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(54) Overcoated photoresponsive devices.

(57) A layered photoresponsive device comprising in the order stated: a substrate (3), a hole transport layer (5) comprised of an arylamine dispersed in a resinous binder composition, a charge carrier photogenerating layer (7), and a protective overcoating layer (9) comprising an ultraviolet light absorbing composition.

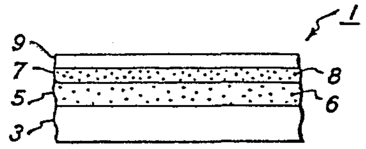

FIG. 1

Croydon Printing Company Ltd

Overcoated photoresponsive devices

This invention is generally directed to a layered photoresponsive device, and more specifically, the present invention is directed to such a device of the kind comprising, in the order stated, a substrate; a hole transport layer comprising an arylamine dispersed in a resinous binder composition; a charge carrier photogenerating layer; and a protective overcoating layer.

Photoresponsive devices, including layered photoresponsive devices containing charge transport layers, and charge generating layers of selenium, selenium alloys, phthalocyanines, and the like are known. Also, photoreceptor materials comprised of inorganic or organic compositions wherein the charge carrier generation and charge carrier transport functions are accomplished by discrete contiguous layers are disclosed in the prior art. Additionally, photoreceptor materials are disclosed in the prior art which include an overcoating layer of an electrically insulating polymeric material, and in conjunction with this overcoated type photoreceptor, there have been proposed a number of imaging methods.

Recently, there has been disclosed layered photoresponsive devices comprised of generating layers and transport layers, reference U.S. Patent 4,265,990, and overcoated photoresponsive materials containing a hole injecting layer, overcoated with a charge transport layer, followed by an overcoating of a photogenerating layer, and a top coating of an insulating organic resin, reference U.S. Patent 4,251,612. Examples of photogenerating compositions disclosed in these patents include trigonal selenium, various phthalocyanines, and the like, while examples of charge transport layers include those comprised of diamines. Additionally, there is disclosed in U.S. Patent 3,041,116 a photoconductive material containing a transparent plastic material overcoated on a layer of vitreous selenium which is contained on a recording substrate. Apparently in operation, the surface of the transparent plastic is electrostatically charged to a desired polarity, followed by exposing the device to activating radiation, which generates a hole electron pair in the photoconductive layer, causing electrons to move to the plastic layer and neutralize the positive charges contained on the free surface of the plastic layer, thus creating an electrostatic image.

In some of the prior art devices, the diamine transport molecules contained in the transport layer can be adversely affected, and degraded by ultraviolet light, and corona exposures, rendering such devices substantially useless for obtaining continuous high quality images. This is particularly a problem with regard to devices containing a top photogenerating layer, which is charged positively.

Apparently, the diamines contained in the transport layer are converted to a cationic radical by ultraviolet light, this radical causing the positive charges contained on the surface of the layered imaging member to be undesirably eliminated. More specifically the overcoating layer of the photoresponsive device of the present invention is comprised of materials that will absorb damaging short wavelength light, while transmitting the longer wavelengths to the photogeneration layer. Since the damaging light radiation extends into the visible, that is wavelength of 450 nanometers the photosensitivity is reduced in the blue by a purely absorptive layer. The photosensitivity at these blue wavelengths can however be restored by using as an overcoat layer materials that are photosensitive to the the short wavelengths they absorb.

Accordingly, there is a need for eliminating the degradation of such diamine molecules. The improved layered photoresponsive device of the present invention accomplishes this important objective.

Additionally, it is known that the application of protective coatings to photoconductive substances, particularly inorganic photoconductive materials, can be effected primarily for the purpose of extending the useful life of these devices. Without such overcoatings, deterioration of the photoconductive member occurs by, for example, the mechanical abrasion attendent to the developing and cleaning processes. In view of this, and for other reasons, various protective overcoatings have been applied to inorganic photoresponsive devices. Thus for example, there is disclosed in U.S. Patent 3,397,982 an electrostatic imaging device comprising a photoconductive layer containing an inorganic glass material, and a photoconductive layer with an overcoating comprised of various oxides, such as germanium oxides, the oxides of vanadium, and silicone dioxides.

Moreover, there is disclosed, for example in US Patent 3 655 377 the use of an arsenic selenium alloy as an overcoating on tellurium selenium alloy photogenerator layer. This prior art, however is silent with regard to protecting the diamine transport molecule from damage by radiation and corona effluents.

Furthermore, there is disclosed in US Patent 2 886 434 processes for protecting selenium photoconductive substances with a thin, transparent film of a material having electrical characteristics comparable to selenium. Examples of materials disclosed as protective layers in this patent include zinc sulfide, silica, various silicates, alkaline earth fluorides, and the like. Nevertheless, there continues to be a need for protective overcoatings, particularly for layered photoresponsive devices containing charge transport layers, and photogenerating layers, which overcoatings also function simultaneously as an ultraviolet light absorber layer for the purpose of preventing degradation of the diamines contained in the charge transport layer.

There also continues to be a need for improved layered photoresponsive devices which not only generate acceptable images but which can be repeatedly used in a number of imaging cycles without deterioration thereof from the machine environment or surrounding conditions. Additionally, there continues to be a need for improved layered imaging devices, wherein the hole transporting compositions selected for use in these devices do not degrade after extended usage. Further, there also continues to be a need for improved photoresponsive devices which contain hole transport layers photogenerating layers, and an overcoating protective layer, which devices are sensitive to visible light and infra-red illumination, thereby allowing these devices to be selected for use in a number of imaging and printing systems.

It is therefore an object of the present invention to provide an improved photoresponsive member which is sensitive to visible light as well as to infra-red light, and which overcomes the above-noted disadvantages.

The present invention provides a photoresponsive device of the kind specified which is characterised in that the overcoating layer comprises an ultraviolet light absorbing composition.

Accordingly there is provided a layered photoresponsive imaging device wherein the aryldiamine molecules that escape from the hole transport layer are prevented from degradation by the protective overcoating layer. The overcoating layer functions as an ultraviolet light absorbant substance, while simultaneously functioning as a visible light photogeneration layer, and as a physical protectant layer for the other layers contained in the device.

The improved photoresponsive devices of the present invention can be prepared by a number of known methods, the process parameters and the order of coating the layers being dependent on the device desired. Thus, for example, the improved photoresponsive device of the present invention can be prepared by providing a conductive substrate, and applying thereto by solvent coating processes, laminating processes, solvent spraying processes, or other methods, a hole transport layer, a photogenerating layer, and a protective overcoating. More specifically, the improved photoresponsive device of the present invention can be prepared by depositing the hole transport layer and photogenerating layers by a solvent spraying process, followed by application of the protective overcoating layer by vacuum deposition. In this process, the hole transport, and photogenerating layers are generally deposited at room temperature, while the overcoating layer is applied at higher temperatures, with the thickness of the layers being controlled for example by the proportions of solvent to hole transport layer or photogenerating layer utilized, and by repeating the coating process as appropriate. Examples of solvents that may be selected in the solvent spraying process include methylene chloride, ethylene chloride, and mixtures thereof.

The improved layered photoresponsive device of the present invention can be selected for use in various imaging systems, and more importantly, can function in imaging and/or printing systems utilizing visible light and/or infrared light. Thus, the improved photoresponsive devices of the present invention can be selected for use in imaging devices where the device is positively charged and wherein the arylamine materials selected for use in the transport layer are not degraded by ultraviolet light. In one embodiment, the imaging method of the present invention involves positively charging the photoresponsive device described herein, subjecting the device to imagewise charging for the purpose of forming an electrostatic latent image thereon, developing the latent image with a developer composition comprised of toner particles and carrier particles, followed by transferring the image to a suitable substrate such as paper, and permanently affixing the image thereto.

In another embodiment of the present invention, the photoresponsive device can be selected for use in printing systems, that is in those apparatuses wherein a laser, such as a gallium arsenide laser, or image bars are used for generating the image to be developed.

For a better understanding of the present invention, and further features thereof, reference is made to the following detailed description of various preferred embodiments wherein:

Figure 1 is a partially schematic cross-sectional view of the improved photoresponsive device of the present invention;

Figure 2 is a partially schematic cross-sectional view of a preferred photoresponsive device of the present invention; and

Figure 3 is a partially schematic cross-sectional view of a preferred photoresponsive device of the present invention.

Illustrated in Figure 1 is the improved photoresponsive device of the present invention, generally designated 1, and comprising a substrate 3, a hole or charge transport layer 5, containing a hole transporting composition dispersed in an inert resinous binder 6, a charge carrier photogenerating layer 7, containing a photogenerating pigment optionally dispersed in an inert resinous binder 8, and a protective overcoating layer 9.

The substrate layer 3 may be opaque or substantially transparent, and may comprise suitable materials having the appropriate mechanical properties. Generally, the substrate is comprised of an insulating material, such as an organic or inorganic polymeric material, a layer of an organic or inorganic material having a semiconductive surface layer arranged thereon, or a conductive material such as for example, aluminum, chromium, nickel, indium, tin oxide, brass, or the like. Examples of insulating layers that can be selected as the substrate include various resinous materials, such as polycarbonates, polyesters, and the like, however, the substrate is preferably comprised of a material commercially available as aluminized Mylar. The substrate may be flexible or rigid, and may have a number of different configurations, including a plate, a cylindrical drum, a scroll, an endless flexible belt, and the like. Preferably, the substrate is in the form of an endless flexible belt, or a rigid cylindrical drum.

The thickness of the substrate layer varies depending upon many factors, including economical considerations, thus this layer may be of substantial thickness, for example, over 10 millimeters, or of minimum thickness, providing there are no adverse effects with the resulting device. In one preferred embodiment, the thickness of this layer ranges from about 3 millimeters to about 10 millimeters.

The hole transport layer 5 can be comprised of a number of suitable materials which are capable of transporting holes, this layer generally having a thickness in the range of from about 5 to about 50 micrometers, and preferably this layer is of a thickness of from about 20 to about 40 micrometers. Transport layer 5 thus comprises an arylamine electron donor dispersed in an inert resinous binder material 6. Illustrative examples of electron donor molecules include those as described in U.S. Patent 4,265,990. Specific illustrative examples of electron donor molecules include aryl amines, such as substituted N,N,N',N'-tetraphenyl-[1,1'-biphenyl]4,4'-diamines of the formula as illustrated in the 4,265,990 patent.

The inert highly insulating resinous binder 6, which has a resistivity of at least 10^{12} ohm-cm to prevent undue dark decay, is a material which is not necessarily capable of supporting the injection of holes from the photogenerator layer, and is not capable of allowing the transport of these holes through the material. However, the resin becomes electrically active when it contains from about 10 to 75 weight percent of the substituted N,N,N',N'-tetraphenyl-[1,1'-biphenyl]4,4'-diamines. Specific examples of such diamines include, N,N'-diphenyl-N,N'-bis(alkylphenyl)-[1,1'-biphenyl]-4,4'-diamine wherein alkyl is selected from the group consisting of methyl, such as 2-methyl, 3-methyl, and 4-methyl, ethyl, propyl, butyl, hexyl, and the like. With halo substitution, the amine is N,N'-diphenyl-N,N'-

bis(halophenyl)-[1,1'-biphenyl]-4,4'-diamine wherein halo is 2-chloro, 3-chloro, or 4-chloro.

Other electrically active donor compositions which can be dispersed in the electrically inactive resin to form a layer which will transport holes include the arylamines, triphenylamine, bis-(4-diethylamino-2-methylphenyl)phenylmethane; bis-(4-diethylaminophenyl)phenylmethane; 1-phenyl-3-(4'-diethylaminostearyl)-5-(4"-diethylaminophenyl) pyrazoline; 4-diethylaminobenzaldehyde-1,1-diphenyl hydrazone; 2,5-bis-(4'diethylaminophenyl)-1,3,4-oxadiazole; and 1,4-bis-[bis(4'-(phenylmethyl)-amino-2'-methylphenyl)methyl] benzene.

A preferred hole transport layer, in a thickness of from about 10 micrometers to about 20 micrometers, is comprised of 35 percent by weight of the diamine N,N'-diphenyl-N,N'-bis(3-methylphenyl)1,1'-biphenyl-4,4'-diamine, dispersed in 65 percent by weight of the polycarbonate resin commercially available as Makrolon.

Illustrative examples of insulating resinous binders 6 for the hole transport layer include in addition to polycarbonate resins commercially available as Makrolon, Merlon and Lexan, polysulfones polystyrene, and the like. Generally, the diamine transport molecule is dispersed in the resinous binder, in an amount ranging from about 25 percent by weight to 70 percent by weight, and preferably in an amount of from about 30 percent by weight to about 50 percent by weight.

The photogenerating layer 7 includes for example, numerous photoconductive charge carrier generating materials providing they are electronically compatible with the charge carrier transport layer, that is, they can inject photoexcited charge carriers into the transport layer and charge carriers can travel in both directions across the interface between the two layers. Thus, the photogenerating layer 7 can be comprised of inorganic photosensitive pigments such as trigonal selenium, mixtures of Groups IA and IIA elements, cadmium selenide, cadmiun sulfur selenide, copper and chlorine doped cadmium sulfide,and trigonal selenium doped with sodium carbonate reference U.S. Patents 4,232,102 and 4,233,283, and the like, optionally dispersed in various resinous binders.

The photogenerating layer can also contain organic charge carrier generating materials such as phthalocyanines, including for example, metal phthalocyanines, metal free phthalocyanines, vanadyl phthalocyanines, squaraine pigments, such as methyl squarilium pigments, hydroxy squarilium pigments, and mixtures thereof, optionally dispersed in resinous binders.

Other photogenerating materials not disclosed herein can be selected for the photoresponsive device of the present invention including, for example, other phthalocyanines, such as copper phthalocyanine, zinc phthalocyanine, magnesium phthalocyanine, the x-form of metal free phthalocyanine, and the like.

The photogenerating pigments are usually dispersed in an inactive resinous binder, 8, illustrative examples of which include polyesters, polycarbonates, polystyrenes, polysulfones, phenoxy resins, epoxy resins, and the like, with polyesters being preferred. Generally, the photogenerating pigment is contained in the resinous binder in an amount of from about 5 percent by weight to about 80 percent by weight, and preferably in an amount of from about 10 percent by weight to about 40 percent by weight. Accordingly, in this embodiment the resinous binder is present in an amount of from about 95 percent by weight to about 20 percent by weight, and preferably in an amount of from about 90 percent by weight to about 60 percent by weight.

The thickness of the photogenerating layer depends on a number of factors including the thicknesses of the other layers, generally, however, this layer ranges in thickness of from about 0.01 micrometers to about 10 micrometers, and preferably is of a thickness of from about 0.1 micrometers to about 1.0 micrometers. The maximum thickness of this layer is dependent primarily on factors such as mechanical considerations, while the minimum thickness of this layer is dependent on for example, the pigment particle size, optical density of the photogenerating pigment, and the like.

The overcoating layer 9, which generally ranges in thickness of from about 0.05 micrometers to about 10 micrometers, and preferably is of a thickness of from about 0.2 micrometers to about 5 micrometers, is comprised of materials that are capable of absorbing ultraviolet light so as to prevent the degradation of the electron donor arylamine materials contained in the transport layer 5, which materials diffuse to some extent into layer 7. Also, this layer can function as a protective layer for the photoresponsive device. Illustrative examples of materials selected for layer 9 include selenium, alloys of selenium, such as arsenic selenium, containing 0.1 to 50 percent by weight of arsenic, and 99.9 to about 50 percent by weight selenium, arsenic selenium alloys containing halogens, such as chlorine or iodine, in an amount of from about 1 part per million to about 1 percent, as well as selenium tellurium alloys, arsenic selenium tellurium alloys, the above selenium alloys containing germanium, and the like.

Other overcoating materials not specifically disclosed herein may also be selected providing the objectives of the present invention are achieved including, for example, other inorganic and organic materials, such as vacuum deposited phthalocyanines, subject to the provision that these materials absorb ultraviolet light, and function as an electrically active charge generating layer. Additionally, solvent coated organic polymers may be used provided they absorb ultraviolet light, or contain ultraviolet absorbing additives, and further, providing that the coating process does not result in the diffusion of the arylamine transport molecule into the overcoating layer 9. Illustrative examples of organic materials that may be selected for the overcoating layer 9 include various polymers containing therein organic and/or inorganic ultraviolet light absorbers. Examples of these materials include polycarbonates, polyesters, silicon polymers, siloxanes, and the like, having dispersed therein ultraviolet light absorbers, such as zinc oxide, amorphous or crystalline particles of selenium, arsenic, or selenium tellurium alloys, phenidone, uvinul, and the like. Generally, the ultraviolet light absorbers are present in the organic material in an amount ranging from about 5 percent by weight to about 40 percent by weight, and preferably in an amount of from about 10 percent by weight to about 20 percent by weight.

While it is not desired to be limited by theory, it is believed that overcoating layer 9 prevents the degradation of the arylamines contained in the charge transport layer that have migrated or diffused into the photogenerating layer during, for example the solvent coating of this layer. The overcoating layer is believed to prevent the penetration into the photoresponsive device of ultraviolet light, and ionized molecules resulting from corona exposure. The action of ultraviolet light and ionized molecules on the charge transport amine molecules is believed to result in the formation of cations. This causes the photoresponsive device to have unstable electricals due to the trapped cation radicals. These unstable electricals cause an increase residual voltage or loss in charge acceptance of the photoresponsive device due to charge sweepout, adversely affecting the device and resulting in images of very low quality.

Addtionally while the primary function of the overcoating layer 9 is to prevent ultraviolet light from migrating to the photogenerating layer, the overcoating layer can also act as a protectant, both physical and chemical, for the photoresponsive device, and further, this overcoating layer prevents ions generated by the corona charging device to reach the photogenerating layer. More specifically, as a protective layer, the overcoating layer prevents the mechanical abrasion and/or chemical damage relating to the developing, charging and cleaning processes selected for electrostatographic imaging methods. Also, this overcoating layer enables broad spectral response of the photoresponsive device in that it combines for example excellent blue and visible photoresponse of the selenium alloy, overcoating layer with excellent red and infrared photoresponse of the phthalocyanine generating layer.

The photoresponsive device of the present invention is useful primarily as an infrared imaging device, that can be selected for incorporation into various imaging systems, wherein light emitted by lasers are utilized. Such a device has sensitivity ranging from about 700 nanometers to about 900 nanomaters, and thus can be selected for use with solid state lasers, including helium-neon lasers, and gallium arsenide lasers. However, as disclosed herein, the photoresponsive devices of the present invention are also sensitive to visible light, that is light having a wavelength of from about 400 nanometers to about 700 nanometers.

Illustrated in Figure 2 is a preferred layered photoresponsive device of the present invention designated 10, and comprised of a substrate 15 of an aluminum drum in a thickness of 4 millimeters, a hole transport layer 17, containing 35 percent by weight of N,N'-diphenyl-N,N'-bis(3-methylphenyl)1,1'-biphenyl-4,4'-diamine dispersed in 18, 65 percent by weight of a polycarbonate commercially available as Merlon, this layer having a thickness of from about 10 micrometers to about 25 micrometers, a photogenerating layer 19, comprised of 30 percent by weight of vanadyl phthalocyanine, dispersed in 20, 70 percent by weight of a polyester material, PE-100, commercially available from Goodyear Corporation, this layer having a thickness of 1 micrometer, and layer 21, the protective layer, comprised of an arsenic selenium alloy, containing 2 weight percent of arsenic, and 98 weight percent of selenium, this layer having a thickness of 1.0 micrometers.

Illustrated in Figure 3 is a another embodiment of the improved photoresponsive device of the present invention designated 25, this device being comprised of a substrate 30, of an electroformed nickel belt in a thickness of 100 micrometers, a charge transport layer 32, having a thickness of 16 micrometers, and containing 40 percent by weight of N,N'-diphenyl-N,N'-bis(3-methylphenyl)1,1'-biphenyl-4,4'-diamine, and 60 percent by weight of a polycarbonate, commercially available as Merlon, a photogenerating layer 34 containing 30 percent by weight of trigonal selenium, dispersed in 33, 70 percent by weight of a polyester material, PE-49,000, commercially available from E. I. duPont Co., this layer having a thickness of 0.8 micrometers, and a protective layer 36, 0.5 micrometers in thickness containing a selenium arsenic alloy, containing 36 weight percent of arsenic, and 64 weight percent of selenium.

This invention will now be described in detail with reference to the specific preferred embodiments thereof, it being understood that these examples are intended to be illustrative only, and the invention is not intended to be limited to materials, conditions, process parameters, and the like recited herein. All parts and percentages are by weight unless otherwise indicated.

Moreover, in the examples that follow, the processing steps were accomplished in a room containing red safe lights so as to not expose the materials, particularly the amine charge transport materials, to light of wavelengths less than 500 Angstroms, in order to prevent ultraviolet light degradation of such materials.

EXAMPLE I

An overcoated photoreceptive device was prepared by applying, with spraying, with a Model No. 21 spray gun, commercially available from Binks, Inc., an amine charge transport layer onto a clean aluminum cylinder having a diameter of 83 millimeters. The spraying was accomplished in a laminar air flow booth designed to process volatile solvents containing an entrance means and exhaust means. This booth also contained a motor driven mandrel with the aluminum cylinder mounted thereon, which cylinder was rotated about the vertical axis of the mandrel at 290 revolutions per minute. The Binks spray gun was located 20 centimeters from the aluminum cylinder, and the spray booth was maintained at a temperature of 20 degrees centigrade and a relative humidity of about 40 percent.

Prior to spraying the aluminum cylinder was cleaned by dipping it into a solution containing 3 percent of sodium carbonate and 3 percent of sodium triphosphate, for 1 minute. Subsequently, the aluminum cylinder was removed from the solution, washed with water and immersed for 0.5 minutes in concentrated nitric acid, 67 weight percent. The cylinder was then removed from the nitric acid and rinsed thoroughly with deionized water.

The charge transport layer applied contained a 4 percent solid solution of a mixture of 65 percent by weight of the polycarbonate resin, Merlon M 39N, and 35 percent by weight of N,N'-diphenyl-N,N'-

bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine. This mixture was prepared by dissolving in a 0.5 liter amber bottle, the polycarbonate resin, Merlon M39N available commercially from Mobay Chemical, in a solution containing 60 percent by volume of methylene chloride and 40 percent by volume 1,1,2-trichloroethane. The polycarbonate resin was dissolved by tumbling the solution mixture for one hour on a paint shaker, and after tumbling the resulting mixture was allowed to stand for about 24 hours at room temperature.

There was then added to the resulting solution N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, which diamine was dissolved therein by tumbling the mixture for two hours on a paint shaker. After tumbling, the resulting mixture was allowed to remain at room temperature for about 24 hours.

The resulting solution was then applied to the aluminum cylinder, by spraying with the Model No. 21 spray gun followed by drying at 40°C for 20 minutes, and 160°C for 60 minutes, the drying being affected in a forced air oven. There resulted an aluminum cylinder containing thereon in a thickness of 15 micrometers, a charge transport layer comprised of 35 percent by weight of the amine indicated, and 65 percent by weight of the polycarbonate resin specified.

There was then applied to the transport layer, by spraying with the above Binks Model No. 21 spray gun, a photogenerating layer containing 30 percent by weight of vanadyl phthalocyanine, dispersed in 70 percent by weight of a polyester.

The photogenerating composition was prepared by mixing 30 percent by of weight vanadyl phthalocyanine, and 70 percent by weight of a polyester, commercially available from Goodyear as PE-

100 polyester. This mixture was placed in a 1 liter amber bottle, containing in a 60/40 volume ratio, a mixture of solvents of methylene chloride and 1,1,2-trichloroethylene. To the bottle was added steel shot, 3 millimeters in diameter. The contents of the bottle were then mixed on a paint shaker for 24 hours.

After removing, the steel shot by filtration there was added to the resulting slurry sufficient additional solvents so as to result in a mixture containing 1 percent solids, of vanadyl phthalocyanine and the PE-100 polyester. This mixture was then sprayed onto the above prepared diamine charge transport layer, with the Binks spray gun.

After spraying, the resulting device was dried at 100°C for 1.25 hours in a forced air oven, resulting in a photogenerating layer having a dry thickness of 1 micrometer.

A top ultraviolet light absorbing overcoating layer was then applied to the above photogenerating layer by placing the aluminum cylinder, containing the charge transport layer, and the photogenerating layer in a vacuum chamber, and vacuum evaporating on the photogenerating layer, an alloy containing 98 percent by weight of selenium and 2 percent by weight of arsenic. The vacuum chamber contained a horizontally rotating, motor driven shaft, a string of four crucibles, longer in length than the aluminum cylinder, these crucibles being of the size of 2.5 x 12.5 cm, which crucibles were placed 30 cm in distance away from the cylinder. There was also included in the vacuum chamber a radiant heater, which was placed above the cylinder, at a distance of 5 centimeters therefrom. These crucibles were loaded with the arsenic-selenium alloy pellets, each crucible containing about two grams of pellets. The vacuum chamber was then evacuated to a pressure of less than a [illegible] Torr, and the aluminum cylinder was rotated at a speed of [illegible] revolutions per minute, while being heated to 70°C with the radiant heaters. The arsenic selenium alloy was caused to evaporate and was deposited on the photogenerating layer by heating each of the crucibles to 300°C.

After cooling, there resulted on the photogenerating layer an overcoating layer of an arsenic selenium alloy, containing 2 percent by weight of arsenic and 98 percent by weight of selenium, which overcoating had a thickness of 1.5 micrometers.

There thus results a photoresponsive device comprised in the order stated of (1) an aluminum substrate, (2) a diamine transport layer, (3) a photogenerating layer of vanadyl phthalocyanine, and (4) and overcoating layer containing a selenium arsenic alloy.

The above prepared device was then charged positively to 800 volts with a corotron and was found to be electrically stable, over 100,000 imaging cycles, in that the device retained a positive charge of 800 volts as measured with an electrostatic voltmeter, commercially available from Monroe Electronics Inc. of Rochester New York. Moreover, the photoresponsive device sensitivity ranged from 90 volts/erg/cm^2 at 400 nanometers to 60 volts/erg/cm^2 at 900 nanometers, as measured with an electrostatic voltmeter, commercially available from Monroe Electronics Inc. of Rochester New York, which indicates that images can be formed on this device over a wavelength ranging from 400 nanometers to 900 nanometers.

The above-prepared photoresponsive device was incorporated as a photoreceptor into a commercially available Xerox 3300 copying apparatus, containing exposure lamps generating visible light, corotrons, a developing station, a fixing station, a transfer station, and a fusing station. Subsequent to development with toner particles containing a styrene n-butylmethacrylate resin copolymer and carbon black there resulted for 2,000 imaging cycles high quality images with excellent solid area coverage and low background, as determined by a visual observation of these images.

Additionally,the above-prepared photoresponsivedevice was incorporated as a photoreceptor into a commercially available Xerox 2700 printing device. The resulting images subsequent to development with toner particles containing a styrene n-butylmethacrylate copolymer and carbon black particles, were of excellent resolution with good solid area coverage for 100,000 imaging cycles, as determined by a visual observation of these images.

Example II

A photoresponsive device was prepared by applying with a Bird applicator gap thickness of 125 micrometers an amine transport layer, onto a clean nickel sheet, having a thickness of 50 micrometers. The nickel sheet was cleaned by repeating the process steps of Example I as they apply to the cleaning of the aluminum cyclinder.

There was then applied to the nickel sheet, with a Bird applicator a solution prepared in a one liter amber bottle containing 8.4 grams of the available polyester resin Makrolon, and 5.6 grams of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine in 62 milliliters of methylene chloride. The device was then dried in a forced air oven at 135^{O}C for 60 minutes, resulting in a transport layer having a thickness of 20 micrometers.

The transport layer was then overcoated with a photogeneration layer as follows:

In a one liter amber bottle, 1.77 grams of Makrolon was dissolved in 15.6 milliliters of methylene chloride. Added to this solution was 0.43 grams of hydroxy squarilium and glass beads for mixing. This mixture was then placed on a paint shaker for 90 minutes and the resulting slurry, after removal of the glass beads by filtration was coated with a Bird applicator to a dry thickness of about 1 micrometer, on the amine transport layer. The device was dried at 120°C for 60 minutes in a forced air oven.

An overcoating layer of arsenic triselenide (As_2Se_3) 39 percent by weight of arsenic, and 61 percent by weight of selenium was applied to the photogenerating layer in a vacuum chamber by vacuum deposition, by repeating the appropriate process steps of Example I. The device was maintained at room temperature while sufficient As_2Se_3 was evaporated to produce an overcoating layer thickness of 0.1 micrometers.

The above-prepared device was then charged positively to 800 volts with a corotron, and was found to be electrically stable, over 30,000 imaging cycles in that the device retained a positive charge of 800 volts as measured with an electrostatic voltmeter, commercially available from Monroe Electronics, Inc. Moreover, the photoresponsive device sensitivity ranged from 10 volts/erg/cm^2, at 400 nanometers, to 30 volts/erg/cm^2, at 900 nanometers, as measured with an electrostatic voltmeter, commercially available from Monroe Electronics, Inc., indicating that images could be formed on this device.

EXAMPLE III

A photoresponsive device was prepared by repeating the procedure of Example I with the exception that the top overcoating layer of the selenium arsenic alloy was not applied to the photogenerating layer, thus resulting in a photoresponsive device comprised in the order stated of (1) an aluminum substrate, (2) a diamine transport layer, and (3) a photogenerating layer of vanadyl phthalocyanine. This device was then incorporated as a photoreceptor into the Xerox 2700 printer, reference Example II, and after 1,000 imaging cycles substantially no images resulted since apparently the amine transport layer, some of the molecules of which diffused into the photogenerating layer, were adversely affected. Subsequent to 2,000 imaging cycles, and exposure of the photoresponsive device to room fluorescent light, electrical measurements of the device with an electrostatic voltmeter, commercially available from Monroe Electronics, Inc., indicated that the charge acceptance of this device without an overcoating layer, undesirably decreased from 850 volts to 100 volts, indicating that no images would be obtainable.

— In contrast, the overcoated photoresponsive device prepared in accordance with Example I was incorporated as a photoreceptor in the same Xerox 2700 printer and after 50,000 images were formed and developed, no image degradation was observed in that the images were of high resolution with good solid background. Further, the overcoated device after 50,000 imaging cycles and exposure to room fluorescent light, showed that the charge acceptance remained at 850 volts with no decrease, as measured by an electrostatic voltmeter, commercially available from Monroe Electronics, Inc.

EXAMPLE IV

Two photoresponsive devices were prepared, by repeating the procedures of Examples I and III, resulting in the photoresponsive device without a selenium alloy overcoating, and a photoresponsive device with a selenium alloy. Both photoresponsive devices were then exposed to light of a wavelength of 400 noanometers, at an intensity of 2 milliwatts/cm^2, for 5 minutes. The device with no selenium alloy overcoating accepted less than 100 volts, as measured with an electrostatic voltmeter, commercially available from Monroe Electronics, Inc., while the device containing the arsenic alloy overcoating, reference the device of Example 1, was unaffected and accepted charge of 800 volts. These measurements indicated that the non-overcoated device would not form images, since charge acceptance was not sufficient, and that the overcoated device would form images.

Further, the photoresponsive devices as prepared in accordance with Examples I-IV, were individually tested for ultraviolet light degradation by exposing these devices to unfiltered light from a 1 kilowatt Xenon lamp for a period of 30 seconds, for the purpose of determining whether the devices would accept charge since acceptance of charge indicates that these devices would form images and were not degraded by ultraviolet light. Measurements were accomplished with an electrostatic voltmeter, commercially available from Monroe Electronics, Inc. Those devices containing the arsenic alloy overcoating, reference the device as prepared in Example I, accepted 800 volts of charge, while those devices that did not contain a selenium alloy overcoating, accepted 0 volts, indicating substantial degradation of the materials in the device.

Claims:

1. A layered photoresponsive device comprising in the order stated: a substrate (3); a hole transport layer (5) comprising an arylamine dispersed in a resinous binder composition; a charge carrier photogenerating layer (7); and a protective overcoating layer (9); characterised in that the overcoating layer comprises an ultraviolet light absorbing composition.

2. A photoresponsive device in accordance with Claim 1 wherein the protective overcoating layer (9) comprises amorphous selenium.

3. A photoresponsive device in accordance with Claim 1 wherein the protective overcoating layer (9) comprises a selenium alloy, and the arylamine comprises a substituted N,N,N',N'-tetraphenyl-[1,1'-biphenyl]-4,4'-diamine dispersed in a resinous binder.

4. A photoresponsive device in accordance with Claim 3 wherein the arylamine is N,N'-diphenyl-N,N'-bis(alkylphenyl)-[1,1'-biphenyl]-4,4'-diamine, or N,N'-diphenyl-N,N', bis(3-methylphenyl)-1,1',-biphenyl-4,4',-diamine.

5. A photoresponsive device in accordance with Claim 3 wherein the protective selenium alloy overcoating contains from 0.1 percent by weight to 50 percent by weight of arsenic, and from 99.9 percent by weight to 50 percent by weight of selenium.

6. A photoresponsive device in accordance with Claim 3 wherein the protective selenium alloy overcoating contains 2 percent by weight of arsenic, and 98 percent by weight of selenium, or wherein the protective selenium alloy overcoating contains 40 percent by weight of arsenic, and 60 percent by weight of selenium.

7. A photoresponsive device in accordance with Claim 3 wherein there is incorporated into the selenium alloy a halogen material.

8. A photoresponsive device in accordance with Claim 7 wherein the halogen is chlorine present in an amount of 20 parts to 200 parts per million.

9. A photoresponsive device in accordance with any one of Claims 1 to 8 wherein the thickness of the substrate (3) ranges from 3 millimeters to 10 millimeters, the thickness of the hole transport layer (5) ranges from 5 micrometers to 50 micrometers, the thickness of the photogenerating layer (7) ranges from 0.01 micrometers to 10 micrometers, and the thickness of the protective overcoating layer (9) ranges from 0.1 micrometers to 10 micrometers.

10. A method of imaging which comprises charging the photoresponsive device of any one of Claims 1 to 9, followed by imagewise exposure of this device, developing the latent electrostatic image formed, transferring the image to a suitable substrate, and optionally permanently affixing the image thereto.

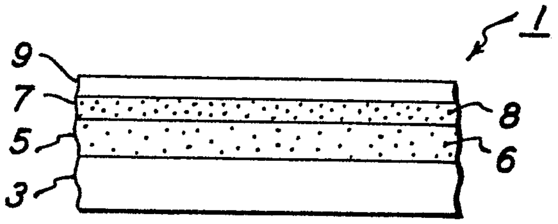

FIG. 1

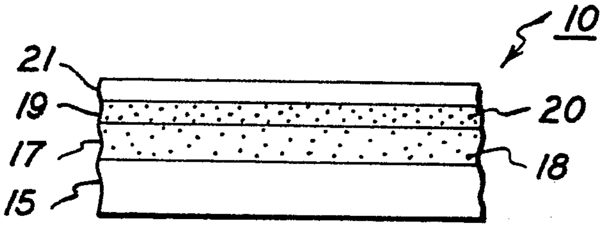

FIG. 2

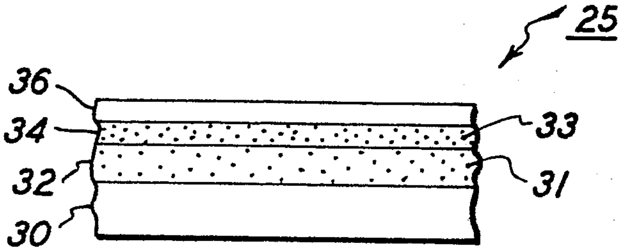

FIG. 3