimethylamino - 1,2 - propanediol, triethanolamine, methyldiethanolamine and the like. The reaction of the vinylbenzyl halide and the tertiary amine proceeds readily at temperatures between about 0° and 60° C., and can be carried out in admixture with, or in the presence of, a solvent or reaction medium such as water, ethyl alcohol, ethylene dichloride, toluene or the like, but a solvent is not required.

The vinylbenzyl quaternary ammonium compounds can be polymerized alone or in admixture with one another, or in admixture with acrylamide or divinylbenzene in the proportions previously stated to form the water-soluble or water-dispersible polymers suitable for use as the electroconductive substance for use in the invention. The polymerization can be carried out in mass, i.e. in the substantial absence of an inert liquid medium, in solvents for the monomers or in a solvent for both the monomer and the polymer. Suitable solvents or polymerization media are water, lower aliphatic alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, or aliphatic ketones such as acetone or methyl ethyl ketone and mixtures of such compounds with water.

The polymerization is accelerated by the use of polymerization catalysts such as heat, ultraviolet light, hydrogen peroxide, sodium perborate, potassium persulfate, sodium persulfate, benzoyl peroxide, lauroyl peroxide, tertiary butyl peroxide, ditertiary butyl peroxide, tertiary butyl perbenzoate, cumene hydroperoxide or diisopropylbenzene hydroperoxide.

The polymerization of the monomers can be carried out at temperatures between 0° and 100° C. and at atmospheric, subatmospheric or superatmospheric pressures, but in all cases is carried out at temperatures below the decomposition temperature of the monomeric material and at pressures sufficient to maintain the monomers in a liquid condition.

In preparing paper having a printing surface containing the electroconductive polymers, the polymer can be incorporated on or with the cellulose web or paper by coating, dipping, brushing, calendering or other usual ways of applying a solution or dispersion of the polymer, preferably an aqueous solution or dispersion of the polymer, to the paper and thereafter drying the same to produce a final product containing the electroconductive polymer in the desired amount. The proportion of the electroconductive polymer can be varied in amount corresponding to from about 0.5 to 5 pounds of the polymer per 1000 square feet of the paper. The amount of the polymer to be incorporated with the paper can be varied by change in the concentration of the polymer in the aqueous solution or dispersion employed for the coating or dipping operation. The electroconductive polymer is preferably applied to the paper or cellulose web as a surface coating or by dipping of the paper in an aqueous solution or dispersion of the polymer, after which the treated paper is dried in usual ways, e.g. by calendering or in an oven.

FIG. 1 of the drawing is an enlarged view of a section of paper having on one side a continuous coating of an electroconductive water-dispersible polymer prepared in accordance with the invention, and FIG. 2 is a similar view of a section of paper coated on both sides with such a polymer, each of which coated papers has a printing surface adapted for electrographic printing.

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. In the examples, procedures identified by the designation "TAPPI" refer to standard methods published in Tentative and Official

Testing Methods, Recommended Practices, Specifications, by the Technical Association of the Pulp and Paper Industry.

EXAMPLE 1

In each of a series of experiments, a sheet of 51 pounds per ream of bleached sulfite base paper, sized on one side, was coated on the sized side with a layer of an aqueous solution containing 20 percent by weight of a homopolymer of vinylbenzyl trimethyl ammonium chloride, then was dried in an air oven at 220° F. for a period of 2 minutes and weighed. The paper contained a coating of the homopolymer corresponding to 1.4 pounds of the homopolymer per 1000 square feet of the coated paper. The homopolymer of vinylbenzyl trimethyl ammonium chloride employed in the experiment had a molecular weight corresponding to a viscosity characteristic of 1.63 centipoises as determined for a 0.5 weight percent solution of the homopolymer in an aqueous 2 weight percent solution of sodium chloride at 25° C. Test pieces were cut from the polymer coated paper. These test pieces were conditioned in air having a relative humidity as stated in the following table, at a temperature of 75° C. for a period of 24 hours, then were tested for surface resistivity employing a procedure similar to that described in ASTM D257–46. Table 1 identifies the experiments and gives the surface resistivity expressed as ohms of the polymer coated paper at the stated relative humidity. The coated paper had a printing surface adapted for electrographic printing.

Table I

Run No.	Relative Humidity, Percent	Surface Resistivity, Ohms×10⁶
1	10	22
2	20	3.7
3	42	1.1
4	55	0.97
5	76	0.58

EXAMPLE 2

In each of a series of experiments, a sheet of 51 pounds per ream of bleached sulfite base paper, sized on one side, was coated with a layer of an aqueous solution of a homopolymer of vinylbenzyl trimethyl ammonium chloride similar to that employed in Example 1, then was dried to obtain a paper having a coating of the homopolymer in amount as stated in the following table. Test pieces were cut from the coated sheet and were tested for surface resistivity at relative humidities as stated in the table employing procedure similar to that employed in Example 1. Table II identifies the experiments and gives the weight of the polymer coating expressed as pounds of the polymer per 1000 square feet of the coated paper. The table also gives the surface resistivity of the polymer coated paper at the stated relative humidity. Each of the coated papers had a printing surface adapted for electrographic printing.

Table II

Run No.	Polymer Coating, lbs./1,000 sq. ft.	Relative Humidity, Percent	Surface Resistivity, ohms×10⁶
1	0.96	10	23
2	1.4	10	19
3	2.2	10	11
4	2.9	10	7.2
5	0.96	20	4.8
6	2.2	20	3.6
7	2.9	20	1.3
8	0.96	42	2.0
9	2.2	42	1.2
10	0.96	55	1.2
11	2.2	55	0.82
12	0.96	76	0.56
13	2.2	76	0.46

EXAMPLE 3

In each of a series of experiments, a sheet of 51 pounds per ream of bleached sulfite base paper, sized on one side, was coated by dipping it in an aqueous solution of a homopolymer of vinylbenzyl trimethyl ammonium chloride similar to that employed in Example 2, which solution contained the homopolymer in a concentration of 20 percent by weight. The dipped paper was passed between squeeze rolls, then was dried in an air oven at 220° F. and was weighed to determine the percent by weight of the homopolymer incorporated in the paper. Test pieces of the impregnated paper were used to determine the surface resistivity at relative humidities as stated in the following table.

Table III

Run No.	Polymer Coating on Paper, Percent	Relative Humidity, Percent	Surface Resistivity, ohms×10⁶
1	11.6	10	76
2	30.9	10	12
3	11.6	20	12
4	30.9	20	2.8

EXAMPLE 4

In each of a series of experiments, a sheet of 51 pounds per ream of bleached sulfite paper, on one side, was coated with a layer of an aqueous solution of a homopolymer of vinylbenzyl trimethyl ammonium chloride, which homopolymer had a molecular weight corresponding to a viscosity characteristic of 1.63 centipoises as determined for a 0.5 weight percent solution of the homopolymer in an aqueous 2 weight percent solution of sodium chloride at 25° C., then was dried in an air oven at a temperature of 220° F. to obtain a coated paper containing an amount of the homopolymer as stated in the following table. Test pieces were cut from the coated paper and were conditioned in air at a relative humidity as stated in the table at 75° C. for a period of 24 hours, then were tested for surface resistivity employing a procedure similar to that described in ASTM D257–46. Table IV identifies the experiments and gives the proportion of the homopolymer expressed as percent by weight of the coated paper. The table also gives the surface resistivity of the coated paper.

Table IV

Run No.	Homopolymer, Percent	Surface Resistivity at Humidity of—			
		10 percent, ohms×10⁶	20 percent, ohms×10⁶	55 percent, ohms×10⁶	76 percent, ohms×10⁶
1	none	6,500,000	60,000	8,600	73
2	3.4	3,900	170	37	4.7
3	6.0	330	33	8.1	2.4
4	17.5	33	3.9	1.7	0.97
5	43.5	6.6	1.4	0.65	0.34

EXAMPLE 5

In each of a series of experiments, a sheet of 51 pounds per ream of bleached sulfite paper, sized on one side, was coated by dipping it in an aqueous solution of a homopolymer of vinylbenzyl trimethyl ammonium chloride similar to that employed in Example 4, and drying the dipped paper in an air oven at a temperature of 220° F. The concentration of the homopolymer in the solution was varied for the individual experiments to provide a coated paper having an amount of the homopolymer incorporated therewith as stated in the table. Test pieces of the impregnated paper were tested employing procedure similar to that employed in Example 4. Table V identifies the experiments and gives the surface resistivity of the coated paper at the relative humidities stated in the table.

Table V

Run No.	Homopolymer, lbs./1,000 sq. ft.	Surface Resistivity at relative humidity of—			
		10 percent, ohms×10⁶	20 percent, ohms×10⁶	55 percent, ohms×10⁶	76 percent, ohms×10⁶
1	0.32	270	17	7.3	2.2
2	0.75	94	6.6	2.1	1.0
3	1.60	23	2.5	1.0	0.58
4	2.30	14	1.4	0.73	0.32
5	3.10	18	1.0	0.87	0.26

EXAMPLE 6

(A) A water-dispersible copolymer containing in the polymer molecules residues corresponding to vinylbenzyl trimethyl ammonium chloride cross-linked with about one percent by weight of divinylbenzene was prepared by polymerizing a mixture of 99 percent by weight of vinylbenzyl chloride and 1 percent of divinylbenzene in an aqueous emulsion employing the recipe:

Ingredients:	Parts by weight
Monomers	100
Water	185
Triton 200 (28 percent liquid solution of sodium salt of alkyl aryl polyether sulfate)	14
Potassium persulfate	0.5

The ingredients were placed in a sealed vessel and were agitated and maintained at a temperature of 30° C. for a period of 16 hours. A coagulum-free latex was obtained in quantitative conversion of the monomers to copolymer. The latex was diluted with six times its weight of water and was mixed with 182 grams of an aqueous 25 weight percent solution of trimethylamine. The resulting mixture was stirred and maintained at 25°–30° C. for a period of 2 hours. A transparent viscous solution of the copolymer containing residues corresponding to vinylbenzyl trimethyl ammonium chloride cross-linked with the divinylbenzene was obtained.

(B) In each of a series of experiments, a sheet of 51 pounds per ream of bleached sulfite paper, sized on one side, was coated with a layer of the solution of the copolymer prepared in part (A) above, then was dried in an air oven at a temperature of 220° F. The dried paper contained 1.1 pounds of the copolymer per 1000 square feet of the paper. Test pieces of the coated paper were conditioned in air at a relative humidity as stated in the following table at 75° C. for 24 hours, then were tested for surface resistivity. The results were as follows:

Relative humidity, percent:	Surface resistivity, ohms×10⁶
10	36
20	6.2
55	1.3
76	0.59

EXAMPLE 7

A sheet of 51 pounds per ream bleached sulfite paper, sized on one side, was coated with a layer of a copolymer of vinylbenzyl trimethyl ammonium chloride cross-linked with 4 percent of divinylbenzene, prepared by procedure similar to that described in part (A) of Example 6, employing procedure similar to that employed in part (B) of said example. The paper had a coating corresponding to 1.1 pounds of the copolymer per 1000 square feet of the paper. The coated paper had a surface resistivity as follows:

Relative humidity, percent:	Surface resistivity, ohms×10⁶
20	9.0
55	2.0
76	0.9

EXAMPLE 8

A sheet of 51 pounds per ream bleached sulfite paper was coated with a layer of an aqueous dispersion of a copolymer of vinylbenzyl trimethyl ammonium chloride cross-linked with 2 percent of divinylbenzene, prepared by procedure similar to that described in part (A) of Example 6. The dried paper contained 1.5 pounds of the copolymer per 1000 square feet of the paper. It was tested and found to have a surface resistivity as follows:

Relative humidity, percent:	Surface resistivity, ohms $\times 10^6$
20	6.8
55	1.2
76	0.71

EXAMPLE 9

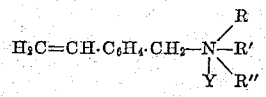
A sheet of 51 pounds per ream of bleached sulfite paper was coated with a layer of an aqueous solution of a homopolymer corresponding to polymerized vinylbenzyl trimethyl ammonium chloride, which polymer was prepared by polymerizing vinylbenzyl chloride in an aqueous emulsion in the presence of 0.1 percent by weight of dodecyl mercaptan and reacting the polymer with the trimethylamine, employing procedure similar to that described in part (A) of Example 6. The paper was coated and tested employing procedures similar to those employed in part (B) of Example 6. The coated paper contained the copolymer in amount corresponding to one pound of the copolymer per 1000 square feet of the paper. It had a surface resistivity as follows:

Relative humidity, percent:	Surface resistivity, ohms $\times 10^6$
10	47
20	8.5
55	1.7
76	0.66

Similar results are obtained when the polymer is incorporated with the paper by dipping the paper in the aqueous solution and thereafter drying the paper.

We claim:

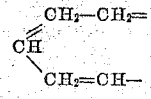
1. A paper having a printing surface adapted for electrographic printing and containing on said surface a continuous coating of an electroconductive water-dispersible polymer consisting of at least one member of the group consisting of (*a*) homopolymers of a vinylbenzyl quaternary ammonium compound having the general formula:



wherein R, R′ and R″ each represents individually a monovalent radical selected from the group consisting of $CH_2OH—CH_2—$, $CH_3—CHOH—CH_2—$,

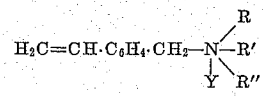
$$CH_2OH—CHOH—CH_2—$$

and alkyl, aryl, cycloalkyl and aralkyl hydrocarbon radicals, and R, R′ and R″ collectively represent the trivalent radical of the formula



wherein the three valences are attached to the nitrogen atom, and Y is an anion, said R groups containing a total of not more than 12 carbon atoms in the substituent radicals, (*b*) copolymers of at least two of such vinylbenzyl quaternary ammonium compounds, (*c*) copolymers of at least 65 percent by weight of at least one of such vinylbenzyl quaternary ammonium compounds and not more than 35 percent by weight of acrylamide, and (*d*) copolymers corresponding to from 95.0 to 99.99 percent by weight of at least one of such vinylbenzyl quaternary ammonium compounds and from 5.0 to 0.01 percent by weight of divinylbenzene, said electroconductive water-dispersible polymer being present in amounts corresponding to from 0.5 to 5 pounds of the polymer per 1000 square feet of the paper.

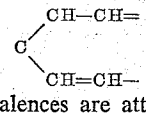
2. A paper having a printing surface adapted for electrographic printing and containing on said surface a continuous coating of an electroconductive water-dispersible polymer consisting of at least one homopolymer of a vinylbenzyl quaternary ammonium compound having the general formula:



wherein R, R′ and R″ each represents individually a monovalent radical selected from the group consisting of $CH_2OH—CH_2—$, $CH_3—CHOH—CH_2—$,

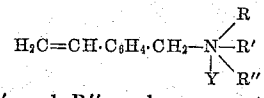
$$CH_2OH—CHOH—CH_2—$$

and alkyl, aryl, cycloalkyl and aralkyl hydrocarbon radicals, and R, R′ and R″ collectively represent the trivalent radical of the formula:



wherein the three valences are attached to the nitrogen atoms, and Y is an anion, said R groups containing a total of not more than 12 carbon atoms in the substituent radicals, said electroconductive water-dispersible polymer being present in amount corresponding to from 0.5 to 5 pounds of the polymer per 1000 square feet of the paper.

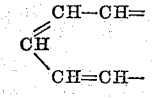
3. A paper having a printing surface adapted for electrographic printing and containing on said surface a continuous coating of an electroconductive water-dispersible polymer consisting of a copolymer of at least 65 percent by weight of a vinylbenzyl quaternary ammonium compound having the general formula:



wherein R, R′ and R″ each represents individually a monovalent radical selected from the group consisting of

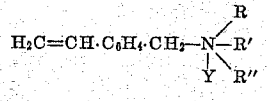
$$CH_2OH—CH_2—,\ CH_3—CHOH—CH_2—$$

$CH_2OH—CHOH—CH_2—$ and alkyl, aryl, cycloalkyl and aralkyl hydrocarbon radicals, and R, R′ and R″ collectively represent the trivalent radical of the formula:



wherein the three valences are attached to the nitrogen atom, and Y is an anion, said R groups containing a total of not more than 12 carbon atoms in the substituent radicals, and not more than 35 percent of acrylamide, said polymer being present in amount corresponding to from 0.5 to 5 pounds of the polymer per 1000 square feet of the paper.

4. A paper having a printing surface adapted for electrographic printing and containing on said surface a continuous coating of an electroconductive water-dispersible polymer corresponding to a copolymer consisting of from 95.0 to 99.99 percent by weight of a vinylbenzyl quaternary ammonium compound having the general formula:

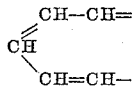


wherein R, R′ and R″ each represents individually a monovalent radical selected from the group consisting of

$$CH_2OH—CH_2—,\ CH_3—CHOH—CH_2—$$

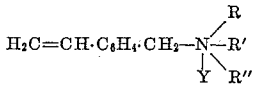
$CH_2OH—CH_2OH—CH—$ and alkyl, aryl, cycloalkyl and

aralkyl hydrocarbon radicals, and R, R′ and R″ collectively represent the trivalent radical of the formula:



wherein the three valences are attached to the nitrogen atom and Y is an anion, said R groups containing a total of not more than 12 carbon atoms in the substituent radicals, and from 5.0 to 0.01 percent of divinylbenzene, said polymer being present in amount corresponding to from 0.5 to 5 pounds of the polymer per 1000 square feet of the paper.

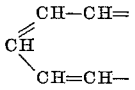
5. A method of making a paper having a printing surface containing an electroconductive water-dispersible polymer and which paper is adapted for electrographic printing, which method comprises contacting at least one of the major surfaces of the paper with an aqueous solution of a water-dispersible polymer selected from the group consisting of (*a*) homopolymers of a vinylbenzyl quaternary ammonium compound having the general formula:



wherein R, R′ and R″ each represents individually a monovalent radical selected from the group consisting of

$CH_2OH—CH_2—$, $CH_2CHOH—CH_2—$

$CH_2OH—CHOH—CH_2—$ and alkyl, aryl, cycloalkyl and aralky hydrocarbon radicals, and R, R′ and R″ collectively represent the trivalent radical of the formula:



wherein the three valences are attached to the nitrogen atom, and Y is an anion, said R group containing a total of not more than 12 carbon atoms in the substituent radicals, (*b*) copolymers of at least two of such vinylbenzyl quaternary ammonium compounds; (*c*) copolymers of at least 65 percent by weight of at least one of such vinylbenzyl quaternary ammonium compounds and not more than 35 percent of acrylamide, and (*d*) copolymers corresponding to from 95.0 to 99.99 percent by weight of at least one of such vinylbenzyl quaternary ammonium compounds and from 5.0 to 0.01 percent of divinylbenzene, and drying said paper, whereby said dried paper contains said polymer on the printing surfact in the form of a continuous coating in amount corresponding to from 0.5 to 5 pounds of the polymer per 1000 square feet of the paper.

6. A method as claimed in claim 5, wherein the water-dispersible polymer is a homopolymer of a vinylbenyl quaternary ammonium compound of group (*a*).

7. A method as claimed in claim 6, wherein the water-dispersible polymer is a homopolymer of vinylbenzyl trimethyl ammonium chloride.

8. A method as claimed in claim 5, wherein the water-dispersible polymer is a copolymer of at least 65 percent by weight of at least one vinylbenzyl quaternary ammonium compound of group (*a*) and not more than 35 percent of acrylamide.

9. A method as claimed in claim 8, wherein the water-dispersible polymer is a copolymer of vinylbenzyl trimethyl ammonium chloride and acrylamide.

10. A method as claimed in claim 5, wherein the water-dispersible polymer is a copolymer of from 95.0 to 99.99 percent by weight of at least one vinylbenzyl quaternary ammonium compound of group (*a*) and from 5.0 to 0.01 percent by weight of divinylbenzene.

11. A method as claimed in claim 10, wherein the water-dispersible polymer is a copolymer of vinylbenzyl trimethyl ammonium chloride and divinylbenzene.

References Cited in the file of this patent

UNITED STATES PATENTS

2,772,310 Morris ---------- Nov. 27, 1956
2,884,057 Wilson et al. ---------- Apr. 28, 1959

UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

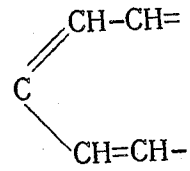
December 5, 1961

Patent No. 3,011,918

Lloyd H. Silvernail et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, lines 23 to 26, the formula should appear as shown below instead of as in the patent:



column 9, line 30, for "$CH_2CHOH-CH_2-$" read -- $CH_2-CHOH-CH_2-$ --; column 10, lines 10 and 11, for "surfact" read -- surface --; line 15, for "vinylbenyl" read -- vinylbenzyl --; line 39, under "References Cited" strike out
"2,772,310 Morris------Nov. 27, 1956".

Signed and sealed this 26th day of June 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

UNITED STATES PATENT OFFICE

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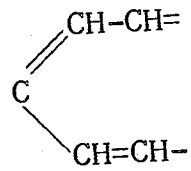

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