

[54] BARRIER LAYERS FOR ELECTROPHOTOGRAPHIC ELEMENTS CONTAINING A BLEND OF CELLULOSE NITRATE WITH A TETRAPOLYMER HAVING VINYLIDENE CHLORIDE AS THE MAJOR CONSTITUENT

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[58] Field of Search.....260/80.8, 17 R; 96/1.5; 117/201, 218

[56]

References Cited

UNITED STATES PATENTS

3,228,770	1/1966	Nodeau et al.....	96/87
3,353,991	11/1967	Shelburg et al.....	117/138.8
3,403,116	9/1968	Ream et al.....	260/8
3,468,660	9/1969	Davenport et al.....	96/1.5

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[57]

ABSTRACT

An electrophotographic element comprised of a support, an electrically conductive layer and an insulating photoconductive layer is provided with a barrier layer composed of a blend of cellulose nitrate with a tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride interposed between the electrically conductive layer and the insulating photoconductive layer. Barrier layers of this composition provide good adhesion to the contiguous layers, so as to permit flexing of the element without damage, as well as excellent electrophotographic properties.

14 Claims, No Drawings

BARRIER LAYERS FOR ELECTROPHOTOGRAPHIC ELEMENTS CONTAINING A BLEND OF CELLULOSE NITRATE WITH A TETRAPOLYMER HAVING VINYLIDENE CHLORIDE AS THE MAJOR CONSTITUENT

This invention relates in general to electrophotography and in particular to electrophotographic elements which include a barrier layer between an electrically conductive layer and a photoconductive insulating layer. More specifically, this invention relates to the use of a blend of cellulose nitrate with a tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride as a barrier layer for electrophotographic elements.

Electrophotographic imaging processes and techniques have been extensively described in both the patent and other literature, for example, U.S. Pat. Nos. 2,221,776; 2,277,013; 2,297,691; 2,357,809; 2,551,582; 2,825,814; 2,833,648; 3,220,324; 3,220,831; 3,220,833 and many others. Generally, these processes have in common the steps of employing an electrophotographic element which is prepared to respond to imagewise exposure with electromagnetic radiation by forming a latent electrostatic charge image. A variety of subsequent operations, now well known in the art, can then be employed to produce a permanent record of the image.

One type of unitary photoconductive element particularly useful in electrophotography is generally produced in a multilayer structure. Such an element is prepared by coating a layer of an insulating photoconductive composition onto a film support previously overcoated with a layer of conducting material. In addition, an insulating or barrier layer is interposed between the conducting material and the photoconductive composition.

One purpose of the barrier layer in an electrophotographic element is to reduce the charge leakage in the absence of activating radiation. Such charge leakage is generally referred to as "dark decay." On the other hand, a suitable barrier layer must not prevent proper charge dissipation in the presence of activating radiation. The barrier layer also helps to reduce the variation in performance upon repeated use of an element. Such a variation in performance of an electrophotographic element upon repeated use is known as "charge fatigue." In essence, the function of a barrier layer is to prevent passage of charge from the conductive layer to the photoconductive insulating layer, thus preventing unwanted discharge of the photoconductive layer.

However, problems are often encountered with prior electrophotographic elements of this type in that there is often considerable difficulty in obtaining good adhesion between the conducting layer and the barrier layer or between the photoconductive insulating layer and the barrier layer. Because of the lack of good adhesion between layers, many prior electrophotographic elements could not be substantially flexed without causing the layers to separate in various places.

It is, therefore, an object of this invention to provide electrophotographic elements having new barrier layers which have improved adhesion to substrates.

It is a further object of this invention to provide novel electrophotographic elements having new barrier layers to which overcoated layers readily adhere.

Still another object of this invention is to provide novel electrophotographic elements capable of forming good quality images having low background.

A further object of this invention is to provide novel electrophotographic elements capable of being electrically charged in a positive or a negative mode.

These and other objects and advantages are accomplished in accordance with this invention with an electrophotographic element having a barrier layer composed of a blend of cellulose nitrate with a tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride. This barrier layer is positioned between a photoconductive layer and a conducting layer on a support.

It is known to use cellulose nitrate as a barrier layer for electrophotographic elements, as shown, for example, by British Pat. No. 1,153,506. It is also known to use other polymeric resins to prepare barrier layers, as shown, for example, by U.S. Pat. No. 2,901,348. However, the essential feature of the present invention is the use of a blend of cellulose nitrate with a tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride to obtain a combination of desirable properties not realizable with either of these resins by themselves.

For the purposes of this invention, the tetrapolymer should be made up of a major proportion of vinylidene chloride on a weight basis and a minor proportion of the other monomers. It is preferred to employ a tetrapolymer consisting of about 5 to about 20 percent by weight methyl acrylate, about 5 to about 20 percent by weight acrylonitrile, about 2 to about 8 percent by weight acrylic acid, and the balance vinylidene chloride, and particularly preferred to employ a tetrapolymer consisting of 10 percent by weight methyl acrylate, 15 percent by weight acrylonitrile, 6 percent by weight acrylic acid and 69 percent by weight vinylidene chloride. The tetrapolymer can be prepared by well known aqueous emulsion polymerization techniques as described, for example, in U.S. Pat. Nos. 2,278,415; 2,698,235; 2,698,240 and 2,762,720. Particularly good results are obtained with a tetrapolymer having an inherent viscosity, as measured at a concentration of 0.25 gram of polymer per 100 milliliters of cyclohexanone and at a temperature of 25° C., in the range from about 0.9 to about 1.8. Optimum performance is achieved with a tetrapolymer having an inherent viscosity of about 1.2.

For use in preparing a barrier layer, the blends of tetrapolymer and cellulose nitrate should consist of a major proportion of the tetrapolymer on a weight basis. It is preferred that the blend consist of about 3 to about 15 parts of the tetrapolymer per part of cellulose nitrate by weight, and more preferably from about 4 to about 8 parts of the tetrapolymer per part of cellulose nitrate. Optimum results have been obtained at a ratio of 4.3 parts of the tetrapolymer to one part of cellulose nitrate. The thickness of the barrier layer can vary widely depending on the particular characteristics required. Typically, the barrier layer coverage on a dry basis will be in the range from about 10 mg./ft.² to about 200 mg./ft.² (corresponding to 4-80 microinches dry thickness) and more preferably in the range from about 30 mg./ft.² to about 50 mg./ft.² (corresponding to 12-20 microinches dry thickness).

The electrophotographic elements of the present invention can be formed on a wide variety of support materials. Suitable support materials would include glass; wood; paper, including coated paper such as polyethylene or polypropylene coated paper, baryta coated paper, etc., polymeric materials such as cellulose acetate, poly(ethylene terephthalate), polyethylene, polypropylene, etc.; and other known support materials.

The conductive coating which is placed on the support can be formed in a variety of ways and from a number of materials. One method of applying such a conductive coating is by evaporation techniques, such as described in U.S. Pat. No. 2,756,165. Another suitable method of forming the conductive layer is by coating onto the support a solution of a conductive or semiconductive material and a resinous binder in a volatile solvent and evaporating the solvent to leave a conductive layer. U.S. Pat. No. 3,245,833 discloses methods for accomplishing this latter technique.

Particularly good conductive layers for use with the present barrier layers utilize a metal-containing semiconductor compound such as cuprous iodide, silver iodide, etc. Conductive layers of this sort can be prepared as described in U.S. Pat. No. 3,245,833. These metal-containing semiconductor compounds can be coated at a wide range of coverages, with particularly useful results being obtained at coverages of from about 4 to about 40 mg./ft.² based on the dry weight of the semiconductor compound.

Similarly, the photoconductive layer in the present electrophotographic elements can be comprised of a variety of materials. Photoconductors suitable for use in the photoconductive layer can include inorganic, organic and organometallic materials. Useful photoconductors include zinc oxide, titanium dioxide, organic derivatives of Group IVa and Va metals such as those having at least one amino-aryl group attached to the metal atom, aryl amines, polyarylalcanes having at least one amino substituent, etc. The following table is a partial listing of U.S. patents disclosing a variety of organic photoconductive compounds and compositions which are useful in accordance with the present invention.

Inventor	U.S. Pat. No.
Schlesinger	3,139,338
Schlesinger	3,139,339
Cassiers	3,140,946
Davis et al.	3,141,770
Ghys	3,148,982
Cassiers	3,155,503
Schlesinger	3,257,202
Sues et al.	3,257,203
Sues et al.	3,257,204
Fox	3,265,496
Kosche	3,265,497
Noe et al.	3,274,000

The photoconductor is usually applied by forming a mixture with a polymeric binder material and coating the mixture over the barrier layer. The photoconductive layer can be applied by a variety of means such as spray coating, swirl coating, extrusion hopper coating, etc. Also, the amount of photoconductor in the layer can be varied from about 10 to about 60 percent by weight of the total solids in the photoconductive layer.

The barrier layers of the present invention can likewise be applied in a variety of ways such as spray coating, dip coating, swirl coating, extrusion hopper coating, bead application on a continuous coating machine, and the like.

The invention is further illustrated by the following example of the preparation of an electrophotographic element comprising a barrier layer composed of a blend of cellulose nitrate and a tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride.

A 4 mil poly(ethylene terephthalate) film was coated with a subcoating of a terpolymer consisting of 15 percent by weight acrylonitrile, 6 percent by weight acrylic acid and 79 percent by weight vinylidene chloride and a conductive layer of cuprous iodide, as described in U.S. Pat. No. 3,245,833, was applied over the subcoating at a dry coverage of 15 mg./ft.² of cuprous iodide. A barrier layer, as hereinbefore described, was then applied over the conductive layer. To prepare the barrier layer, a tetrapolymer consisting of 10 percent by weight methyl acrylate, 15 percent by weight acrylonitrile, 6 percent by weight acrylic acid and 69 percent by weight vinylidene chloride was dissolved, with vigorous stirring, in methyl ethyl ketone in an amount sufficient to form a 3 percent by weight solution. To 4.3 parts by weight of this solution, there was added, slowly and with vigorous stirring, one part by weight of a 3 percent by weight solution of cellulose nitrate prepared by diluting with methyl alcohol a 16 percent by weight concentrate of cellulose nitrate in a 1 to 9 isopropyl alcohol/methyl alcohol mixture. The resulting 3 percent by weight solution of a 4.3 to 1 blend of the tetrapolymer and cellulose nitrate was coated over the cuprous iodide conductive layer and dried to provide a clear barrier layer with a coverage of 30 mg./ft.² dry solids. To complete the preparation of the electrophotographic element, an insulating photoconductive layer was applied over the barrier layer using a photoconductive coating composition prepared in the manner described in British Pat. No. 1,153,506. To prepare the photoconductive coating composition, 300 grams of a polycarbonate resin formed from the reaction between phosgene and a dihydroxydiarylalcanes (available from General Electric Company

under the trademark Lexan 105), 200 grams of 4,4'-benzylidenebis(N,N-diethyl-m-toluidine), and 10 grams of 4-(4-dimethylaminophenyl)2-6,diphenylthiapyrylium perchlorate were dissolved, with 2 hours of stirring, in 1,700 grams of methylene chloride and 1133.3 grams of 1,1,2-trichloroethane and the resulting solution was sheared in a high-speed blender. The photoconductive coating composition was coated over the barrier layer from an extrusion hopper at a dry coverage of 1.1 gm./ft.².

To determine the electrophotographic speed, the element is electrostatically charged under a corona source until the surface potential, as measured by an electrometer probe, reaches 600 volts. The charged element is then exposed to a 3,000° K. tungsten light source through a standard stepped density gray scale. The exposure causes reduction of the surface potential of the element under each step of the gray scale from its initial potential, V_0 , to some lower potential, V , whose exact value depends on the actual amount of exposure in meter-candle-seconds received by the area. The results of these measurements are then plotted on a graph of surface potential V vs. log exposure for each step. The actual positive or negative speed of the element can then be expressed in terms of the reciprocal of the exposure required to reduce the surface potential to any fixed arbitrarily selected value. Herein, the actual positive or negative speed is the numerical expression of 10^4 divided by the exposure in meter-candle-seconds required to reduce the 600-volt charged surface potential to a value of 500 volts (100-volt shoulder speed) or to a value of 100 volts (100-volt toe speed). The positive and negative 100-volt shoulder and toe speeds measured in this manner are 8,000 and 3,200, respectively, for the electrophotographic element described hereinabove.

In addition to electrophotographic speed, other important properties include "dark decay," i.e., the charge leakage in the absence of activating radiation, and the adhesion between contiguous layers. The "dark decay" can be measured by an electrometer probe placed immediately after the corona charge and following the voltage decay in the dark. The electrophotographic element described hereinabove has less than 100 volts decay in 30 seconds when the initial charge is 600 volts. A measure of the adhesion between the layers can be obtained by scoring the surface of the element, applying a pressure-sensitive tape to the scored area, and rapidly pulling the tape away. Any large area separation in this test would be considered to represent poor adhesion that would render the element unfit for use. Good adhesion between the layers is important to allow the electrophotographic element to be flexed without layer separation and to permit it to be treated with developing solutions without being adversely affected. With the electrophotographic element described hereinabove good adhesion is obtained, i.e., no separation of the layers occurred when the element was tested in the aforesaid manner.

The use of a blend of cellulose nitrate and a tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride as a barrier layer was unexpectedly found to provide a desirable combination of both good adhesion to the adjacent layers and good "dark decay" characteristics; whereas barrier layers known heretofore, such as a layer of cellulose nitrate, do not provide satisfactory properties with regard to both of these features. Barrier layers composed of each of the two individual components of the blend of this invention were prepared and found to be incapable of providing both adequate adhesion and suitable "dark decay" characteristics. In particular, use of a barrier layer composed solely of cellulose nitrate provides satisfactory "dark decay" but poor adhesion, i.e., when an electrophotographic element employing this barrier layer was subjected to the test with pressure-sensitive tape previously described, separation of the layers occurred. On the other hand, use of a barrier layer composed solely of a tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride provides good adhesion but poor "dark decay" characteristics. i.e., an electrophotographic element with this barrier layer exhibits about 400 volts

decay in 30 seconds when the initial charge is 600 volts. Barrier layers were also prepared from (1) a terpolymer of 35 percent by weight methyl acrylate, 2 percent by weight itaconic acid and 63 percent by weight vinylidene chloride, (2) blends of terpolymer (1) with cellulose nitrate, (3) 1 terpolymer of 15 percent by weight acrylonitrile, 6 percent by weight acrylic acid and 79 percent by weight vinylidene chloride, and (4) blends of terpolymer (3) with cellulose nitrate. Each of these four barrier layers provided good adhesion, but in each case the "dark decay" properties were unsatisfactory. Furthermore, the blends of cellulose nitrate and a tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride of this invention have other important advantages, for example, they can be readily dissolved in solvents which will not adversely affect the conductive layer and the components of the blend are fully compatible so that a solvent solution of the blend can be coated with reproducible results. A barrier layer composed of the aforesaid blend is also particularly advantageous in that it provides essentially the same amount of "dark decay" when the element is charged positively as when it is charged negatively.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. In an electrophotographic element comprising an electrically conducting support, a barrier support contiguous with said conducting layer and a photoconductive layer contiguous with said barrier layer, the improvement wherein said barrier layer consists essentially of a blend of cellulose nitrate with a tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride; said tetrapolymer being composed of a major proportion by weight of vinylidene chloride and said blend being composed of a major proportion by weight of said tetrapolymer.

2. An electrophotographic element as described in claim 1 wherein said blend consists of about 3 to about 15 parts of said tetrapolymer per part of cellulose nitrate by weight.

3. An electrophotographic element as described in claim 1 wherein said blend consists of about 4 to about 8 parts of said tetrapolymer per part of cellulose nitrate by weight.

4. An electrophotographic element as described in claim 1 wherein said blend consists of about 4.3 parts of said tetrapolymer per part of cellulose nitrate by weight.

5. An electrophotographic element as described in claim 1 wherein said tetrapolymer is composed of about 5 to about 20 percent by weight methyl acrylate, about 5 to about 20 percent by weight acrylonitrile, and about 2 to about 8 percent by weight acrylic acid, with the balance being vinylidene chloride.

6. An electrophotographic element as described in claim 1 wherein said tetrapolymer is composed of 10 percent by

weight methyl acrylate, 15 percent by weight acrylonitrile, 6 percent by weight acrylic acid and 69 percent by weight vinylidene chloride.

7. An electrophotographic element as described in claim 1 wherein said tetrapolymer has an inherent viscosity, as measured at a concentration of 0.25 gram of polymer per 100 milliliters of cyclohexanone and at a temperature of 25° C., in the range from about 0.9 to about 1.8.

8. An electrophotographic element as described in claim 1 wherein said tetrapolymer has an inherent viscosity, as measured at a concentration of 0.25 gram of polymer per 100 milliliters of cyclohexanone and at a temperature of 25° C., of about 1.2.

9. An electrophotographic element as described in claim 1 wherein the barrier layer coverage on a dry basis is in the range from about 10 to about 200 mg./ft.².

10. An electrophotographic element as described in claim 1 wherein the barrier layer coverage on a dry basis is in the range from about 30 to about 50 mg./ft.².

11. An electrophotographic element comprising a support having coated thereon a conductive layer of a metal-containing semiconductor compound, said conductive layer having in contiguous relationship therewith a barrier layer consisting essentially of a blend of cellulose nitrate with a tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride, said tetrapolymer being composed of a major proportion by weight of vinylidene chloride and said blend being composed of a major proportion by weight of said tetrapolymer, and coated on said barrier layer a photoconductive layer containing an organic photoconductor.

12. An electrophotographic element as described in claim 11 wherein the metal-containing semiconductor compound is cuprous iodide.

13. An electrophotographic element as described in claim 12 wherein said blend consists of about 4 to about 8 parts of said tetrapolymer per part of cellulose nitrate by weight and said tetrapolymer is composed of about 5 to about 20 percent by weight methyl acrylate, about 5 to about 20 percent by weight acrylonitrile, about 2 to about 8 percent by weight acrylic acid, with the balance being vinylidene chloride, and has an inherent viscosity, as measured at a concentration of 0.25 gram of polymer per 100 milliliters of cyclohexanone and at a temperature of 25° C., in the range from about 0.9 to about 1.8.

14. An electrophotographic element as described in claim 12 wherein said blend consists of about 4.3 parts of said tetrapolymer per part of cellulose nitrate by weight and said tetrapolymer is composed of 10 percent by weight methyl acrylate, 15 percent by weight acrylonitrile, 6 percent by weight acrylic acid, and 69 percent by weight vinylidene chloride and has an inherent viscosity, as measured at a concentration of 0.25 gram of polymer per 100 milliliters of cyclohexanone and at a temperature of 25° C., of about 1.2.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,640,708 Dated February 8, 1972

Inventor(s) Wesley D. Humphriss and Lawrence C. Bartlett

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

Col. 5, line 5, change "1" (second occurrence) to --a--.

Claim 1, line 2, change "support" to --layer--;
line 3, change "layer" (first occurrence) to --support--.

Signed and sealed this 8th day of August 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents