

[54] CONDUCTIVE PAPERS

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[58] Field of Search..... 117/155 UA, 201, 64 C, 117/155 R, 155 L; 260/89.7 R, 89.7 N

[56] **References Cited**

UNITED STATES PATENTS

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[57]

ABSTRACT

Electrically conductive paper is made by coating or impregnating paper with a polymer containing at least 70 percent quaternised dialkylamino methylene acrylamide or methacrylamide groups, and then curing the polymer. The polymer must also have another property. Thus it may be defined as containing also methylolated acrylamide or methacrylamide units. Preferred polymers are made by the Mannich reaction. The polymers used cure under moderate conditions and are then resistant to leaching by moisture.

9 Claims, No Drawings

CONDUCTIVE PAPERS

It is frequently required to produce paper which has, amongst other properties, the property of low electrical resistance.

This property is required for instance in the production of punch tapes and cards for use in conjunction with computers in order to eliminate the troublesome effects which would otherwise occur due to the accumulation of static electrical charge. Another increasingly important requirement for papers of high electrical conductivity is for their use in the various systems of photo-electric reprography.

It is well known to manufacture papers having low electrical resistance by impregnating or coating the paper with, for example, organic or inorganic salts, humectants or polyelectrolyte resins or combinations of such materials.

It is generally required that the conductive material fulfills several important parameters for it to be acceptable, chief amongst which are that it provides low electrical resistance at low percentage add-on at all environmental humidities above the level of about 15 percent relative humidity and that this effect must be achieved at an economical treatment cost.

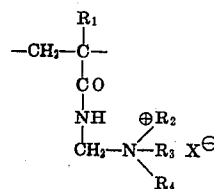
Surprisingly few materials have been found to meet these requirements and most interest has centred around two or three products selected from the class of water soluble cationic polyelectrolyte resins of high charge density and which also have good film-forming properties.

It is becoming increasingly important that the materials used to confer electrical conductivity on the paper should be capable of being rendered insoluble in water after they have been applied to the paper to prevent their being leached away and rendered less effective or to prevent the water leached materials contaminating other areas of the paper or the equipment in which they are used. Commercially available resins supplied for conferring high conductivity to the paper do not possess this property to any reasonable degree.

This water insolubility is desirable when the paper is stored at high humidity or when the paper is to receive an additional coating, e.g., a photo conductive coating, applied from a coating mix containing water, or when the paper is to be used for an electro-photographically produced offset printing master copy where such a copy is repeatedly contacted with water in the course of its use on the printing press.

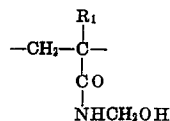
It is known to achieve water insolubility by using a conductive additive comprising a water soluble cationic polyelectrolyte to which is added cross-linking agents which are chemical substances capable of reacting with the polyelectrolyte to form within or on the paper a water insoluble matrix. Careful selection of cross-linking agent has to be made to ensure its compatibility with the system generally, to ensure that it has no adverse effects such as colour development or the development of acidity. Further it is often a matter of some difficulty to ensure that the cross-linking agent is sufficiently reactive chemically as to achieve its cross-linking effect under relatively mild conditions such as could be used in drying or curing the paper and yet sufficiently low in reactivity to prevent undue instability in the coating or impregnating mix prior to application.

According to this invention conductive paper is made by coating or impregnating paper with compositions comprising particular polymers in which at least 70 percent of the recurring units of the polymer have the formula:



where R_1 is hydrogen or methyl, R_2 , R_3 and R_4 may be the same or different and are C_{1-4} alkyl and X^- is Br^- or, preferably, Cl^- , and curing the polymer.

The polymers used in the invention must have at least one further characteristic in addition to containing at least 70% of the recurring units of the formula shown above. This characteristic can be expressed in various ways. Most conveniently, it can be defined as being that the polymer should also include recurring methylolated acrylamide or methacrylamide units. Such methylolated units can be expressed as having the formula:



where R_1 is as defined above. The amount of methylolated units in the polymer must be sufficient to permit adequate cross-linking occurring under the very mild conditions that are permissible in the drying and curing of conductive papers. Usually therefore there are at least 5 percent of the methylolated units in the polymer but of course there cannot be more than 30 percent. Usually the amount of methylolated groups is from 5 to 20 percent, most preferably 10 to 15 percent.

The polymers defined above can be made by polymerising methylol acrylamide or methylol methacrylamide with dialkylamino methylene acrylamide or dialkylaminomethylene methacrylamide, or a quaternary salt of one of these, in the desired proportions and then, if the dialkylamino monomer was not a quaternary salt, quaternising the resultant polymer. Polymerisation conditions similar to those used conventionally for the production of polyacrylamide or polymethacrylamide can be used, for example polymerisation in the presence of a free radical catalyst. The dialkylamino methylene acrylamide or methacrylamide may be made by subjecting acrylamide or methacrylamide to the Mannich reaction, i.e., reaction with formaldehyde and a secondary amine.

Analysis of polymers of the type used in the invention can be rather difficult and so it is convenient to define them instead by their method of preparation rather than their chemical structure. Accordingly polymers for use in the invention can be defined as having at least 70 percent of the recurring units of Formula I quoted above and as having been made by a process comprising subjecting polyacrylamide or polymethacrylamide to the Mannich reaction, i.e., reaction with formalde-

hyde and a secondary amine (i.e., a dialkylamine). It is believed that during the reaction although the majority of amide groups are converted to dialkylamino methylene amide groups some are converted to methylolated amide groups of Formula II. Thus, for example, from 70 to 90 percent of the starting amide groups may be converted to dialkylamino methylene amide groups while from 5 to 25 percent of the starting amide groups may be converted to methylol amide groups of Formula II and the balance, if any, of the amide groups remain unreacted.

The degree of reaction and the end product will depend, in part, upon the proportions of formaldehyde and amine used.

Preferably the amount of formaldehyde, and the amount of secondary amine, is a substantially equimolar amount based on the amount of amide present. Preferably from 1 to 1.5 mols of each of formaldehyde and the secondary amine are used per mol of amide. Preferably the molar proportion of formaldehyde:amine is substantially 1:1.

The polymers used in the invention may contain units other than the specified units of Formulae I and II and amide units but such other monomeric units usually tend to reduce the conductivity of the final product and so should not be present in large amounts, and usually will not be present in amounts of more than 10 percent, or at the most 20 percent, of the units of the polymer.

The preferred method of making polymers for use in the invention is to form a polymer of acrylamide or methacrylamide (i.e., a homopolymer or copolymer of these), optionally containing also a small amount of other monomeric units, by conventional polymerisation processes, for example in the presence of a free radical catalyst, until a polymer of the desired molecular weight is formed, and then subjecting the polymer to the Mannich reaction and then quaternising the aminomethyl groups introduced into the polymer by reaction with a quaternising agent. Suitable quaternising agents for use in this reaction, or in the quaternisation of a monomer (as discussed above) are alkyl bromides and chlorides.

The polymers used in the invention can have a wide range of molecular weights. Usually high molecular weights are, however, avoided as the application of high molecular weight polymers can be rather difficult because of the high viscosity of their solutions. Usually very low molecular weights, for example 10,000 or below, are avoided as coatings of them may tend to be slightly tacky. Preferably therefore the molecular weights will be intermediate values, for example 100,000 to 250,000. In preference to quantifying the preferred molecular weights in this manner it can be stated that the intrinsic viscosity, measured in 3 molar sodium chloride, is preferably between about 0.2 and 1.

The polymers may be applied to suitable paper, in any convenient manner, and are usually applied in the form of an aqueous solution. Any suitable concentration of solution may be used. Usually it is from 5 to 40 percent. Usually the polymers are applied in a composition that contains other ingredients useful for giving the paper selected properties.

A variety of papers may be coated by use in the invention; it will be appreciated that the paper does not have to be a relatively thin flexible paper but can be pa-

perboard. Preferred paper for use in the invention is electrophotographic base paper.

The solution may contain various additives, such as clay or other thickeners, especially when the solution is to be coated onto the paper rather than being impregnated into the paper.

The polymeric materials used in the invention are capable of self cross-linking under mild conditions, i.e., temperatures of up to 120°C and at a substantially neutral pH, to a state in which they are substantially incapable of being leached away by the presence of moisture. Thus they may self cross-link merely upon drying the coating or impregnant in conventional manner on heated rolls and thus do not require the presence of a second agent to render them insoluble. Further, the materials have all the other desirable attributes of a conductive resin listed above.

The polymers used in the invention are distinguished from the polymers described in, for example, U.S. Pat. Specification No. 3,486,932 by, inter alia, the facts that although the latter may contain units of formula I they do not contain any methylolated amide groups, that they are not made by the Mannich reaction and, in particular, that they are not able to give the high water resistance obtained in the invention.

The following are some examples of the invention.

EXAMPLE 1

Acrylamide is polymerised as a 25 percent solution in water in the presence of ammonium persulphate as initiator at 60°C to give a polyacrylamide resin having an intrinsic viscosity of about 1. The resultant 25 percent solution is subjected to the Mannich reaction using formaldehyde and dimethylamine in essentially equimolar proportions relative to the amide groups in the polyacrylamide resin, the reaction being conducted by heating the mixture for 4 hours at 40°C. The product was then quaternised by heating with an equimolar quantity of methyl chloride in an autoclave at 100°C for 5 hours.

Referring to formula I, the resultant polymer has R₁ representing hydrogen and R₂, R₃ and R₄ each representing methyl and X representing chloride ion.

EXAMPLE 2

Methacrylamide may be subjected to the Mannich reaction by heating with substantially equimolar proportions of formaldehyde and dimethylamine, relative to the amide groups to form dialkylamino methylene methacrylamide. A mixture of 90 percent of this monomer with 10 percent methylolacrylamide may then be subjected to polymerisation in water containing ammonium persulphate as initiator at 60°C to produce a resin having an intrinsic viscosity of about 1. The product may then be heated with a substantially equimolar quantity of methyl chloride to effect quaternisation.

EXAMPLE 3

Samples of electrophotographic base paper were treated by immersion with 7 percent aqueous solution of the polymer made in Example 1, Polymer A, and with polydimethylamino ethyl methacrylate salt, which is a conventional conductive water resistant polymer, (Polymer B) and dried in an oven for 3 minutes at 105°C. The surface resistance of each paper was determined after conditioning at a relative humidity of 15 percent for 24 hours. The papers were then soaked in

water for 24 hours, redried at 100°C and conditioned at 15% r.h. The surface resistance was again determined. The loss of weight was also noted.

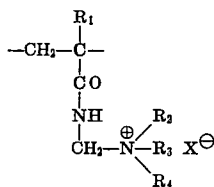
The results appear in the following table:

Material	Coat Wt. (g/m ²)	Surface Resistance (log ohms/sq)		Loss in weight on weighing (g/m ²)
		Before washing	After washing	
Polymer A	2.47	10.9	10.9	1.4
Polymer B	2.27	10.5	12.3	4.7

The polymer used in the present invention was not removed by washing, as indicated by the conductivity figures, and the coated paper suffered no loss in conductivity whereas the paper treated with the conventional resin suffered an appreciable loss in conductivity, its electrical resistance increasing by a factor of approximately one hundred. In addition the paper treated with the polymer of the present invention lost a much smaller amount of other soluble constituents, i.e., starches, and hence can be expected to preserve certain important properties such as strength and dimensional stability.

We claim:

1. Electrically conductive paper which is coated or impregnated with a composition containing as the essential electroconductive component thereof a cross-linked polymer formed from a polymer in which at least 70 percent of the recurring units have the formula



wherein R₁ is hydrogen or methyl, R₂, R₃, and R₄ may be the same or different and are C₁₋₁₄ alkyl and X is Br or Cl and which also includes 5 to 30 percent of methylolated acrylamide or methacrylamide units.

2. Electrically conductive paper according to claim 1 in which the polymer contains at least 10 percent of the methylolated groups.
3. Electrically conductive paper according to claim 1 in which R₁ represents hydrogen.
4. Electrically conductive paper according to claim 1 in which R₂ and R₃ both represent methyl.
5. Electrically conductive paper according to claim 1 in which R₂, R₃, and R₄ each represent methyl.
6. Electrically conductive paper according to claim 1 in which X is Cl.
7. Electrically conductive paper according to claim 1 in which the polymer has been made by a process comprising reacting a polyacrylamide or polymethacrylamide with formaldehyde and a secondary amine.
8. Electrically conductive paper according to claim 1 in which the polymer has been made by reacting a polyacrylamide or polymethacrylamide with from 1 to 1.5 moles of each of formaldehyde and secondary amine relative to the amide groups in the polymer.
9. Electrically conductive paper according to claim 1 in which the polymer was applied as an aqueous solution having a substantially neutral pH and the paper was then dried and the composition cured to effect crosslinking of the polymer on the paper.

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