

[54] **METHOD OF ELECTROPHOTOGRAPHIC SENSITIVE PAPER**

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[73] Assignee: **Xerox Corporation**, Stamford, Conn.

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Related U.S. Application Data

[62] Division of Ser. No. 52,311, July 6, 1970, Pat. No. 3,720,514.

[52] U.S. Cl. **117/218, 96/1.5, 117/200, 117/213, 162/138**

[51] Int. Cl. **B44d 1/18, G03g 5/00, B44d 1/10**

[58] Field of Search **117/218; 96/1.5; 162/138, 181, 162/181 C**

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Primary Examiner—J. Travis Brown

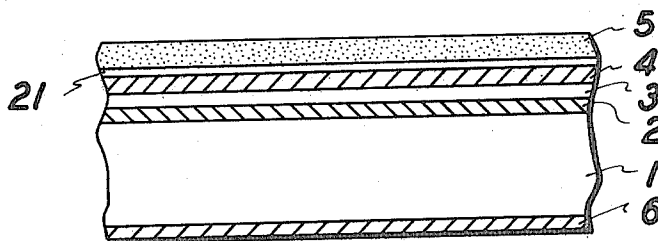
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[57] ABSTRACT

Electrophotographic paper is provided which comprises a waterproof paper treated with inorganic colloidal oxide dispersion having an electroconductive layer coated on the treated surface and a photoconductive insulating layer residing on the surface of the electroconductive layer.

2 Claims, 3 Drawing Figures



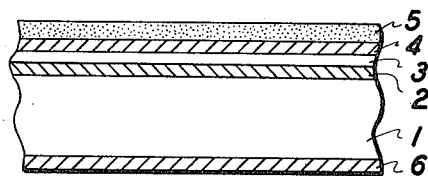


FIG. 1

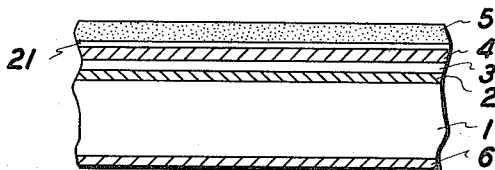


FIG. 2

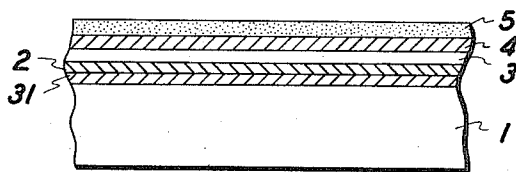


FIG. 3

METHOD OF ELECTROPHOTOGRAPHIC SENSITIVE PAPER

This application is a divisional of co-pending application Ser. No. 52,311, filed July 6, 1970, now U.S. Pat. No. 3,720,514.

BACKGROUND OF THE INVENTION

This invention relates to electrophotography and more specifically to electrophotographic members and methods for providing same.

In the well known art of electrophotography, commonly called xerography, more fully described in U.S. Pat. No. 2,296,671, it is known that a visible image may be formed by employing sensitized and unsensitized paper. Where unsensitized paper is employed an electrophotographic member, normally a photoconductive member, is charged, exposed, and developed and then the image so formed is transferred to the unsensitized paper and normally fused thereon using appropriate means. When it is desired to form an image directly on the paper eliminating the transfer step a sensitized paper is employed which is charged and selectively illuminated and then developed. Such electrophotographic sensitive paper or electrostatic recording paper medium usually comprises a base paper which is given a special treatment so as to acquire a high degree of electroconductivity in a particularly wide range of humidity and an insulative recording layer formed thereover by spreading or other means. Treatments usually employed for conferring such electroconductivity are broadly divided into two classes: to one class belongs the methods by which such substances as hygroscopic inorganic salts, hygroscopic polyhydroxy compounds, cationic active agents, or quaternary ammonium salt polymers are caused to impregnate the fiber structure of the paper through its entire thickness; and the other class of treatment given for conferring electroconductivity is such that a continuous film of low resistance is formed on the surface of the side closer to the recording layer. The former compound may be used either alone or in combination. Film forming agents may be employed such as polyacrylic acid, salts thereof or polyvinyl alcohol. However, since these substances have relatively low electroconductivity in an environment having low humidity, recent methods have come to employ polymers derived from monomers containing the structure of quaternary ammonium salts. Polymers of this type are able to form films which exhibit a high degree of electroconductivity in a wide range of humidity. It has been found, however, that where it is desired to obtain an image of continuous tone equivalent in quality to that of the conventional silver halide process by electrophotography, methods of treatment of the base paper known in the art often prove unsatisfactory in terms of performance. Inadequacy of performance is due to a number of problem areas which exhibit themselves in the unsatisfactory quality of reproduction obtained.

When it is desired to obtain a continuous tone image by developing an electrostatic latent image employing a liquid developing agent comprising extremely fine toner particles, it is found that the nature of the base employed affects the highlight areas of the reproduction so obtained. If the base employed has insufficient smoothness or the electroconductive film is not a complete continuous film in the lateral direction, it is found

that the highlight area for example fails to be developed to a low density uniformly. This is caused by the toner depositing in fine or finer areas to a relatively higher density apparently in conformity to the structure of the base giving rise to an extremely objectionable appearance. It is found that if the smoothness and electrical quality of the base are not adequate there may result a slight variation in thickness and electrostatic capacity of the sensitive layer which may cause corona discharge depriving the surface charge density of uniformity and, consequently, making photosensitivity non-uniform. This absence of uniformity becomes conspicuous when substantially all surface charge is removed and only a small portion of it is permitted to remain as a consequence of exposure to light. This explanation is found to agree with experimentation and satisfactorily explains why such unevenness is observed clearly in about two stages of the highlight area having a very low density and not observed either in the area of high density or in the completely discharged or when, for example, an optical wedge is developed on an electrophotographic sensitive paper. That roughness of the highlight area of the print obtained will substantially affect the clarity of the print is known. This shortcoming tends to become detrimentally conspicuous particularly when obtaining a multi-color image with continuous tone as compared with a monochromatic image. In order to remedy this problem, i.e. to obtain adequate smoothness of the paper base and the proper electroconductive properties, a polished metal layer or a vacuum deposited metal overlying a smooth plastic base or the like may be employed. Thus, it is seen that a base having a high smoothness and extremely high degree of electroconductivity is particularly preferable for the reproduction of continuous tone images. However, it is extremely difficult to fabricate such a base from paper material which is porous and characteristically has fiber-like rough surfaces and is inherently less electroconductive than metals.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide electrophotographic recording media devoid of the above noted disadvantages.

Another object of this invention is to provide electrophotographic sensitive paper having the advantages of a smooth, metallic base in the reproduction of continuous tone images.

Still another object of this invention is to provide an electrostatic paper recording medium which is particularly suitable for the reproduction of continuous tone multi-color images.

Yet, another object of this invention is to provide a method whereby electrophotographic recording media comprising paper may be rendered suitable for the reproduction of continuous tone images.

Still another object of this invention is to provide a novel electrophotographic system.

Yet, another object of this invention is to provide a novel method for producing electrophotographic paper.

These and other objects are accomplished in accordance with the system of the present invention by providing an electrophotographic paper comprising treating a waterproofed paper with a processing liquid comprising colloidal silica and/or colloidal alumina having a non-volatile content of at least 70 percent by weight

forming on the treated surface of the base an electroconductive layer having as a principal ingredient a member selected from the group consisting of quaternary ammonium salt polymers, polyvinyl benzene sulfonic acid, and the water-soluble salt of said acid, then forming an electrophotographic sensitive layer on the electroconductive layer so obtained. It is known that to provide water resistance to paper generally involves the impregnation by a water resistant binding agent and inorganic pigment particles, such as, for example, clay or barium sulfate, resulting in a water resistant paper which when immersed in an organic solvent, is found not to substantially impede the penetration by organic solvents. Further, such water resistant paper as above described has been shown to provide insufficient electroconductivity and, therefore, is found to be unsuitable without further modification as a base paper for electrophotography. In order to improve the electroconductivity of the base paper, a resin layer is provided which overlies the water resistant layer. The water resistant layer is usually composed of clay in combination with materials, such as, starch, casein, styrene-butadiene copolymers or butadiene-acrylester copolymers serving as a binding agent. Since the aqueous solution of this resin possesses a high water repellence, it cannot be applied to the base because it is repelled very strongly. It is difficult to solve this problem by changing the solvent since any resin having high electroconductivity is sparingly soluble in organic solvents and, therefore, can only be dissolved using water so that a surface active agent may be employed to subdue or eliminate this repellence. Since the pigment layer is porous, the solution as spread is found to penetrate into the pigment layer more quickly and as a consequence thereof a laterally continuous film cannot be formed. Consequently, when an electrophotographic layer is formed thereon, there is observed a heavy deposition of toner particles in the areas of low charged density.

Without resorting to constant adjustment as hereinbefore mentioned the system of the present invention contemplates employing a water type inorganic colloidal solution which when applied to a smooth water resistant layer may be spread thereon without being repelled at all and is able to fill voids present in the porous structure conferring strong hydrophillic properties to the surface thereof. The aqueous solution of the resin to be employed having a high electroconductivity may be spread uniformly without resort to the use of a surface active agent. It is found that the film formed upon drying is perfectly continuous in the lateral direction. Although it is seen that a two step treatment is involved, the conductive paper base obtained as a result of the treatment has been found to have a smoothness equal to a plastic film covered by a layer of vacuum deposited metal and, consequently, may serve as an ideal base in the reproduction of continuous tone images.

Although any suitable inorganic colloidal solution may be employed in the system of the present invention, colloidal silica and colloidal alumina are preferred. Of these two, colloidal alumina is found to form a film having a higher degree of electroconductivity than the silica film in a wide range of humidity conditions. It is, therefore, more desirable to employ colloidal alumina in an environment where there is a requirement for a base of particularly low resistance. Water dispersions of both colloidal alumina and colloidal silica are commercially available. If desired, a small quan-

tity of film forming substance may be added to the colloidal dispersion. However, it is preferred to control the addition of any such film forming substance to a maximum of up to about 30 percent by weight of the inorganic colloidal dispersion. The film forming substance so added may be in the form of a water emulsion of a water-insoluble resin or of a resin which becomes insoluble upon hardening. Since colloidal silica offers a higher degree of colloidal stability, it is found to permit the incorporation of many substances without disturbing the dispersion. In the case of colloidal alumina, on the other hand, it is found desirable to employ the substance by itself. The colloid may be employed in a concentration of about 0.1 grams (g) to 3 g per meter squared (M^2) of the area covered and preferably from about 0.2 g to about 1.5 g per M^2 . It is found in the case where the inorganic colloid is employed alone that a coating of excessive thickness is undesirable because the colloidal layer tends to form cracks and in subsequent coatings tends to become brittle and break.

In the normal course of manufacture, a binding agent is not added to the inorganic colloidal layer since no advantage is gained by the addition thereof. Such binding agents are normally preferred to be and are found to be water insoluble so that no particular advantages are obtained since the subsequent application of an electroconductive layer is accomplished normally with water. It is, therefore, found to be more desirable to use the colloidal solution, for example, colloidal silica or colloidal alumina by itself.

When colloidal silica is spread at a rate of about 1 g per M^2 on the surface of a machine coat paper, the surface resistance upon drying is found to have a resistance of about 5×10^9 ohms per square in an atmosphere of about 40 percent relative humidity. A coating of colloidal alumina spread at about the same concentration results in a surface resistance having a value decreased by a power of 100. It is permissible to incorporate into the inorganic colloidal layer a hygroscopic inorganic salt or a hygroscopic polyhydro compound. However, in the case of colloidal alumina dispersions an electroconductive layer is obtained having highly desirable properties so that it is not necessary to incorporate such additives. Therefore, alumina dispersions are generally preferred.

The surface of the inorganic colloidal dispersions obtained are found to be highly hydrophillic and, therefore, is highly desirable for use in connection with an aqueous solution to be spread thereover. The electroconductive layer applied thereover is accomplished with facility because it is a hydrophillic resinous layer. Any suitable hydrophillic resinous layer may be employed to provide the desired electroconductivity. Cationic polymers obtained from monomers incorporated in the quaternary ammonium salt, polyvinyl benzene sulfonic acid and salts thereof, and sulfonates of polystyrene are preferred resins because they possess a high degree of electroconductivity over a wide range of humidities and form ideal surfaces capable of completely preventing permeation of organic solvents. In addition, where a pretreatment is made such as with alumina colloid, the resin solution is found to be spread easily on the surface without being repelled and does not permeate excessively into the porous layer of the surface, but results in a laterally continuous film. The film of resinous material so applied is spread in a concentration of from about 1 g to about 4 g per M^2 . Polyvinyl benzene

potassium sulfonate is a preferred resin because it forms a film more resistant to permeation of solvent than cationic polymer resins. The electroconductive resin layer may also contain a polyhydric alcohol, a hygroscopic inorganic salt, a miscible resin having still higher resistance, and still other components. Polyvinyl alcohol is particularly inexpensive and provides a satisfactory film and, therefore, is preferred for use over other additives. Since the addition of large quantities of substances, such as, polyvinyl alcohol which has a relatively low electroconductivity results in a degraded electroconductivity at lower humidities it is desirable to avoid the addition of such quantities.

The general nature of the invention having been set forth, the invention will now be described illustratively in terms of the following specification and the drawings in which:

FIG. 1 illustrates one embodiment of the electrophotographic sensitive paper produced in accordance with the system of the present invention.

FIG. 2 represents the same structure as seen in FIG. 1 with the exception that an extremely thin insulating barrier 21 has been added.

FIG. 3 represents the structure as illustrated in FIG. 1 with the exception that a highly electroconductive carbon layer 31 has been provided.

In FIG. 1 is seen one embodiment of the electrophotographic sensitive paper of the present invention, wherein the paper base 1 has coated thereover a clay layer 2 which may comprise a baryta layer or a machine coat layer or the like having coated thereover a film composed mainly of colloidal silica or colloidal alumina 3 having coated thereover an electroconductive water soluble resinous layer 4, and finally, having coated thereover an electroconductive sensitive layer 5. Layer 6 underlying the fibrous paper layer 1 is included to illustrate the application of a curl-balancing layer which may be employed when desired. When so employed this layer is selected so that it possess a high degree of electroconductivity.

In FIG. 2 is seen the structure as illustrated in FIG. 1 with the exception that an extremely thin insulative barrier layer 21 is provided between layers 4 and 5. This layer is hardened and designed so as not to be dissolved by the solvent which is used in coating the sensitive layer 5.

In FIG. 3 is seen a structure as illustrated in FIG. 1 with the exception that a highly electroconductive carbon layer 31 is provided below layer 2, the black color of the carbon layer being completely masked by layer 2.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

To further define the specifics of the present invention the following examples are intended to illustrate and not limit the particulars of the present system. Parts and percentages are by weight unless otherwise indicated.

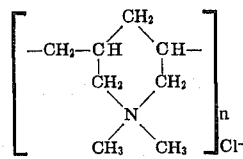
EXAMPLE I

A black electroconductive paint comprising a water emulsion of vinyl acetate resin and carbon black is spread on the non-art surface of a one face art paper having a thickness of about 90 microns. To the art surface of a portion of this paper is applied about a 10 percent aqueous solution of polyvinyl benzene potassium

sulfonate resulting in the appearance of small spot-shaped beads repelled by the surface indicating that the solution may not be spread uniformly thereover. To another portion of the paper the same solution is coated with the addition of a small quantity of surface active agent resulting in greatly improved wettability. However, it is found that the film after drying has no luster indicating that the solution has penetrated into the clay layer. To a third portion of this paper a water dispersion containing colloidal alumina at about 5 percent by weight is spread to a concentration of about 0.5 g per M² on the art layer and then dried. Over this is spread the 10 percent aqueous solution of polyvinyl benzene potassium sulfonate as previously used resulting in an extremely smooth uniform film. An electrophotographic sensitive layer comprising zinc oxide and an alkyd resin is spread with toluene over the polyvinyl benzene potassium sulfonate layer over portions of the paper both treated and not treated with the colloidal alumina. The material is then dried and adapted to darkness. When both portions of the paper are charged and exposed utilizing methods as hereinbefore described and developed employing a liquid developing agent, it is found that on the treated paper the uniformity of density in the low density area is very good wherein in the case of the untreated paper, uneven density is conspicuously present in the low density areas.

EXAMPLE II

A water dispersion of colloidal alumina is spread to a concentration of about 1 g per M² on both surfaces of a two surface art paper having a thickness of about 100 microns. Calgon Conductive Polymer 261, a 40 percent aqueous solution of a conductive polymer having the formula:



is diluted with water and applied to only one side of the surfaces resulting in an extremely smooth surface. To this is applied an electrophotographic layer similar to that as described in Example I. When the paper is imaged as in Example I, an excellent reproduction of a continuous tone image is obtained.

EXAMPLE III

The same procedure as outlined in Example I is performed with the exception that colloidal silica is used in place of colloidal alumina and the electroconductive layer comprising polyvinyl benzene potassium sulfonate is substituted by a film comprising about 10 parts of polyvinyl benzene potassium sulfonate and about 10 parts of glycerin. When this paper is imaged as in Example I, an excellent continuous tone image is obtained.

EXAMPLE IV

The method as outlined in Example II is performed with the exception that the colloidal alumina is substituted by a mixture of 8 parts of colloidal silica with about 2 parts of polyvinyl alcohol. When employed in an imaging process as in Example I there is obtained an excellent continuous tone image.

EXAMPLE V

An electrophotographic paper is provided as in Example I with the exception that an insulative layer having the thickness of about 1 micron comprising a mixture of styrene-maleic anhydride copolymer with epoxy resin is formed on the electroconductive layer of polyvinyl benzene potassium sulfonate prior to the formation of the electrophotographic sensitive layer, heated at about 80° C for about 1 hour and then coated with the sensitive layer. When this paper is imaged utilizing techniques similar to those as employed in Example I, an excellent reproduction of a continuous tone image is obtained.

EXAMPLE VI

A layer comprising gelatin and carbon black is applied to one surface of paper. Over this layer is applied a baryta layer such as that generally employed in photographic printing paper. This paper is then treated as in Example I with a colloidal dispersion and then coated as in Example I with an electroconductive layer and then finally with an electrophotographic sensitive layer. This electrophotographic sensitive paper when imaged as in Example I results in an extremely high quality reproduction when liquid development is employed.

EXAMPLE VII

A solution comprising about 10 parts alumina sol, and 90 parts methanol is spread on the art layer of a one surface art paper having a weight of about 1 to 30 g per M² so that upon drying the weight of the coating is found to be about 2 g per M². About a 10 percent aqueous solution of polyvinyl benzene potassium sulfonated is spread thereover forming an extremely smooth film. Over this electroconductive layer an electrophotographic sensitive layer similar to that of Example I is formed. When imaged employing techniques as employed in Example I, an excellent reproduction of a

continuous tone image is obtained.

Although the present examples were specific in terms of conditions and materials used, any of the above listed typical materials may be substituted when suitable in the above examples with similar results. In addition to the steps used to carry out the process of the present invention, other steps or modifications may be used if desirable. For example, other layers may be employed to the non-imaging surface of the electrophotographic paper to desirably adjust colloidal properties. In addition, other materials may be incorporated in the system of the present invention which will enhance, synergize or otherwise desirably affect the properties of the systems for their present use. For example, other layers employed on the imaging surface may also be applied to the underside or non-image surface of the paper as desired.

Anyone skilled in the art will have other modifications occur to him based on the teachings of the present invention. These modifications are intended to be encompassed within the scope of this invention.

What is claimed is:

1. In a method for preparation of an electrophotographic paper suitable for use in continuous tone imaging wherein a waterproofed paper substrate is provided having coated on at least one surface thereof an inorganic colloidal oxide resin, the inorganic colloidal oxide resin being further overcoated with an electroconductive hydrophillic resinous layer, said electroconductive layer being further overcoated with a photoconductive insulating layer,

the improvement comprising providing the uncoated surface of the paper substrate with an electroconductive curl-balancing layer.

2. In a process for preparation of an electroconductive paper suitable for use in continuous tone imaging wherein a waterproofed paper substrate is provided having coated on at least one surface thereof an inorganic colloidal oxide resin, the inorganic colloidal oxide being further overcoated with an electroconductive hydrophillic resinous layer, said electroconductive layer being further overcoated with a photoconductive insulating layer,

the improvement comprising providing an electrically insulating barrier layer interposed between the photoconductive insulating layer and the electroconductive layer.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3787235 Dated January 22, 1974

Inventor(s) Satoru Honjo; Yasuo Tamai

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

1. Column 1, line 46--The word "hage" should be--have--.
2. Column 2, line 4--The word "denisty" should be--density--.
3. Column 6, line 56--The word "tome" should be--tone--.
4. Column 7, line 19--The word "utilzing" should be
--utilizing--.

Signed and sealed this 17th day of September 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHLL DANN
Commissioner of Patents