United States Patent

Rowe

[15] **3,652,268**

[45] **Mar. 28, 1972**

[54] **BARRIER COATED ELECTROPHOTOGRAPHIC SHEET SUITABLE FOR LIQUID DEVELOPMENT**

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[22] Filed: **Mar. 16, 1970**

[21] Appl. No.: **19,954**

[52] **U.S. Cl.** .....**96/1.5**, 96/1 R, 117/37, 117/201, 117/204, 117/218, 162/138

[51] **Int. Cl.** **G03g 5/04**

[58] **Field of Search** 96/1.5, 1.8, 1; 162/138; 117/201, 204, 218, 37

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[57] **ABSTRACT**

An electrophotographic reproduction process and copy sheet therefor for development of a latent electrostatic image on the copy sheet by a liquid developer wherein the copy sheet comprises a conductive base sheet having a thin barrier coating on each side thereof, the coating comprising a highly dielectric insulating material and a conductor material which is either a polymeric quaternary ammonium halide or an ammonium salt of an alkyl aryl sulfonate, and one side having a second coating thereon comprising a thin insulating coating or a photoconductor coating for receiving an electrostatic image.

23 Claims, 3 Drawing Figures

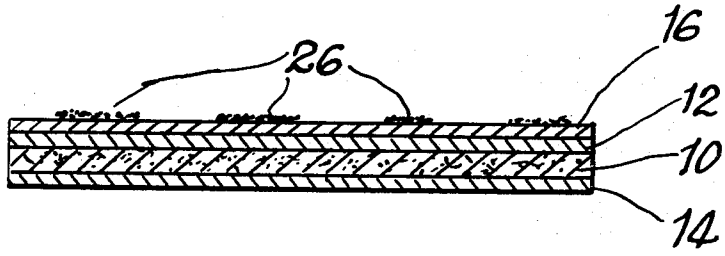


FIG. 1

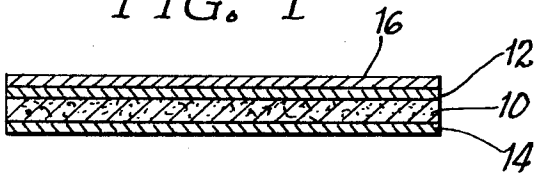


FIG. 2

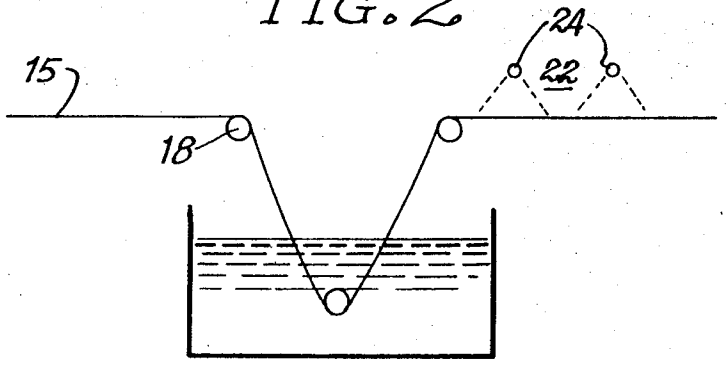
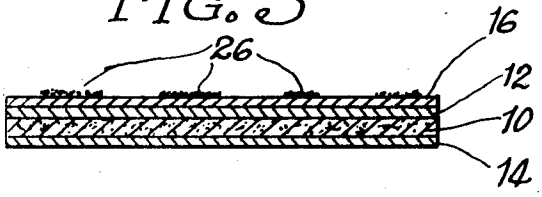


FIG. 3



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BARRIER COATED ELECTROPHOTOGRAPHIC SHEET SUITABLE FOR LIQUID DEVELOPMENT

This invention relates to an electrostatic copy process and more particularly to copy paper for use in electrostatic reproduction processes, such as the Videograph process of the A. B. Dick Company, or the Electrofax process.

In the Borden et al. U.S. Pat. No. 2,879,422, Crews U.S. Pat. No. 2,928,973, Borden U.S. Pat. No. 2,978,607, Barnes et al. U.S. Pat. No. 2,996,573, Evans et al. U.S. Pat. No. 3,017,625, and Relph et al. U.S. Pat. No. 3,075,859, description is made of the process identified as the Videograph process. Briefly described, use is made of a cathode ray tube which directs a video signal onto an array of conductive wires extending through the face of the tube. The wires discharge onto a grounded writing medium having a dielectric insulating coating, during advancement of the writing medium adjacent the face of the tube, to form a latent electrostatic image which is retained on the dielectric insulating coating until developed by toner particles in accordance with conventional electrostatic copy technique.

A writing medium suitable for use in the practice of the Videograph copy process is described in the aforementioned patent of Relph et al. in which the writing medium comprises a paper base sheet having a continuous dielectric insulating coating on one surface and in which the paper base sheet is rendered more conductive as by modification to include a humectant and/or a water soluble, water stable, ionizable metal salt uniformly distributed throughout the base sheet.

The paper base sheet itself is sufficiently conductive but the conductivity can be stabilized against change in response to change in humidity and otherwise rendered more conductive by the modification described or by other techniques, such as impregnation to include conductive carbon in the base sheet or by wetting the base sheet with aqueous or other liquid electrolyte immediately prior to receiving the electrostatic discharge from the cathode ray tube.

A writing medium of the type described has been found to be suitable for use in the development of copy with dry toners wherein the dry toner particles are dusted, cascaded, or otherwise applied over the surface containing the latent electrostatic image whereby toner particles are retained by the imaged portions for visual development while the non-imaged portions remain free of toner particles. Thus, clean and clear copy is produced without noticeable background color.

When the latent electrostatic image is developed by means of a liquid developer, such as described in the Metcalfe et al. U.S. Pat. No. 2,907,674, or the Mayer U.S. Pat. Nos. 2,891,811 and 2,877,133, a considerable amount of discoloration occurs in the copy sheets. It is believed that this stems, at least in part, from the exposure of the back side of the paper base sheet to the liquid developer whereby the paper base sheet becomes impregnated with developer during development of the latent electrostatic image. Such liquid developer is retained in the paper base sheet whereby toner particles remain to effect the described discolorations.

In copending application, Ser. No. 859,949, filed Sept. 22, 1969, and entitled "Copy Process for Electrostatic Printing," description is made of an electrostatic reproduction process using a copy sheet which comprises a conductive base sheet having a thin continuous insulating coating on one side for receiving the electrostatic image and which is preferably treated on the other side or back side with a humectant to increase the electrical conductivity of the base sheet. Thereafter the back side is further treated to provide a thin, continuous coating thereon which serves as a barrier to provent absorption of developer liquid and which has an electrical resistivity of not more than 1.0×10^9 ohms per square centimeter. The copy sheet described in the aforementioned copending application represents a significant improvement over copy sheets heretofore known in that it virtually eliminates discoloration of the copy sheets during development thereof by absorption of developer liquid. However, the copy sheet is expensive to prepare in that it is necessary to provide three separate treatments for its preparation.

It is accordingly an object of the present invention to provide an electrostatic reproduction process and copy sheet therefor wherein the copy sheet is coated on both sides with a conductive barrier coating composition and is thereafter top coated to provide a dielectric insulating coating or a photoconductive coating which receives the latent electrostatic image.

It is a related object of the present invention to provide a process of the type described wherein use is made of a copy sheet which retains the desired characteristics of a highly dielectric insulating coating or a photoconductive insulating layer on an electrically conductive base sheet for receiving and retaining the electrostatic image; in which dry copy can be produced within a short period of time after development of the latent image; and, in which good clean copy can be produced by electrostatic techniques.

These and other objects and advantages of the invention will appear hereinafter, and, for purposes of illustration, but not of limitation, an embodiment of the invention is shown in the accompanying drawing wherein:

FIG. 1 is a sectional view of a copy sheet embodying the concepts of the invention;

FIG. 2 is a schematic view of the visual development of the latent electrostatic image on a copy sheet of the type shown in FIG. 1; and,

FIG. 3 is a sectional view similar to that of FIG. 1 after development of the latent electrostatic image.

The concepts of the present invention reside in an electrostatic reproduction process and copy sheet for use in same wherein the copy sheet comprises a conductive base sheet which has been coated on both sides thereof with a composition comprising a material which is a barrier to the penetration of liquid and a water soluble conductor material selected from the group consisting of a polymeric quaternary ammonium halide and an ammonium salt of an alkyl aryl sulfonate to provide a thin, continuous conductive barrier coating on the copy sheet. Thereafter, one side of the treated base sheet is provided with a conventional coating adapted to receive the electrostatic image. For example, for use in the Videograph process, the copy sheet is provided with a dielectric insulating coating which operates to retain the latent electrostatic image formed thereon. For use in the Electrofax process, the copy sheet is provided with a photoconductive layer or coating which forms a latent electrostatic image in response to a corona discharge followed by exposure to light modulated by an image.

It has been found that the conductive barrier coating on the conductive base sheet imparts the desired conductivity to the base sheet paper, and at the same time prevents absorption of the liquid developer composition by the base sheet to thereby provide good clean copy on development of the latent electrostatic image.

A wide variety of materials may be used to provide the barrier coating in accordance with the invention, such as polyvinyl acetate, acid-modified polyvinyl acetate such as crotonic acid-modified polyvinyl acetate, polyethylene, wax, unmodified or oil-modified alkyd resins, nitrocellulose, ethyl cellulose, carboxymethyl cellulose, cellulose acetate, shellac, polyester resins, organo silicon resins, polyvinyl chloride, copolymers of butadiene and styrene, polyvinyl butyral, acrylic acid polymers and copolymers as well as a variety of other dielectric materials known to those skilled in the art. However, it is generally preferred in the present invention to make use of polyvinyl alcohol since it appears to be more compatible with the conductor material, and is easier to work with owing to its solubility in water.

The water soluble conductor materials useful in accordance with the invention include polymeric quaternary ammonium halides, and particularly the chlorides, and ammonium salts of alkyl aryl sulfonates. Preferred polymeric ammonium halides are the polydialkyl divinyl and polydialkyl diallyl ammonium halides wherein the alkyl group contains one to four carbon atoms, such as methyl, ethyl, propyl, etc. Particularly suitable is polydimethyl diallyl ammonium chloride which is commercially available under the trademark "Calgon 261."

A wide variety of ammonium alkyl aryl sulfonates are similarly suitable for use in the present invention, and particularly those where the alkyl group contains 1–20 carbon atoms and the aryl group is either a benzene or naphthalene group. Particularly preferred is RP 505 from Monsanto which is the ammonium salt of an alkylated benzene sulfonate.

It is possible, and frequently preferred, to include, in the coating various filler and extender materials which operate to increase the stability of the coating and the increase of its conductivity. For this purpose, use can be made of vinyl acetate emulsion, such as vinyl acetate emulsion 25-1025 from National Starch, and/or hydrated ammonium silicates.

The relative proportions of the dielectric material, the conductive material and the filler and/or extender, when present, in the composition for treating the conductive base layer are not critical. It is generally sufficient that the barrier material and the conductive material each be present in an amount within 0.1 and 20 percent by weight, and that the vinyl acetate emulsion, when present, constitute between 1 and 25 percent by weight of the composition. The hydrated ammonium silicates preferably constitute between 1 and 15 percent by weight.

Having described the basic concept of the invention, reference is now made to the following examples, which are provided by way of illustration, and not by way of limitation of specific embodiments of the invention. All parts given are parts by weight.

EXAMPLE 1

10 parts	Ammonium alkyl benzene sulfonate (RP 505-Monsanto)
10 parts	6% solution of polyvinyl alcohol in water (Evanol 7251-DuPont)
250 parts	Water

The foregoing composition is used to impregnate both sides of a paper base sheet in dry coating weights of 2–3 pounds per 3,000 square feet of paper on each side. The resulting paper has a resistivity of 4×10^{12} ohm-cm. at 90° F. and 10 percent relative humidity, and 8×10^{7} ohm-cm. 72° F. and 50 percent relative humidity.

EXAMPLE 2

1080 parts	12% solution of polyvinyl alcohol in water
270 parts	Polydimethyl diallyl ammonium chloride
900 parts	25% hydrated ammonium silicate clay in water (KCS Georgia Koolinite Clay)
450 parts	Vinyl acetate emulsion (National Starch emulsion 25-1025)
900 parts	Water

The foregoing composition is applied to both sides of a base sheet by means of a blade to provide a coating of 2 to 4 lbs. per 3,000 square feet on each side. Tests at 72° F. and 50 percent relative humidity and revealed a surface resistance of 10^{8} ohms-cm and 90° F. and 10 percent relative humidity.

EXAMPLE 3

1,100 parts	12% solution of polyvinyl alcohol in water
295 parts	Ammonium alkyl benzene sulfonate(RP 505-Monsanto)
930 parts	25% hydrated ammonium silicate in water
480 parts	Vinyl acetate emulsion
1,000 parts	Water

The foregoing composition may be applied to a base sheet by conventional procedure to apply a uniform coating across the base sheet in a coating weight of 2–14 lbs. per 3,000 square feet of surface area per side, followed by air drying or drying at an elevated temperature within the range of 125° to 250° F.

A sectional view of a base sheet treated in accordance with the present invention is shown in FIG. 1, and comprises a conductive base sheet **10** formed of conventional paper having a thin coating **12** and **14** on each side of the base sheet comprising one of the compositions of Examples 1–3. The coating **12** and **14** may be applied in a conventional manner, and contain between 5–50 percent of the barrier material, 1.0–75 percent of the conductive material, and, when present, 15–40 percent of the hydrated ammonium silicate and up to 40 percent by weight of vinyl acetate plus emulsifier.

As shown in FIG. 1, the copy sheet also includes a second coating on one surface thereof wherein the section coating **16** comprises either a thin insulating coating or a photoconductor coating for receiving an electrostatic image. For example, when the copy sheet is to be used in the Videograph process, the treated base sheet having the thin conductive barrier coatings **12** and **14** thereon is provided with a second coating **16** on one surface thereof wherein the coating **16** is formed of a high dielectric insulating material which operates to retain the latent electrostatic image on the copy sheet. For this purpose, use can be made of polyvinyl acetate or a polyvinyl acetate acidic polymer, such as polyvinyl acetate with crotonic acid.

As described in the aforementioned patent of Relph et al., the dielectric insulating coating **16** can also be formulated of polyethylene, wax, unmodified or oil-modified alkyd resin, nitrocellulose, ethylcellulose, cellulose acetate, shellac, polyester resin, organo-silicon resin, polyvinyl chloride, butadiene-styrene copolymer, polyvinyl butyral, acrylic acid polymer or copolymer. Such high dielectric insulating materials may be applied onto the base sheet from solvent solution or from an aqueous dispersion in coating weights of from 2 to 4 pounds per 3,000 square feet of surface area. Instead of providing the dielectric insulating layer **16** by coating technique, a film of the dielectric insulating material can be laminated onto the one side of the paper base sheet.

The following examples are provided by way of illustration of the preparation of a high insulating layer on a base sheet which has been treated on both sides with one of the compositions of Examples **1–3**.

EXAMPLE 4

36.5% by weight	Oil-modified alkyl resin (50% solids) (Aroplaz 7424 of Archer-Daniels-Midland
12.01% by weight	Resin(Piccopale 100-Pennsylvania Industrial Chemical Company)
21.0% by weight	Xylene
30.5% by weight	Barium sulphate

EXAMPLE 5

1.40% by weight	Barium sulphate
0.8% by weight	Ammonium hydroxide
69.1% by weight	Water
14.01% by weight	Polyvinyl acetate copolymer
0.1% by weight	Nopco JMY(Diamond-Shamrock Co.)
2.0% by weight	Butanol

Application of the coating composition can be made onto the paper base sheet by conventional coating procedure to apply a uniform layer across the base sheet in a coating weight of 2–14 pounds per 3,000 square feet of surface area, followed

by air drying or drying at an elevated temperature within the range of 125°–250° F.

For use in the Electrofax process, the base sheet is treated in accordance with the concept of the present invention and thereafter provided with a thin coating of an inorganic or organic photoconductor, which is preferably admixed with an insulating material of the type described above which operates as a binder for the photoconductor material. Such binders preferably have a resistivity greater than 10^{12} ohm cm. In addition to the foregoing materials, use can also be made of other resinous binders, such as a Union Carbide resin, identified as VMCH, which is formulated of 86 percent by weight vinyl chloride, 13 percent by weight vinyl acetate and 1 percent by weight maleic acid, polystyrene, acrylate and methacrylate ester polymers, Acryloid A10 and chlorinated rubber, such as Parlon.

A wide variety of photoconductors may be used in preparing the photoconductive layer. For example, use can be made of conventional zinc oxide photoconductors as described in the Grieg U.S. Pat. No. 3,052,539, or in the Middleton U.S. Pat. No. 3,121,006. Use can also be made of organic photoconductors, including polymers of N-vinyl carbazole or the dimer of an N-vinyl carbazole as described in copending application, Ser. No. 612,432, with or without various sensitizers.

The following examples are provided by way of illustration of the preparation of a photoconductive layer on a base sheet which has been preferably treated with one of the compositions of Examples 1–3.

EXAMPLE 6

150 parts by wt.	Zinc oxide
100 parts by wt.	Alkyd resin (Rhodene L9/50)
100 parts by wt.	Toluene solvent

EXAMPLE 7

1.0 gram	N-vinyl carbazole dimer
	Vinyl chloride (86%)-vinyl acetate(13%)-maleic acid (1%) resin (VMCH)
20 cc.	Methylene chloride resin

The foregoing compositions are applied to the treated base sheet so as to provide a coating weight of within the range of 0.25–25 pounds per 3,000 square feet of surface area.

A copy sheet prepared in accordance with the concept of the present invention can be completely immersed in the liquid developer for development of the latent electrostatic image without discoloration of the back side of the copy sheet. As shown in FIG. 2, the copy sheet 15 which has been treated in accordance with the present invention is advanced over roller 18 into a bath of the liquid developing composition whereby toner particles are retained by the electrostatically imaged portions of sheet 15. The retained diluents on the copy sheet are rapidly eliminated by advancing the developed copy sheet through a hot zone 22, to which heat may be supplied by conventional means, such as the infra-red lamps 24, or by conventional electrical resistivity heaters or a circulating hot air stream.

The resulting developed copy sheet is shown in FIG. 3 wherein the coating 16 on one side of the conductive base sheet 10 contains the visual image in the form of toner particles 26 which are attracted to the coating 16 in the areas corresponding to the areas of the coating 16 containing the latent electrostatic image.

It will be apparent from the foregoing that I have provided a new and improved electrostatic copy process and copy sheet for use therein which can be employed in either the Videograph process or the Electrofax process to provide good clean copy without discoloration of the copy sheet caused by absorption of the liquid developer in the copy sheet.

It will be understood that various changes and modifications may be made in the details of formulation, application and use without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. An electrophotographic reproduction sheet for development of a latent electrostatic image by a liquid developer comprising a conductive base sheet having a thin continuous conductive barrier coating on each side thereof, said coating comprising a resinous material which is a barrier to the penetration of liquid and a conductor material selected from the group consisting of a polymeric quaternary ammonium halide selected from the group consisting of polydialkyl divinyl ammonium halides and polydialkyl diallyl ammonium halides and an ammonium salt of an alkyl aryl sulfonate, and a second coating on one side of said base sheet, said second coating comprising a material adapted to receive an electrostatic image.

2. A reproduction sheet as defined in claim 1 wherein said barrier material is polyvinyl alcohol.

3. A reproduction sheet as defined in claim 1 wherein said conductor material is polydimethyl diallyl ammonium chloride.

4. A reproduction sheet as defined in claim 1 wherein the conductor material is an ammonium salt of an alkyl aryl sulfonate in which the aryl group is selected from a group consisting of a benzene group and a naphthalene group and contains one or more alkyl groups having 1–20 carbon atoms.

5. A reproduction sheet as defined in claim 1 wherein coating contains 5–50 percent by weight of said barrier material and 1–75 percent by weight of said conductor material.

6. A reproduction sheet as defined in claim 1 wherein said barrier coating includes vinyl acetate.

7. A reproduction sheet as defined in claim 6 wherein said vinyl acetate is present in an amount up to 40 percent by weight of said coating.

8. A reproduction sheet as defined in claim 1 wherein said barrier coating includes a hydrated ammonium silicate.

9. A reproduction sheet as defined in claim 8 wherein said ammonium silicate is present in an amount within the range of 15–40 percent by weight of said coating.

10. A reproduction sheet as defined in claim 1 wherein said barrier coating is present in a dry coating weight of 2–14 pounds per 3,000 square feet of surface area.

11. A reproduction sheet as defined in claim 1 wherein said material for receiving the electrostatic image is selected from the group consisting of a high insulating material and a photoconductive material.

12. An electrostatic copy process in which use is made of a liquid developer for visual development of a latent electrostatic image comprising the steps of forming a latent electrostatic image on a copy sheet formed of a conductive base sheet, said base sheet having a thin continuous conductive barrier coating on each surface comprising a resinous barrier material which is a barrier to the penetration of liquid developer and a comductor material selected from the group consisting of a polymeric quaternary ammonium halide selected from the group consisting of polydialkyl divinyl ammonium halides and polydialkyl diallyl ammonium halides and an ammonium salt of an alkyl aryl sulfonate, and a second coating on one surface, said second coating comprising a material adapted to receive an electrostatic image and wetting the copy sheet with the developer liquid whereby the latent electrostatic image becomes visually developed without development of excessive color in the base sheet.

13. The process as defined in claim 12 wherein said barrier material is polyvinyl alcohol.

14. The process as defined in claim 12 wherein said conductor material is polydimethyl diallyl ammonium chloride.

15. The process as defined in claim 12 wherein the conductor material is an ammonium salt of an alkyl aryl sulfonate in

which the aryl group is selected from a group consisting of a benzene group and a naphthalene group and contains one or more alkyl groups having 1–20 carbon atoms.

16. The process as defined in claim 12 wherein coating contains 5–50 percent by weight of said insulating material and 1–75 percent by weight of said conductor material.

17. The process as defined in claim 12 wherein said conductive barrier coating includes vinyl acetate.

18. The process as defined in claim 17 wherein said vinyl acetate is present in an amount up to 40 percent by weight of said coating.

19. The process as defined in claim 12 wherein said coating includes a hydrate ammonium silicate.

20. The process as defined in claim 19 wherein said ammonium silicate is present in an amount within the range of 15–40 percent by weight of said coating.

21. The process as defined in claim 12 wherein said coating is present in a dry coating weight of 2–14 pounds per 3,000 square feet of surface area.

22. The process as defined in claim 12 wherein said second coating is adapted to receive an electrostatic image and is selected from the group consisting of a high insulating material and a photoconductive material.

23. An electrophotographic reproduction sheet for development of a latent electrostatic image by a liquid developer comprising a conductive base sheet having a thin continuous conductive barrier coating on each side thereof, said coating comprising polyvinyl alcohol, a conductor material selected from the group consisting of a polymeric quaternary ammonium halide selected from the group consisting of polydialkyl divinyl ammonium halides and polydialkyl diallyl ammonium halides and an ammonium salt of an alkyl aryl sulfonate, vinyl acetate and a hydrated ammonium silicate, and a second coating on one side of the said base sheet, said second coating comprising a material adapted to receive an electrostatic image.

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