Nov. 12, 1963 T. DOGGETT ET AL 3,110,621

ELECTROSTATIC RECORDING PAPER

Filed Feb. 1, 1960

Fig. 1

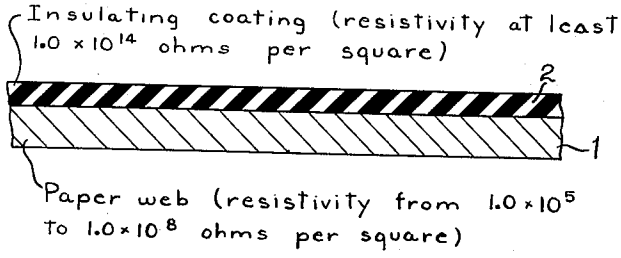
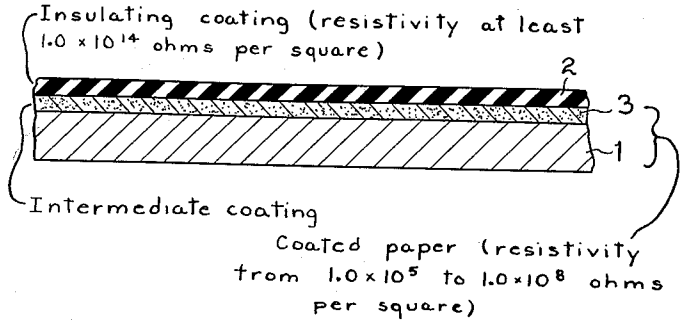


Fig. 2



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ELECTROSTATIC RECORDING PAPER

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This invention relates to a coated paper product adapted for use in electrostatic printing, particularly that form thereof sometimes called "electrographic" printing, and to a method of making such a coated paper product.

In one form of electrostatic printing a paper web having a dielectric or insulating surface, while being carried upon a grounded support, is passed into close proximity but not in actual contact with styli which can be electrically energized as desired. Each time a stylus is energized it charges the surface of the paper in a single spot directly beneath the stylus. By selection of styli to be energized, charged spots in the pattern of a letter or other image can be formed on the surface of the paper. The charged spots are then treated or developed with a colored resinous powder which clings to the charged areas but does not adhere to or is easily removed from the uncharged areas. The paper is thereafter heated to fuse the colored powder to the spots to form a permanent visible image or print. This method of printing is capable of very high speeds, as many as 1,000 characters per second being easily obtainable.

It is apparent that for successful operation in this method of printing the paper receiving the print must have a surface that is dielectric or non-conducting to a very high degree so that it will hold an electrostatic charge for at least several minutes. The surface must be free from contamination by conductive matter and it must be substantially unaffected by variation in the moisture of the ambient atmosphere. Paper with a sheet of extruded polyethylene film laminated thereto has been used in this process. Also paper has been used which has been coated with a layer of resin such as polystryene applied as a lacquer or varnish in a volatile organic solvent. Hitherto, however, it has not been found possible to make a paper satisfactory for this process by coating the paper with an aqueous coating composition. It is apparent that use of an aqueous vehicle is much to be desired for several important reasons including freedom from fire hazard, freedom from toxicity, and considerably lower cost. Coatings containing the usual hydrophilic adhesives, which are necessarily affected by humidity changes will not give satisfactory results. It has been found that emulsification of non-hydrophilic resins in an aqueous vehicle has likewise not given satisfactory coatings, possibly because of the presence of emulsifying or dispersing agents required to produce stable aqueous dispersions of such resins.

The present invention provides a coated paper product having a dielectric surface deposited from an aqueous vehicle. The resulting product will hold an electrostatic charge satisfactorily for several minutes and long enough to permit visible development and fixation of latent electrostatic images impressed thereon. The product, however, will permit the gradual dissipation of charges over an extended period so that static charges inadvertently picked up during processing or handling will not be permanently retained to interfere with proper performance of the paper in its intended use.

The product of the invention is a coated paper, the paper base of which has a low but controlled degree of conductance, said base carrying, on one side only, a substantially non-conductive or dielectric resinous layer comprising the insoluble decomposition residue of a reaction product of a copolymer of vinyl acetate and crotonic

acid with ammonia or a water-soluble, volatile substituted ammonia (i.e. an amine). Said layer should be free from mineral pigment, water-sensitive or conductive surface-active agents, and all matter having a dielectric constant substantially lower than that of said decomposition product.

The product is made by first forming a sized paper web containing a small quantity of conductive matter to provide a slight degree of conductance in the web. There are no unusual strength characteristics needful in the paper web for fulfilment of its intended use. Hence a web of approximately 75 grams per square meter (50 pounds (50 pounds per ream 25" x 38—500) with the strength characteristics of ordinary book paper is satisfactory for use.

It is desirable, however, that regardless of weight the conductance of the paper shall fall within certain limits. One way to measure the conductance of a sheet of paper is to cement to the surface of the web by use of conductive adhesive two metal electrodes having straight edges of equal length in parallel side-by-side relationship. The distance between the inside edges of the parallel electrodes should be exactly the same as the length of the electrodes. In this way there is a square area of the paper bounded on two sides by the electrodes and on the other two sides by imaginary lines connecting the ends of the opposite electrodes. When voltage is impressed between the electrodes current passes through the square of paper. If the paper is uniform in thickness and quality the size of the square is unimportant, for the conductance will be the same for a square of any size. Since for paper the conductance is actually rather low, it is actually more convenient or meaningful to report the electrical property as resistance in ohms per square centimeter or merely per square. A resistance of about 5×10^6 ohms per square has been found very satisfactory. The resistance is not extremely critical, however, because papers having resistances per square of 1×10^8 ohms and 1×10^5 ohms have been found usable. Resistance of this magnitude is high enough to prevent formation of an arc if a hole or flaw exists in the top dielectric coating; at the same time it is low enough to ensure dissipation of charges inadvertently acquired by the sheet while it is being processed or handled and also is low enough to permit charging of the dielectric surface without excessive voltage. It may be noted that a clear film of dielectric resinous coating material when measured in the same fashion would show a resistance of at least 1×10^{14} and usually of 1×10^{15}. Thus the resistance of the dielectric coating is at least one million times as great as that of the paper web, and usually is about 100 million times as great.

In paper intended for use only in humid atmospheres the desired conductance can be imparted by including in the paper a simple electrolyte such as a chloride of sodium or of lithium. This is not an entirely satisfactory procedure, however, for in many cases use in dry atmospheres is also desired. Carbon black incorporated in the paper web will provide conductivity therein substantially unaffected by variation in atmospheric conditions, but carbon black imparts objectionable discoloration to the web. Moreover, the conductivity of carbon black is so high that considerable care is required when it is used to be sure that the conductance of the paper web actually falls in the desired range. Hence although inclusion of a simple electrolyte or of carbon black in the paper will result in a paper base which in many cases is useful according to the invention, it is nevertheless preferred to use as conductive material a substance (1) which is less affected by humidity changes than are the simple electrolytes and (2) which does not, like carbon black, impart objectionable color. There are substantially color-

less resinous polymers of quaternary ammonium salts which are found very suitable for inclusion in the paper web to impart the desired degree of conductivity thereto. An example of such a conductive resinous polymer is polyvinyl benzyl trimethyl ammonium chloride. If desired the resinous polymer may be the only agent added to impart conductance to the sheet.

The top or dielectric coating may be applied directly to such uncoated paper base. Alternatively a base-coat or prime-coat may be first applied to the paper base to provide a more level surface thereto. In the latter case it is important that such a base-coat shall also be given a conductivity of substantially the same magnitude as that possessed by the uncoated paper base.

The insulating or dielectric coating layer is applied to the surface of the conductive paper base, which, as stated above, may, if desired, also have thereon a layer of conductive prime-coat, in the form of an aqueous ammoniacal coating composition containing the dissolved ammonium salt of a vinyl acetate-crotonic acid copolymer. The coating may be applied by coating devices conventional for use with aqueous coating compositions, for instance by an air-knife coater.

It is essential that sufficient of the resin shall be applied in dissolved condition so that it will be deposited on the paper in a continuous film. It is likewise essential that after application, during drying or other treatment, the resinous film shall become insoluble in water and substantially non-conductive electrically. Vinyl acetate-crotonic acid copolymers dissolve readily in aqueous solutions of alkalis. Presumably a soluble salt of the copolymer is thus formed. If a volatile alkali is used, e.g. ammonia or morpholine, the salt, upon being dried and heated, is thereby decomposed, permitting the volatile alkali to escape into the atmosphere and leaving an insoluble residue of resinous acidic polymeric substance which may be identical with or very similar to the original copolymer before it was dissolved.

From consideration of cost ammonia is the preferred volatile alkali for use. Ammonia may be replaced by substituted ammonias, i.e. amines, which are water soluble and which boil at temperatures to which paper can safely be subjected. Preferably the boiling point of the amine should not exceed 140° C. and more desirably it should be below 100° C. Volatile aliphatic amines such as ethylamine, butylamine, and hexylamine are usable as are also heterocyclic amines such as morpholine and pyridine. Primary, secondary, and tertiary amines are usable, provided that they are readily water-soluble and boil below 140° C. The preferred amine is diisopropylamine. Amines which boil below about 140° C. are referred to herein as volatile amines.

As used herein, whenever the context permits "ammonia" includes substituted ammonias or amines, and "ammonium" includes substituted ammonium.

It is known that resinous copolymers of vinylacetate can be made soluble in dilute ammonia solution by incorporation of carboxyl groups therein by inclusion in the polymer of from about 2% to about 15% of crotonic acid based on the weight of the copolymer. The viscosity of the ammoniacal solutions may vary somewhat depending upon the exact ratio of crotonic acid to vinyl acetate in the copolymer, and/or upon the degree to which polymerization has been carried. To be useful in the present invention the polymerization obviously must be carried far enough to yield a resinous product sufficiently hard not to be tacky to the touch. With that one proviso all the copolymer resins described above are usable according to the invention. The prefered copolymers contain from 3 to 7% of crotonic acid.

Commercial resins found to have essential properties substantially identical with those of the resins described include "Elvadex" resin made by E. I. du Pont de Nemours and Company of Wilmington, Delaware; "Stymer LF 25" made by Monsanto Chemical Company of St. Louis, Missouri; "Lemac 541" made by The Borden Company of New York City; "Gelva C–3" made by Shawinigan Resins Corporation of Springfield, Massachusetts; and "Vinac ASB" made by Colton Chemical Company of Cleveland, Ohio.

The coating composition for producing the dielectric layer or coating is preferably made by stirring finely powdered resin into an aqueous medium. The water may contain ammonia dissolved therein, or alternatively ammonia can be added after the powdered resin has been stirred into the water. In some cases substantially all of the resin may dissolve in the ammoniacal solution. In any case a substantial portion of the resin must dissolve and must be enough to carry into suspension any resin remaining undissolved and do this without addition of other emulsifying or dispersing agent. The composition preferably should not contain any mineral filler or any material of which the dielectric constant is appreciably below that of the vinyl acetate-crotonic acid copolymer.

The aqueous coating composition should be spread over the paper base in quantity sufficient to give a continuous film after it has become dry. The minimum quantity required in any particular case will depend to some extent upon the characteristics of the paper base being used. In some cases as little as 3 grams per square meter (or 2 pounds per ream) will give satisfactory coverage. In no case has it been found worthwhile to use more than 13 grams per square meter.

It is desirable to keep sharp the demarcation between the dielectric coating and the paper base. That is, it is preferable to prevent penetration of the top or dielectric coating composition into the paper base. One way of reducing such penetration is to make a surface application of a water-repellent substance to the surface of the paper base prior to application of the dielectric coating. For example, a surface size of starch containing a small quantity of emulsified wax can be used on the paper base. Or a prime coat of mineral filler and adhesive also containing a small quantity of emulsified wax can be applied. In such a case it is advisable also to add sufficient conductive material to make the conductivity of the coating about equal to that of the underlying paper web.

The two embodiments of the invention described above are illustrated in the accompanying drawings in which

FIG. 1 is a diagrammatic cross-section of a sheet of coated paper consisting of the paper web and the dielectric coating, and

FIG. 2 is a diagrammatic cross-section of a sheet of coated paper consisting of the paper web, an intermediate coating and the top dielectric coating.

In both FIGS. 1 and 2 the reference numeral **1** marks the paper web and **2** marks the dielectric coating and in FIG. 2 the reference numeral **3** marks the intermediate coating. As stated above the paper web **1** and the intermediate coating **3** should have a resistance within the range from 1×10^5 to 1×10^8 ohms per square while the dielectric coatings **2** should have a resistance of at least 1×10^{14} per square.

Examples of a product made according to the invention were made as follows:

Example 1.—A paper web was made from a moderately beaten paper-making furnish containing 60 parts of bleached fibers from hard-wood trees and 40 parts of bleached fibers from coniferous trees, the fibers having been obtained by an alkaline pulping process. The paper web weighing about 75 grams per square meter was impregnated with an aqueous composition containing 1½ of emulsified wax size and 5% of a resinous homopolymer of vinyl benzyl trimethyl ammonium chloride. The web was then dried and calendered. The resulting sheet weighed about 80 grams per square meter. It was found to have a resistivity of about 8×10^6 ohms per square. The impregnated web was finally coated with

an aqueous composition containing 20% by weight of "Elvadex," a resinous copolymer of vinyl acetate and about 5% of crotonic acid, the resin being solvated by means of 10% by weight, based upon the copolymer, of 28% ammonia. The coating film applied amounted to 10 grams per square meter after it had dried. The dried coating was found to be water-insoluble and to be sufficiently dielectric to accept an electrostatic charge and hold it for several minutes. The coating may be dried for instance by air-drying over night at room temperature or in hot-air at 150° C. for two minutes.

Example 2.—In another example an impregnated and dried paper web similar to the one used in the preceding example, before the application of the dielectric coating, was given on one side of a priming- or base-coat amounting to 8 grams per square meter of an aqueous composition containing (in parts dry weight) 100 parts of clay, 40 parts of starch adhesive, 2 parts of emulsified paraffine wax and 7.5 parts of resinous polyvinyl benzyl trimethyl ammonium chloride. The base-coated web was dried and calendered. It was found to have a resistance of 5×10^6 ohms per square. The base-coated web was finally coated by means of an air-knife coating device with an aqueous composition containing 19% by weight of a resinous copolymer of 95 parts of vinyl acetate and 5 parts of crotonic acid, the resin being solvated by means of 10% by weight, based upon the copolymer, of 28% ammonia. The dry weight of dielectric coating so applied amounted to 5 grams per square meter. The layer of dielectric coating, after it had been dried, was entirely insoluble in water. The surface accepted an electrostatic charge nd held it for a considerable length of time. The coating may be dried for instance by air-drying over night at room temperature or in hot-air at 150° C. for two minutes.

Example 3.—A paper web weighing 75 grams per square meter was impregnated with an aqueous composition containing 1.5% of emulsified paraffine wax and 5% of a resinous homopolymer of vinyl benzyl trimethyl ammonium chloride sufficient to amount to 5 grams per square meter dry weight. The paper was dried and calendered. It was then coated on one side with 5 grams per square meter, dry weight, of an aqueous solution containing 19% by weight of a resinous copolymer of 95 parts vinyl acetate and 5 parts crotonic acid, and 10% by weight, based upon the copolymer of diisopropylamine. The coated sheet was dried in a current of hot air at 150° C.; thereafter the coating was entirely insoluble in water. The surface accepted an electrostatic charge and held a substantial charge for over 30 minutes.

The following amines have been successfully substituted in eyual weights for the diisopropylamine in the foregoing example: normal butylamine, propylenediamine, ethylenediamine and dimethylaminopropylamine.

The invention provides a method whereby a paper base is impregnated with a substance to lower its resistivity to between 1×10^5 and 1×10^8 ohms per square centimeter and is sized to make it somewhat water-resistant; the web is dried and smoothed and then is coated with an aqueous composition containing dissolved therein a resinous copolymer of from 85 to 98 parts of vinyl acetate and from 15 to 2 parts of crotonic acid, said resinous copolymer being solvated by volatile alkali; the so-coated web is then dried to convert the resinous copolymer to a water-insoluble and highly dielectric condition.

The product of the invention is a coated paper product which comprises a sized paper web having a resistance between 1×10^5 and 1×10^8 ohms per square centimeter, and having on one surface a continuous dielectric layer amounting to from 3 to 15 grams per square meter dry weight, and comprising resinous dielectric matter having electrical properties substantially identical with those of a resin formed by copolymerization of from 85 to 98 parts vinyl acetate and from 2 to 15 parts of crotonic acid. In spite of the said dielectric layer having been deposited from aqueous medium, the layer is highly insulating and capable of accepting an electrostatic charge and of holding said charge for at least several minutes. Another advantage of the invention is that waste printed sheets, trimmings and torn sheets of the paper product may be reworked into pulp in alkaline water so that said waste can be again used in a paper-making process instead of being a total loss as in the case of papers coated with varnish or lacquer.

This application is a continuation-in-part of our application Ser. No. 821,677 filed June 22, 1959, now abandoned.

We claim:

1. An electrostatic recording paper which comprises a sized paper base having per se a resistance of about 5×10^6 ohms per square, said paper base bearing on one side an insulating layer of from 3 to 15 grams per square meter of a resinous copolymer of about 95 parts vinyl acetate and about 5 parts of crotonic acid, said insulating layer being free mineral pigments.

2. An electrostatic recording paper which comprises a paper base impregnated with a resinous homopolymer of vinyl benzyl trimethyl ammonium chloride and having an electrical resistance within the range from 1×10^8 to 1×10^5 ohms per square, said paper having on one side an insulating layer consisting essentially of a resinous copolymer of from 93 to 97 parts of vinyl acetate and from 7 to 3 parts of crotonic acid, said insulating layer being free of mineral pigment.

3. Process of making a paper product adapted for electrostatic printing which comprises preparing a sized paper web containing electrically conductive material, drying said web, said sized and dried web having an electrical resistance within the range from 1×10^8 to 1×10^5 ohms per square, thereafter applying to one side of said web a continuous layer of aqueous composition containing a resinous copolymer of from 85 to 98% of vinyl acetate and from 15 to 2% of crotonic acid and a base selected from the group consisting of ammonia and water soluble volatile amines in quantity equivalent to from 3 to 15 grams dry weight of said resinous copolymer per square meter, drying said layer at a temperature sufficient to evaporate water and said base thereby depositing a dielectric layer of resinous matter having electrical properties substantially identical with those of the resin formed by copolymerization of from 85 to 98 parts of vinyl acetate and from 15 to 2 parts of crotonic acid said aqueous composition and said dielectric layer being free of mineral pigment.

4. Process as defined in claim 3 in which the base is ammonia.

5. Process as defined in claim 3 in which the base is diisopropylamine.

6. Process of making a paper product adapted for electrostatic recording which comprises impregnating a paper web with an aqueous composition containing an electroconductive water-dispersible polymer of a vinylbenzyl quaternary ammonium compound and a small but effective quantity of a water-repellent sizing agent, drying the web, said impregnated sized and dried web having an electrical resistance within the range from 1×10^8 to 1×10^5 ohms per square, thereafter coating one side of said web with an aqueous composition containing a copolymer of from 93 to 97 parts of vinyl acetate and from 7 to 3 parts of crotonic acid, said copolymer being solvated by ammonia, drying the coated web and regenerating the resinous copolymer in the form of a water-resistant electrically insulating surface layer free of mineral pigment.

7. Process of making a paper product adapted for electrostatic recording which comprises forming a paper web,

impregnating said web with an aqueous composition comprising a sizing agent and a resinous homopolymer of vinyl benzyl trimethyl ammonium chloride, drying and calendering the paper web, coating the dried and calendered web with an aqueous ammoniacal dispersion of a resinous copolymer of from 85 to 98 parts of vinyl acetate and from 5 to 2 parts crotonic acid and drying the coated web, said dispersion being free of mineral pigment.

8. Process of making a paper product adapted for electrostatic recording which comprises impregnating a paper web with an aqueous composition comprising emulsified wax and a resinous homopolymer of vinyl benzyl trimethyl ammonium chloride, drying said web, coating said web with an aqueous composition comprising clay, starch, paraffine wax and resinous polyvinyl benzyl trimethyl ammonium chloride in the weight ratio of about 100 parts of clay, 40 parts of starch, 2 parts of paraffine and 7.5 parts of resinous polyvinyl benzyl trimethyl ammonium chloride, drying and calendering said coated web and then coating said web with an ammoniacal aqueous composition comprising a resinous copolymer of from 85 to 98 parts of vinyl acetate and from 5 to 2 parts of crotonic acid and drying said coated web, said last recited composition being free of mineral pigment.

9. A paper product adapted for electrostatic printing which comprises a sized paper web and a continuous layer of insulating coating on one side only thereof, said sized paper web containing an electrically conductive ingredient and having a greater electrical conductivity than said coating, the electrical resistance of the sized paper web being within the range from 1×10^{8} to 1×10^{5} ohms per square, said coating comprising the water-insoluble and electrically insulating evaporation residue of an aqueous composition containing a resinous copolymer of from 85 to 98 parts by weight of vinyl acetate and from 15 to 2 parts by weight of crotonic acid and a base selected from the group consisting of ammonia and water-soluble volatile amines in quantity sufficient to solubilize said resinous copolymer, said coating having a dielectric constant at least as high as that of said resinous copolymer and being free of mineral pigment.

10. A paper product as defined in claim 9 in which said conductive ingredient in the paper web is polyvinyl benzyl trimethyl ammonium chloride.

11. A paper product as defined in claim 10 in which the paper web is sized with paraffine wax.

12. A paper product as defined in claim 9 in which said insulating coating has a resistance of at least 1×10^{14} ohms per square.

13. A paper product as defined in claim 9 comprising a prime coating between said paper web and said insulating coating said prime coating, having a resistance within the same range as said paper web.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,110,621 November 12, 1963

Towers Doggett 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 6, line 23, for "free mineral pigments." read -- free of mineral pigment. --.

Signed and sealed this 28th day of April 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents