

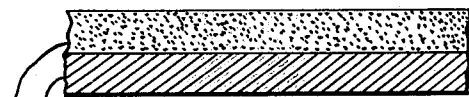
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ELECTROPHOTOGRAPHIC RECORDING PAPER AND METHOD OF MAKING

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PAPER BASE

COATING OF PHOTOCONDUCTIVE
ZINC OXIDE AND EVAPORATION
RESIDUE OF AQUEOUS SOLUTION
OF COPOLYMER VINYLACETATE-
CROTONIC ACID AND VOLATILE
AMINE OR AMMONIA

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**ELECTROPHOTOGRAPHIC RECORDING PAPER
AND METHOD OF MAKING**

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This invention relates to a coated paper product adapted for use as an electrophotographic recording or printing medium or receptor, and to a method for producing the same.

In the known electrophotographic recording and printing process it is necessary to have a surface which will accept an electrostatic charge and hold it for at least several minutes in the dark. Exposure of the charged surface to actinic radiation makes the exposed areas conductive and permits dissipation of the charge from those areas. To carry out the electrophotographic recording or printing process the entire photoconductive surface, while protected from light, is given an electrostatic charge as by friction or more commonly by exposure to an electrical corona discharge. The charged surface is then exposed to a pattern of actinic-radiation as through a transparency or by reflection from a patterned surface, which discharges the exposed areas but leaves the unexposed areas still charged in the form of a latent image. The exposed surface is then brought into contact with a colored resinous powder which preferably has a charge opposite to that of the still charged areas of the surface. The powder clings to the charged areas of the latent image but does not adhere to, or is easily removed from, the discharged or exposed areas. Thus a visible image is formed on the charged areas; this visible image may be transferred to another surface or it may be heated and fused in place on the areas of the original latent image.

It is apparent that for successful operation in this method of recording or printing the paper to be charged must have a surface which in the dark is dielectric or non-conducting to a very high degree so that it will hold an electrostatic charge for at least several minutes when not exposed to actinic light. The surface must be free from contamination by conductive matter and it must be substantially unaffected by variation in the moisture content of the ambient atmosphere.

It is known how to produce a paper with an electrophotographic coating by applying to the paper base a layer of photoconductive zinc oxide in a vehicle of volatile organic solvent containing an insulating resin dissolved therein. Hitherto, however, it has not been found possible to make a paper which is satisfactory for this process by coating the paper base with an aqueous coating composition. It is apparent that use of an aqueous vehicle is much to be preferred 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 resinous adhesives in an aqueous vehicle likewise has not given satisfactory insulating coatings, possibly because of the presence therein of emulsifying or dispersing agents required to produce stable aqueous dispersions of such resins.

The present invention provides a coated paper product having an electrophotographic coating layer deposited from an aqueous vehicle. The resulting product will

take and hold an electrostatic charge in the dark; it will when exposed to actinic light in certain areas release its charge in such areas but still retain the charge in unexposed areas for at least several minutes and long enough to permit visible development and fixation of the latent image formed by the unexposed charged areas.

An embodiment of the invention is illustrated in the accompanying drawing.

The paper product of the invention as illustrated in the drawing comprises a paper web or sheet having on one side thereof a layer or coating of finely particulate photoconductive zinc oxide, said layer being permeated, in at least its surface portion, by a water-insoluble, insulating decomposition residue of an aqueous solution of the reaction product of a resinous copolymer of from 85 to 98% by weight of vinyl acetate and from 2 to 15% by weight of crotonic acid with ammonia or a volatile amine, said decomposition having taken place in situ in the coating layer in the presence of and in contact with the finely divided zinc oxide particles.

No important strength characteristics are required in the use of this paper. Paper is strong enough if it possesses the strength of ordinary book paper weighing 75 to 90 grams per square meter. The surface of the paper should be level and it should be sized and/or coated sufficiently to hold the electro-photographic coating well on its surface without significant penetration thereof into the paper base. To ensure levelness and good hold-up of the electrophotographic coating it is preferred, but not essential, to interpose a layer of base coating between the paper and the electrophotographic layer and to calender said base coating. The paper base is not necessarily non-conductive but it should not contain soluble matter which might dissolve in the photoconductive coating and render it conductive in the dark.

A suitable paper base is one weighing from 75 to 90 grams per square meter and made from a moderately beaten paper-making furnish of bleached chemical wood pulp, clay filler, and rosin size precipitated by aluminum sulfate. Desirably this web is also coated on one side with a layer of base-coating amounting to 15 to 20 grams per square meter. A typical coating composition for use as base coat is the following:

BASE COAT FORMULA I

	Parts dry weight
Clay	100
Casein	13
Styrene-butadiene copolymer	5
Urea-formaldehyde resin	2
Sulfonated tallow	1
Tributyl phosphate	0.13
Water to make solids content 42%.	

Another suitable base coat has the following formulation:

BASE COAT FORMULA II

	Parts dry weight
Clay	60
Fine calcium carbonate	40
Soy protein	7
Styrene-butadiene copolymer	10
Melamine-formaldehyde resin	1.5
Spermaceti	2
Tributyl phosphate	0.015
Water to make solids content 40%.	

The paper base whether or not it bears a base coat thereon should be calendered to render it level before the electrophotographic coating is applied.

It is known that copolymers of vinyl acetate and crotonic acid containing from 98 to 85% by weight of vinyl acetate and from 2 to 15 percent by weight of copolymerized crotonic acid may be reacted with an aqueous solution of an alkali to form an aqueous solution of the crotonic acid copolymer. 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 solely of cost, ammonia is the preferred volatile alkali for use. In some cases ammonia may advantageously 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 such temperature should not exceed 150° 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. 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.

When an aqueous solution of a resinous copolymer as described above is spread upon a surface and dried, the salt decomposes, ammonia or amine is released and vaporized, and a water-insoluble film results. It is now found that the resulting film is an excellent electrical insulator or dielectric, and consequently the aqueous solution can be used in conjunction with zinc oxide pigment to yield a composite coating layer which is strongly insulating or dielectric in the absence of actinic radiation. Such a film can easily be given an electrostatic charge which will be held for a considerable period of time in the dark. When the surface is exposed to actinic light, the charge on the exposed area is dissipated. Areas not exposed still retain their charge. Thus although the copolymer itself is a non-conductor, it serves as a binder between the photoconductive particles for holding them together in the coating in substantially electrically conductive relation so that the application of actinic light to the zinc oxide particles renders the coating conductive in places where the light reaches the zinc oxide. The higher the crotonic acid content of the copolymer the more ammonia or amine must be used to dissolve it. In general copolymers containing from 97 to 93% by weight of vinyl acetate and from 3 to 7 percent by weight of crotonic acid are found to be very satisfactory for use.

Commercial resins which have essential properties substantially identical with those of the vinyl acetate-crotonic acid copolymers described above include the following: "Elvadex" resin made by E. I. du Pont de Nemours and Company of Wilmington, Delaware; "Stymer LF 25" resin 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.

It is generally conceded in the art that zinc oxide prepared by the French process appears to be better suited for use in electrophotographic coatings than is that made by the American process but zinc oxide made by the American process or in any other way which gives an equivalent product may be used.

Example 1

One example of a usable coating composition was made

by adding 2 parts by weight of 28% ammonia water to 100 parts of water. In the resulting solution was dissolved 20 parts of "Gelva C-3 V10" a vinyl acetate-crotonic acid copolymer containing about 5% of crotonic acid. Into this was stirred 120 parts of French process zinc oxide. No dispersing agent was used and the resulting suspension was grainy. Continuous agitation kept the pigment in suspension, however. The composition was applied as a top coating in amount equivalent to 25 grams, dry weight, per square meter to a sized, coated and calendered paper web as previously described, said web having thereon a base coating according to Base Coat Formula I. The top coating when dried at a temperature sufficiently high to vaporize the ammonia was water-insoluble and slightly grainy or sandy. The sheet was then calendered to render the surface smooth. The finished product was found to accept and hold an electrostatic charge in the dark. When exposed to light over parts of its area, the charge on the exposed surface area was dissipated, but a charge still remained on the unexposed surface area. The charged areas were developed by application of electroscopic powder which was thereafter fused in place to form a permanent image in the known manner.

In the foregoing Example 1 it is noted that the resinous copolymer served as the sole adhesive material binding the zinc oxide particles together and to the underlying base. For this purpose it is preferred to use from 15 to 20 parts by weight of said copolymer to each 100 parts by weight of zinc oxide.

If the tendency towards graininess or sandiness mentioned in Example 1 preceding is found objectionable it may be decreased or substantially obviated by using a volatile water-soluble amine instead of ammonia to react with the vinyl acetate-crotonic acid copolymer. The resin can be dissolved in water containing the volatile amine, preferably to yield a solution having a pH value above 8 and below 9.5 and very suitably about 9.0. Into this solution the zinc oxide pigment, preferably already in aqueous dispersion, can be stirred with the stirring being continued until the mixture becomes smooth.

Example 2

A solution was prepared by dissolving 1.75 parts by weight of normal butylamine in 100 parts of water. In this solution there was then dissolved 20 parts of a resinous copolymer of 97 parts vinyl acetate and 3 parts crotonic acid. Into the resin solution so formed was stirred 120 parts of French process zinc oxide, and stirring was continued until the composition was smooth and free from lumps. The composition was applied as a top coating in amount equivalent to 33 grams, dry weight, per square meter to a sized, coated and calendered paper web as previously described, said web having thereon a base coating according to Base Coat Formula I. The top coating was dried at 150° C. and calendered and was thereafter found to be water-insoluble. The finished product was found to accept and hold an electrostatic charge in the dark. When exposed to light over parts of its area the charge on the exposed surface area was dissipated but a charge still remained on the unexposed surface area. The latent image, or the charged areas, were then developed by application of electroscopic powder.

Example 3

Into 80 parts by weight of water were stirred 2 parts of diisopropylamine and 20 parts of a resinous copolymer made from 95 parts of vinyl acetate and 5 parts of crotonic acid. A clear solution resulted. A separate slurry was made from 50 parts of water, 120 parts of French process zinc oxide and 0.2 part of Tamol 731 (dispersing agent, said to be a sodium salt of a carboxylated polyelectrolyte made by Rohm & Haas Company). The two mixtures were then stirred together until smooth. The resulting composition was applied as a top coating in

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amount equivalent to 27 grams, dry weight, per square meter to a sized, coated and calendered paper web as previously described, said web having thereon a base coating according to Base Coat Formula II. This coating was dried at about 150° C. and calendered. It accepted and held an electrostatic charge in the dark. When exposed to light over parts of its area, the charge on the exposed area was dissipated, but a charge still remained on the unexposed surface area. The still charged areas subsequently were developed by application of electroscopic powder thereto.

Example 4

The procedure of Example 3 was repeated, except that this time the volatile amine morpholine was used in place of diisopropylamine. The resulting product was substantially identical with the product of Example 3.

If desired the electrophotographic coating may be applied in two steps as shown by the following Example 5, in which all parts are parts by weight.

Example 5

French process zinc oxide, 100 parts, was dispersed in 55 parts of water containing dissolved therein 0.2 part of Tamol. To this was then added 1.5 parts of polyvinyl alcohol adhesive dissolved in 11 parts of water. The resulting liquid was applied to a calendered base-coated paper web in amount equivalent to 22 grams, dry weight, per square meter. The coated sheet was dried and then given a wash coat of an aqueous solution containing 5% by weight of the ammonium salt of the resinous product made by copolymerizing 95 parts of vinyl acetate and 5 parts of crotonic acid. About 3 grams, dry weight, per square meter of resin was applied by this treatment. The coated surface after being dried was water-insoluble. It was smooth and level. Part of the web was calendered to increase its gloss to some extent. The calendering did not appear to affect the electrical properties of the sheet. Both the calendered and the uncalendered portions of the sheet were found to accept an electrostatic charge and hold it in the dark. When part of the charged area was exposed to light the charge on that area was dissipated, but a charge still remained on the unexposed area. The still charged areas were then developed in the known manner by application of electroscopic powder which was thereafter fused in place to form a permanent image.

In the foregoing example 5 it will be noted that the zinc oxide is first bound loosely to the paper base by means of a small quantity of adhesive (polyvinyl alcohol) other than the insulating copolymer of vinyl acetate and crotonic acid. The quantity of such other adhesive must be so low that the zinc oxide layer is sufficiently porous to allow penetration by the later-applied solution of the ammonium or amine salt of vinyl acetate-crotonic acid copolymer. The wash-coating of copolymer salt should be of sufficiently low viscosity so that it can penetrate into the layer of zinc oxide rather than remain substantially on the surface of the zinc oxide layer. Hence it is preferred to use wash-coat solutions containing not over 10% by weight of the copolymer. The copolymer salt in the wash-coat can be formed by reacting the vinyl acetate-crotonic acid copolymer with ammonia or with a water-soluble volatile amine as desired.

Adhesives other than polyvinyl alcohol may be used provided that they do not adversely affect the photoconductive properties of the zinc oxide. Casein has been found to be less satisfactory than, e.g., starch, carboxymethyl cellulose, and polyvinyl acetate emulsion.

This application is a continuation-in-part of my application Serial No. 821,678, filed June 22, 1959, and now abandoned.

I claim:

1. Process for the production of a paper product adapted for electrophotographic use which comprises coating a surface of a paper base with an aqueous dispersion

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consisting essentially of water, finely divided photoconductive zinc oxide and a relatively small amount compared to said zinc oxide of a water dispersible adhesive, drying said coating and applying thereto a coating consisting essentially of an aqueous solution of the salt of a volatile base selected from the group consisting in ammonia and volatile amines and a resinous copolymer of from 98 to 85% by weight of vinyl acetate and from 2 to 15% by weight of crotonic acid and drying the last named coating.

2. Process as defined in claim 1 in which the volatile base is ammonia.

3. Process as defined in claim 1 in which the volatile base is an amine.

4. Process for the production of paper adapted for use for electrophotographic printing which comprises coating a paper base with an aqueous solution of the salt of a volatile base selected from the group consisting in ammonia and volatile amines and a resinous copolymer of from 98 to 85% by weight of vinyl acetate and 2 to 15% by weight of crotonic acid, said solution containing a major proportion compared to said copolymer of finely divided photoconductive zinc oxide suspended therein and drying said coating.

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

6. Process as defined in claim 4 in which the volatile base is an amine.

7. An electrophotographic printing receptor comprising: a base and a coating on said base comprising a major proportion of a pigment consisting essentially of finely divided photoconductive particles and a minor proportion compared to said pigment of a binder for said particles consisting essentially of a water-insoluble and electrically insulating evaporation residue of an aqueous solution of a water soluble salt of a copolymer of vinyl acetate and crotonic acid and a volatile base selected from the group consisting in ammonia and volatile amines, and said particles being held together by said binder in substantially electrically conducting relation.

8. The electrophotographic printing receptor defined in claim 7 further characterized by said copolymer consisting of from 98 to 85% by weight of vinyl acetate and from 2 to 15% by weight of crotonic acid.

9. An electrophotographic printing receptor comprising: a base and a photoconductive layer on said base consisting of a major proportion of a multiplicity of finely divided photoconductive particles in substantially electrically conducting contact, and a minor proportion of means for binding said particles to each other and to said base and preventing said particles from adsorbing atmospheric moisture comprising a coating on said particles of the water-insoluble evaporation residue of an aqueous solution of a water soluble salt of a copolymer of vinyl acetate and crotonic acid and a volatile base selected from the group consisting in ammonia and volatile amines.

10. The electrophotographic printing receptor defined in claim 9 further characterized by said copolymer consisting of from 98 to 85% by weight of vinyl acetate and from 2 to 15% by weight of crotonic acid.

11. An electrophotographic printing receptor comprising: a base, a layer of photoconductive pigment on said base, and means for preventing said pigment from adsorbing atmospheric moisture comprising a coating on said pigment of the water-insoluble evaporation residue of an aqueous solution of a water soluble salt of a copolymer of vinyl acetate and crotonic acid and a volatile base selected from the group consisting in ammonia and volatile amines, the amount of said pigment being greater than the amount of said evaporation residue.

12. The electrophotographic printing receptor defined in claim 11 further characterized by said copolymer consisting of from 98 to 85% by weight of vinyl acetate and from 2 to 15% by weight of crotonic acid.

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