United States Patent [19]

Lee

[11] **3,891,435**

[45] **June 24, 1975**

[54] **HETEROPHASE ADHESIVE COMPOSITIONS CONTAINING CHLOROSULFONATED POLYETHYLENE FOR METAL-SELENIUM COMPOSITES**

[75] Inventor: **Lieng Huang Lee**, Webster, N.Y.

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

[22] Filed: **Aug. 17, 1973**

[21] Appl. No.: **389,283**

[52] **U.S. Cl.** **96/1.5**; 117/200; 117/218

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

[58] **Field of Search** 96/1.5; 117/200, 218

[56] **References Cited**

UNITED STATES PATENTS

3,713,821	1/1973	Angelini	96/1.5
3,723,110	3/1973	Goffe	96/1.5
3,738,833	6/1973	Merrill	117/218

OTHER PUBLICATIONS

"Organic Coatings for Electronics" Products Finishing, July, 1971, pp. 74–80, Licari and Brands.

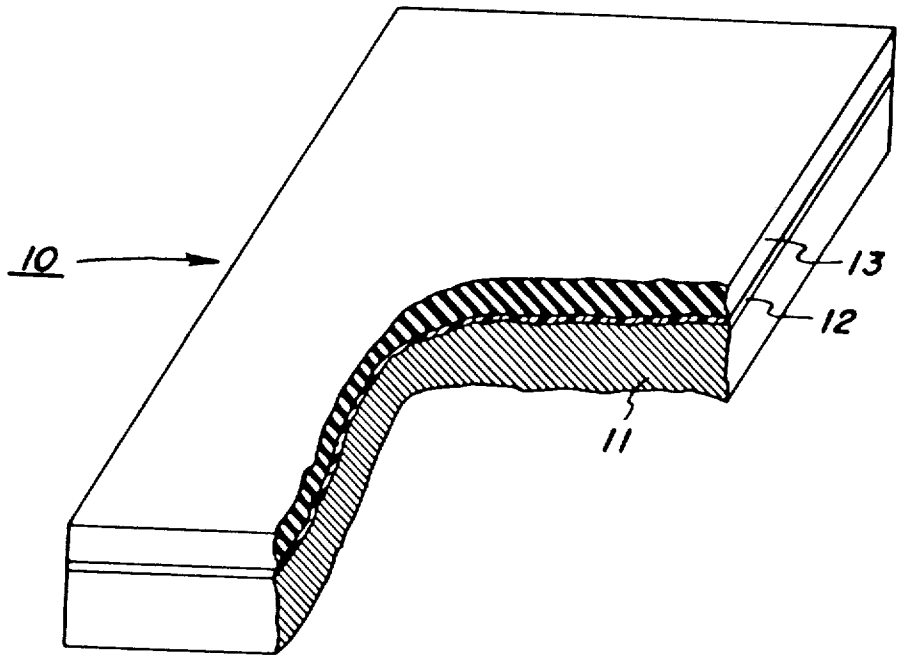
Primary Examiner—Norman G. Torchin

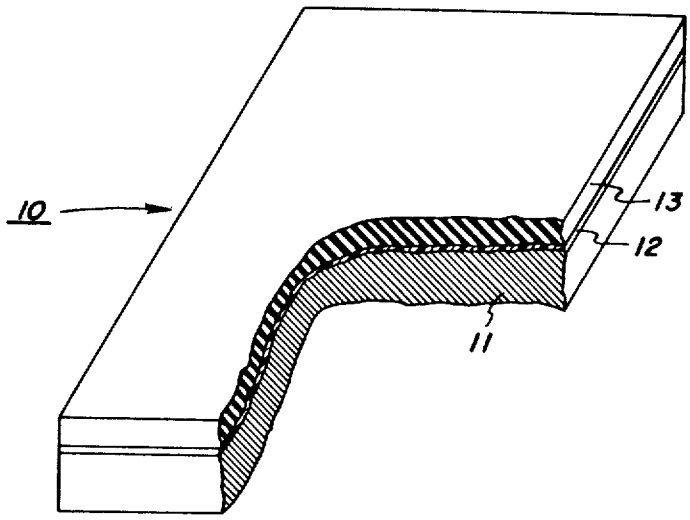
Assistant Examiner—Judson R. Hightower

[57] **ABSTRACT**

A xerographic member which comprises a conductive substrate having thereon an interfacial barrier layer in a thickness of about 0.5 to 3.0 microns. The barrier layer comprises a polymer blend or mixture of a polycarbonate, a polyether-ester-urethane, and a chlorosulfonated polyethylene and is overcoated with a photoconductive layer about 10 to 200 microns in thickness.

12 Claims, 1 Drawing Figure




10
13
12
11

HETEROPHASE ADHESIVE COMPOSITIONS CONTAINING CHLOROSULFONATED POLYETHYLENE FOR METAL-SELENIUM COMPOSITES

BACKGROUND OF THE INVENTION

This invention relates in general to xerography, and in particular, to an improved interfacial layer for a xerographic member.

In the art of xerography, a xerographic plate containing a photoconducting insulating layer is first given a uniform electrostatic charge in order to sensitize its surface. The plate is then exposed to an image of activating electromagnetic radiation, such as light, which selectively dissipates the charge in the illuminated areas of the photoconductive insulator while leaving behind a latent electrostatic image in the non-illuminated areas. The latent electrostatic image may be developed and made visible by depositing finely divided electroscopic marking particles in the surface of the photoconductive layer. This concept was originally described by Carlson in U.S. Pat. No. 2,297,691 and is further amplified and described by many related patents in the field.

Conventionally, a xerographic member or plate normally includes a conductive base or support which is generally characterized by the ability to conduct electricity for charging or sensitization of a composite member and to accommodate the release of electric charge upon exposure of the member to activating radiation such as light. Generally, this conductive support must have a specific resistivity of less than about 10^{10} ohm-cm, and usually less than about 10^{5} ohm-cm. The conductive support should also have sufficient structural strength to provide mechanical support for the photosensitive member thus making it readily adaptable for xerographic machines suitable for commercial use.

The conventional xerographic plate normally has a photoconductive insulating layer overlaying a conductive support. The photoconductor may comprise any suitable material known in the art. For example, vitreous selenium, or selenium modified with varying amounts of arsenic is one example of one suitable reusable photoconductor which has wide use in commercial xerography. In general, the photoconductive layer must have a specific resistivity greater than about 10^{10} ohm-cm in the absence of illumination and preferably at least 10^{13} ohm-cm. The resistivity should drop at least several orders of magnitude in the presence of activating radiation or light. In general, the photoconductive layer should support an electrical potential of at least about 100 volts in the absence of radiation and may vary in thickness from about 10 to 200 microns.

A plate having the above configuration, normally under dark room conditions, exhibits a reduction in potential or voltage leak in the absence or activating radiation which is known as "dark decay" and exhibits a variation in electrical performance upon repetitive cycling which is described in the art as "fatigue". The problems of "dark decay" and "fatigue" are well known in the art and have been remedied by the incorporation in the plate structure of a barrier layer which comprises a thin dielectric material only a fraction of the thickness of the photoconductive layer. This barrier or interfacial layer is inter-disposed between the conductive substrate and the photoconductive insulating layer. U.S. Pat. No. 2,901,348 to Dessauer et al contemplates such a layer and suggests the use of a thin layer or film of aluminum oxide in a thickness range of about 25 to 200 angstroms; or an insulating resin layer, such as polystyrene, in the order of about 0.1 to 2 microns in thickness. These barrier layers function to allow the photoconductive layer to support a charge of high field strength with minimum charge dissipation in the absence of illumination. When activated by illumination, the photoconductive layer becomes conductive, thereby causing a migration of the appropriate charges through said photoconductive layer and the appropriate dissipation of charge in the radiation or illumination struck areas.

In addition to the electrical requirements of a barrier layer, it is also necessary that such a layer meets certain requirements with regard to mechanical properties such as adhesion to the photoreceptor and overall flexibility. For example, when using a flexible photoreceptor, such as a continuous belt, both the photoconductor and interface must be properly matched so as to have the required electrical characteristics and mechanical stability. It has been demonstrated that after a great deal of flexing, many interfaces tend to spall or crack, resulting in the flaking off or spalling of sections of the photoreceptor rendering it no longer suitable for use in xerography. Therefore, there is a continuing need for improved barrier layers which meet both the required electrical characteristics and mechanical properties for use in applications in which a flexible xerographic member or belt is used.

OBJECTS OF THE INVENTION

It is, therefore, an object of the invention to provide a new and improved photoreceptor barrier layer which overcomes the above noted disadvantages.

It is another object of this invention to provide a photoreceptive member which exhibits improved electrical characteristics and mechanical properties.

It is another object of this invention to provide an improved interfacial barrier layer.

SUMMARY OF THE INVENTION

The foregoing objects and others are accomplished in accordance with this invention by providing a photoconductive member which exhibits improved electrical characteristics and mechanical properties, and which includes a novel interfacial barrier layer which comprises a heterophase adhesive composition containing a polycarbonate, a polyether-ester-urethane, and a chlorosulfonated polyethylene. More specifically, the interfacial layer comprises either a polymer blend or mixture of a polycarbonate, a polyether-ester-urethane, and a chlorosulfonated polyethylene which is sandwiched between a photoconductive insulating layer and a supporting substrate. One of the advantages of this interfacial composition is that it exhibits improved tensile strength, elongation, modulus of elasticity, adhesive properties, and electrical characteristics which in many instances exceed the properties of individual organic components presently employed in the art.

BRIEF DESCRIPTION OF THE DRAWING

The advantages of the instant invention will become apparent upon consideration of the following disclosure of the invention, especially when taken in conjunction with the accompanying drawing wherein:

The FIGURE represents a schematic illustration of one embodiment of a xerographic member as contemplated for use in the instant invention.

DETAILED DESCRIPTION OF THE DRAWINGS

In the drawing, reference character **10** illustrates one embodiment of an improved photoreceptor device of the instant device. Reference character **11** designates a support member which is preferably an electrically conductive material. The support may comprise a conventional metal such as nickel, nickel alloys, brass, aluminum, steel or the like. The support may also be of any convenient thickness, rigid or flexible and in any suitable form such as a sheet, web, cylinder, or the like. The support may comprise other materials such as metalized paper, plastic sheets covered with a thin coating of aluminum or copper iodide, or glass coated with a thin conductive layer of chromium or tin oxide. A preferred substrate for use in the instant invention comprises a seamless flexible xerographic belt which comprises a metal such as nickel, nickel alloys or brass, and which is formed by the method described in Applicant's copending application, Ser. No. 7,289 filed on Jan. 30, 1970, now abandoned.

Substrate **11** is overlayed with an organic interfacial layer **12**, which comprises a polymer blend or mixture of a polycarbonate, polyether-ester-urethane and chlorosulfonated polyethylene. The polycarbonate may be present in a concentration of from about 30 to 80 weight percent with the two elastomers comprising a combined concentration from about 20 to 70 weight percent. Preferably the polycarbonate should be present in an amount from about 70 to 80 weight percent. The polyether-ester-urethane and chlorosulfonated polyethylene are preferably present in a combined concentration of about 10 to 30 weight percent. Interfaces which comprise a polymer blend of the above three components have been found to exhibit particularly outstanding electrical and mechanical properties at both extremes of operation temperatures (−20° to 100°F) and therefore comprise a desirable interfacial material for use in xerography.

Typical polycarbonates suitable for use in the instant invention comprise Merlon polycarbonate available from Mobay; Makrolon polycarbonate available from Bayer; and Lexan polycarbonate available from General Electric.

Typical polyether-ester-urethanes suitable for use in the instant invention comprise Estane 5702 F-2 available from Goodrich and TPU polyurethane available from Goodyear.

Typical chlorosulfonated polyethylenes suitable for use in the instant invention comprise Hyperlon 30 or Hyperlon 20 available from duPont.

The interfacial layer may be made by any convenient technique. For example, the appropriate proportions of the polycarbonate and elastomers are normally dissolved in a solvent and the solution coated onto a supporting substrate. The solvent is then allowed to evaporate leaving a dried coating contained on the supporting substrate. Residual solvents may be driven off by oven drying at 150° to 300°F for about 5 minutes. Typical coating techniques which are suitable for forming the interfacial layer include spray coating, draw coating, dip coating or flow coating. In general, the dried thickness of the interfacial layer should be about 0.5 to 3.0 microns. Thicknesses less than about 0.5 microns are undesirable in that they do not give a uniformly cover substrate roughness. In addition, they are difficult to charge and tend to leak electrical charge. Thicknesses above about 3.0 microns sometimes result in non-charge dissipation. in general, the composite resistivity of these interfacial layers range from about 10^{11} to 10^{14} ohm-cm.

In addition to the above compositions, other additives may be added to the mixture. These additives include small amounts of conductive or photoconductive pigments such as copper phthalocyanine, zinc oxide (electrography grade), cadmium sulfoselenide, and metal-free phthalocyanine. In general these additives are used to control the resistivity of the interfacial barrier layer, and in some cases are even believed to improve the mechanical properties of layer.

Although the exact structure of the interface is not completely understood, it is believed that the elastomeric polymers form a discrete dispersed phase in a polycarbonate matrix. It is also believed that it is essential to form such a discrete phase by agitating the polymeric solution prior to its application in the form of the interfacial layer. At concentrations of the elastomeric phase greater than about 35 weight percent, it is believed that this two phase structure begins to undergo a phase inversion and the desired properties both electrical and mechanical are drastically different after the phase inversion. For example, the elongation reaches a minimum in the phase inversion region, and the resistivity increases steeply in or around the phase inversion region.

It has also been found that when many organic resins are used alone as interfacial layers, the desirable combination of mechanical and electrical properties cannot be maintained. For example, polycarbonate alone is not a suitable barrier layer in that its resistivity is too high. Similarly, many elastomeric materials when used alone also do not yield the desired combination of mechanical and electrical properties. For example, interfacial layers comprising polyurethane alone do not have the required mechanical properties such as high modulus of elasticity and therefore are not suitable as interfaces for flexible xerographic photoreceptors when used alone. Similarly, interfacial layers comprising chlorosulfonated polyethylene alone also do not yield the required mechanical properties with regard to high modulus of elasticity. Electrically, these elastomers alone are somewhat too conductive, but the conductivities are greatly reduced by the incorporation of the high resisitivity polymers in the matrix.

A preferred application of the instant invention includes the use of the instant interface on a flexible seamless belt which may typically comprise a conductive material such as nickel, nickel alloys or brass. In addition to the required electrical characteristics, it is essential that the interfacial layers of the instant invention have a high degree of flexibility at extremes of application temperature and forms a satisfactory adhesive interface between the photoconductive layer and the supporting substrate.

Photoconductive insulating layer **13** overlays interfacial layer **12.** The photoconductor may comprise any suitable photoconductive insulator which is compatible with the composition of the interfacial layer and forms an adherent layer which properly bonds the photoconductive layer to the substrate. Suitable photoconductive materials include vitreous selenium or selenium alloyed with materials such as arsenic, antimony, tellurium, sulfur, bismuth and mixtures thereof. A preferred photoconductor comprises a vitreous alloy of selenium containing arsenic in an amount from about 0.1 to 50 percent by weight. The thickness of the photoreceptor layer is not particularly critical and may range from about 10 to 200 microns. In general, thicknesses in the range from about 20 to 80 microns are particularly satisfactory for use in conventional xerography. The photoreceptor layer may be prepared by any suitable technique. A preferred technique includes vacuum evaporation wherein the appropriate material or alloy is evaporated over the interfacial layer. In general, a selenium or selenium-arsenic alloy layer thickness of about 60 microns is obtained when vacuum evaporation is continued for about 1 hour at a vacuum of 10^{-5} Torr. at a crucible temperature of about 280°C. U.S. Pat. Nos. 2,803,542 to Ullrich; 2,822,300 to Mayer et al, 2,901,348 to Dessauer et al and 2,753,278 to Bixby all illustrating vacuum evaporation techniques which are suitable in the formation of selenium or selenium alloy layers of the instant invention.

In order to gain added sensitivity when using selenium-arsenic layers, a halogen dopant such as chlorine or iodine, may be added in order to improve the electrical characteristics. This concept is more fully described by U.S. Pat. No. 3,312,548 to Straughan.

PREFERRED EMBODIMENTS

The following examples further specifically define the present invention with respect to a method of making a photoreceptor member having an interfacial barrier layer. The percentages in the specification, examples and claims are by weight unless otherwise stated. The examples below are intended to illustrate various preferred embodiments of the instant invention.

EXAMPLE I

The coating solution for forming organic interfacial barrier layer is prepared by dissolving equal proportions by weight (1:1:1) of a polycarbonate resin, an amorphous polyether-ester-urethane elastomer and chlorosulfonate polyethylene as follows:

Part A-polymer 6 parts by weight
ethylene dichloride-100 parts
dioxane-100 parts

The above coating solution is further diluted as follows:

Part B-(Part A 250 parts by volume)
cyclohexanone (100 parts by volume)
tetrachloroethylene (100 parts by volume)

This coating solution is coated onto a continuous flexible nickel belt .0045 inches thick approximately 16½ inches wide and 65 inches in circumference by spray coating using an air spray in a Binks electrostatic spray gun. The coating is allowed to dry and forms a smooth interfacial film about 1 to 2 microns in thickness. The coated nickel substrate is then mounted on a circular mandrel and then inserted into a vacuum chamber. An alloy source containing about 99.67 weight percent selenium and .33 weight percent arsenic and containing 30 parts per million chlorine is inserted in a stainless steel crucible beneath the coated nickel substrate. During vacuum evaporation the substrate is rotated about its longitudinal axis at a rate of about 6 to 12 revolutions per minute. The vacuum chamber is evacuated to a vacuum of about 5×10^{-4} Torr. The crucible contained in the selenium-arsenic alloy is then heated to a temperature of about 300°C and evaporation continued for about 40 minutes resulting in the formation of a 50 micron vitreous selenium-arsenic alloy photoconductive layer being coated over the interfacial barrier layer.

EXAMPLE II

The photoreceptor belt member made by Example I is electrically tested as follows: The belt is mounted on a tri-roller assembly adapted to rotate the belt over each roller. A corotron charging device is located at a point along the path of travel of the belt and a 15 watt cool white erase lamp is located at a point 0.25 inches from the charging unit. The belts are tested for electrical charge acceptance by charging to a potential of about 900 volts. The charge is then erased by exposure to the erase lamp. The charging and exposure cycle is carried out 100 times with the dark discharge being measured after the first cycle. The initial charge acceptance after the first cycle is 870 volts; the charge acceptance after the 100th cycle was 920 volts. The residual voltage was 40 volts and the contrast potential available for development was 880 volts. The dark discharge after the first cycle was 2 percent. These electrical properties are deemed acceptable for commercial xerographic photoreceptor.

Before and after forming the photoconductive layer, the interface and photoconductive selenium alloy were subjected to a scratch test. This test is conducted to determine the degree of adhesion of the interfacial layer to the substrate and the degree of adhesion of the selenium layer to the interfacial layer. This test is conducted by hand by scraping a pronged metallic device over the surface of the appropriate layer. Both layers exhibited good adhesion when subjected to this test.

The belt of Example I is also subjected to a cold test to determine adhesion and resistance to cracking at low temperature. The belt is wrapped in aluminum foil and placed in an ice chest filled with ice for 24 hours. After 24 hours, the selenium layer remained intact with no evidence of cracking or spalling away from the interface.

Although specific components and proportions have been stated above in the above description of the preferred embodiments of this invention, other suitable procedures and materials such as those listed above, may also be used with similar results.

Other modifications and ramifications of the present invention would appear to those skilled in the art upon reading the disclosure. These are also intended to be within the scope of this invention.

What is claimed is:

1. A xerographic member which comprises a conductive substrate having thereon an interfacial barrier layer having a thickness of about 0.5 to 3.0 microns, said barrier layer comprising a polymer blend or mixture of a polycarbonate, a polyether-ester-urethane, and a chlorosulfonated polyethylene, with the polycarbonate being present in a concentration of about 30 to 80 weight percent and the poly-urethane and chlorosul-

fonated polyethylene being present in a combined concentration of about 20 to 70 weight percent, with said interfacial layer having a composite resistivity of about 10^{11} to 10^{14} ohm-cm., and a photoconductive layer about 10 to 200 microns in thickness overlaying said interfacial layer.

2. The member of claim **1** in which the photoconductor comprises a vitreous alloy of selenium and arsenic.

3. The member of claim **1** in which the arsenic is present in an amount of about 0.1 to about 50 percent by weight with the balance substantially selenium.

4. The member of claim **1** in which the photoconductive layer comprises about 99.67 weight percent selenium and 0.33 weight percent arsenic.

5. The member of claim **4** in which the selenium-arsenic photoconductor contains a chlorine dopant.

6. The member of claim **1** in which the photoconductive layer comprises vitreous selenium.

7. The member of claim **1** in which the photoreceptor member is in the form of an endless flexible belt.

8. The member of claim **7** in which the flexible belt substrate is made of nickel.

9. The member of claim **7** in which the belt substrate is made of brass.

10. The member of claim **7** in which the belt substrate is made of a material selected from the group consisting of nickel, brass, aluminum and stainless steel.

11. The member of claim **8** in which the photoreceptor comprises about 99.67 weight percent selenium and 0.33 weight percent arsenic.

12. The member of claim **11** in which the selenium-arsenic photoconductor contains a chlorine dopant.

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