

United States Patent [19]

Staudenmayer et al.

[11] 3,753,709

[45] Aug. 21, 1973

[54] **CROSSLINKED RESIN OVERCOATED
ELECTROPHOTOGRAPHIC ELEMENTS
USEFUL IN LITHOGRAPHY**

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[22] Filed: **Feb. 25, 1971**

[21] Appl. No.: **119,050**

[52] U.S. Cl. **96/1.5, 96/1 R, 96/33,**
101/457, 101/462, 117/161 UB, 117/161 UE

[51] Int. Cl. **G03g 5/06**

[58] Field of Search..... **96/1, 1.5, 1.8;**
101/457, 462

[56] **References Cited**

UNITED STATES PATENTS

3,669,657 6/1972 Adams et al. 96/1.8

3,507,647 4/1970 Sanders 96/1.5
3,140,174 7/1964 Clark 96/1.8
3,482,970 12/1969 Solodar et al. 96/1.5
3,438,773 4/1969 Hayashi et al. 96/1.5
3,407,064 10/1968 Bach et al. 96/1.5 X

OTHER PUBLICATIONS

DuBois, "Plastics", 1943, Amer. Tech. Soc., pp.
335-337

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[57] **ABSTRACT**

Electrophotographic elements are provided with a conversion-free overcoat of a layer comprising a cross-linkable polymer and a crosslinking agent therefor. These elements are useful as lithographic printing masters without the need for a separate conversion step after development.

18 Claims, No Drawings

CROSSLINKED RESIN OVERCOATED ELECTROPHOTOGRAPHIC ELEMENTS USEFUL IN LITHOGRAPHY

This invention relates in general to electrophotography and in particular to an electrophotographic element having a novel overcoat layer which can be used to prepare a lithographic printing plate. More specifically, this invention relates to an electrophotographic element capable of being converted solely by electrophotographic imaging techniques to a lithographic printing plate and to the method of conversion thereof.

It has been known for many years to utilize electrophotographic imaging to provide plates for use in lithography. One way of accomplishing this is to transfer a hydrophobic powder image, which has been formed upon a photoconductive insulating layer by conventional procedures, to a lithographic support. A number of methods have also been developed to eliminate the need for transferring the image by forming a printing surface on the electrophotographic element itself which is hydrophobic in the areas which are to receive the printing ink and hydrophilic in the adjacent areas. Thus, for example, it is known to coat the photoconductive layer over a hydrophilic layer, form a hydrophobic powder image on the photoconductive layer, and then remove the non-imaged areas of the photoconductive layer to expose the underlying hydrophilic layer. It is also known to utilize as a binder for the photoconductor an electrically-insulating, film-forming resin which can be rendered hydrophilic by hydrolysis, or by reaction with a metal salt and after forming the hydrophobic powder image, treating the surface to make the non-imaged areas hydrophilic. In an alternative procedure, the photoconductor in the non-imaged areas is rendered hydrophilic by treatment with a bath containing agents which react with the photoconductor. In yet another method, zinc oxide is employed as the photoconductor and the photoconductive layer is overcoated with a thin layer of a resin which reacts with the zinc oxide to give a hydrophilic surface. An overcoat layer can also be prepared from cellulose acetate and after image formation, the areas which are not covered by the powder image can be rendered hydrophilic by hydrolyzing the cellulose acetate. Included among the many patents pertinent to the adaptation of electrophotographic imaging techniques to the preparation of lithographic printing plates, and to which reference may be made for details of the aforesaid techniques, are U.S. Pat. Nos. 2,952,536 by Kurz, issued Sept. 13, 1960; 2,957,765, by Resetich, issued Oct. 25, 1960; 3,001,872 by Kurz, issued Sept. 26, 1961; 3,107,169 by Bornarth, issued Oct. 15, 1963; 3,407,064 by Bach et al, issued Oct. 22, 1968; and 3,445,224 by Bach et al., issued Oct. 20, 1969.

Copending Yoerger and Staudenmayer U.S. Ser. No. 69,176, filed Sept. 21, 1970 now abandoned, and entitled OVERCOATED ELECTROPHOTOGRAPHIC ELEMENTS ADAPTED TO THE PREPARATION OF LITHOGRAPHIC PRINTING PLATES describes an electrophotographic element from which a lithographic printing plate can be readily made. The element described therein comprises a conventional electrically conductive support bearing a photoconductive insulating layer, which in turn bears a thin overcoat layer of (1) a copolymer of vinyl acetate with a member selected from the group consisting of the alpha-

beta ethylenically unsaturated carboxylic acids and the anhydrides and partial alkyl esters thereof or (2) a blend of a vinyl acetate polymer and a polymer of a member selected from the group consisting of the alpha-beta ethylenically unsaturated carboxylic acids and the anhydrides and partial alkyl esters thereof. These polymers, or polymer blends, were found to provide an advantageous combination of properties for an overcoat layer, including strong adhesion to the photoconductive layer and good film-forming properties. The printing plate made therefrom, however, required a separate conversion step to render it hydrophilic.

In accordance with the present invention, it has been discovered that an improved printing plate can be obtained from an electrophotographic element comprising a conductive support bearing a layer of an organic photoconductive material by overcoating the photoconductive layer with a novel overcoat layer, and forming a toned image on the element thus produced using a hydrophobic toner in the normal electrophotographic process. The overcoat which is coated over the electrophotographic element to form the novel overcoated element of the invention is comprised of a cross-linkable polymeric material such as (a) a copolymer of vinyl acetate with a member selected from the group consisting of the alpha-beta ethylenically unsaturated carboxylic acids and the anhydrides and partial alkyl esters thereof, or (b) a blend of a vinyl acetate polymer with a polymer of a member selected from the group consisting of the alpha-beta ethylenically unsaturated carboxylic acids and the anhydrides and partial alkyl esters thereof, together with a cross-linking agent for the polymeric material. The phrase "partial ester" has reference to the half acid, half ester of an alpha-beta ethylenically unsaturated dicarboxylic acid.

The vinyl acetate polymer in the blend may be a homopolymer of vinyl acetate, or if desired, it may be a copolymer of vinyl acetate with one or more monomers with which it is capable of forming a copolymer. Such other monomers include, for example, N-vinyl-2-pyrrolidone, crotonic acid and other polymerizable acids containing a vinyl group. The ethylenically unsaturated carboxylic acids which can blend or copolymerize with the vinyl acetate-containing moiety generally include those acids having one or two carbon atoms between the ethylenic bond and the carboxyl group, as is well-known. Suitable acids include, for example, acrylic acid, methacrylic acid, crotonic acid, itaconic acid and maleic acid. The anhydrides include, for example, maleic anhydride and its methyl ester. Certain ethers containing a vinyl group can also enter into the polymerization reaction to form the overcoated element of the invention, such as, for example, vinyl methyl ether. Esters of unsaturated carboxylic acids are also suitable. Other monomers producing crosslinkable polymers include monomers containing active methylene groups. Particularly useful are monomers containing crosslinkable active methylene groups as described in Smith, U.S. Pat. No. 3,459,790 issued Aug. 5, 1969. Representative of a useful alkyl ester of an alpha-beta ethylenically unsaturated carboxylic acid containing an active methylene group would be acetoacetoxyethyl methacrylate. The polymer mixtures, combinations with which one skilled in the polymer art is very familiar, and all such combinations are intended to be included within the scope of the invention. The printing plate resulting from the overcoating of an electropho-

tographic element with the novel overcoats disclosed herein is converted into a printing plate by merely forming a hydrophobic image on its surface by conventional electrophotographic imaging techniques, as the surface of the element itself is hydrophilic without further treatment such as with hydrolyzing baths of the known types. Thus, the imaged element can be put directly on a lithographic printing press employing a conventional fountain solution without the conversion normally required. The overcoat layer confers to the electrophotographic element good abrasion resistance, long wearing characteristics, and simplicity of operation, while exerting no significant adverse effects on the electrophotographic properties of the element to which it is applied. The overcoat layer applied to form the element of this invention is useful with both inorganic photoconductors and organic photoconductors, but is particularly advantageous with photoconductive layers comprised of an organic photoconductor in an electrically insulating polymeric organic film-forming binder. Electrophotographic elements including the novel overcoat layer described herein can be made up solely of the electrically conductive support, the photoconductive insulating layer and the overcoat layer, or may also include auxiliary layers between the support and the photoconductive layer, if desired.

The novel overcoated electrophotographic elements of the present invention can comprise any electrically conductive support suitable for use in electrophotography. For example, the support can be a sheet material having the appropriate conductivity, such as metal foil or conductive paper, on which the photoconductive insulating layer is coated. Alternatively, the support can be comprised of a polymeric film, such as a film of cellulose acetate, polyethylene, polypropylene, poly(ethylene terephthalate), and the like, covered with a conductive coating. Materials such as glass, wood, metal, fabric, paper, resin-coated paper, etc. can be utilized in place of the aforesaid polymeric film. A number of different compositions and techniques are known for forming the conductive coating on the support. For example, the conductive coating can be applied by evaporative deposition of a suitable metal, such as nickel, or by applying a solution of a conductive or semi-conductive material and a resinous binder in a volatile solvent and evaporating the solvent to form the coating, or by vacuum deposition of the conductive or semi-conductive material. Metal-containing semi-conductor compounds, such as cuprous iodide or silver iodide, provide conductive coatings with particularly good characteristics. Supports formed from conductive paper are also particularly useful with the elements described herein and represent a preferred embodiment of the invention.

Any of the insulating photoconductive layers utilized in electrophotography can be employed in the practice of this invention. Thus, for example, the photoconductors can be inorganic, organic, (including both polymeric and non-polymeric types), or organo-metallic compounds. Particularly useful photoconductors include zinc oxide, zinc sulfide, titanium dioxide, cadmium sulfide, cadmium selenide, lead oxide, derivatives of Group IVa and Va metals having at least one aminoaryl group attached to the metal atom, arylamines, polyaryllkanes as well as any of the photoconductors disclosed in Contois and Merrill Belgian Pat. No. 748,511, dated June 15, 1970. A wide variety of

polymeric resins are known for use as binders in the photoconductive layers employing organic photoconductors; examples of such binders including silicone resins, acrylic resins, polycarbonate resins, polyester resins, phenolic resins, and mixtures thereof. Similarly, polymeric photoconductors such as a poly(vinyl carbazole) can also be used. As is well known in the art, various photosensitizing agents can also be incorporated in the photoconductive layer to effect a change in the sensitivity or speed of the system or a change in its spectral response characteristics. Examples of particularly effective photosensitizing agents include the pyrylium dyes, such as pyrylium and thiapyrylium dye salts.

To promote the adhesion between contiguous layers of the electrophotographic element, it may be desirable to employ one or more subbing layers. For example, a subbing layer can be provided between the film support, such as a film of poly(ethylene terephthalate), and the conductive coating, such as a layer of evaporated nickel, or a subbing layer can be provided between the conductive coating and the photoconductive insulating layer. Particularly useful subbing layers are composed of interpolymers of vinylidene chloride, such as vinylidene chloride/acrylonitrile/acrylic acid terpolymers or vinylidene chloride/methyl acrylate/itaconic acid terpolymers.

In accordance with the present invention, the photoconductive insulating layer is coated with a thin polymeric overcoat layer of a copolymer of vinyl acetate and an alpha-beta ethylenically unsaturated carboxylic acid or its anhydride or partial alkyl ester, such as a copolymer of vinyl acetate and maleic anhydride, a copolymer of vinyl acetate and acetoacetoxyethyl methacrylate or a copolymer of vinyl acetate and crotonic acid, together with a cross-linking agent for the polymeric layer. Alternatively, the overcoat layer can be a blend of two polymers, one of these polymers being a vinyl acetate polymer and the other a cross-linkable polymer of an alpha-beta ethylenically unsaturated carboxylic acid or its anhydride or partial alkyl ester, together with a cross-linking agent. The vinyl acetate polymer serving as a component of the blend can be poly(vinyl acetate), i.e., a homopolymer of vinyl acetate, or it can be a copolymer of vinyl acetate with one or more ethylenically unsaturated hydrocarbon monomers which are copolymerizable with vinyl acetate, such as maleic anhydride, styrene, acrylic acid, methacrylic acid, crotonic acid, vinyl pyrrolidone, and the like. The second polymer of the blend can be a polymer of any of the alpha-beta ethylenically unsaturated carboxylic acids, for example, acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, and the like. It can be a homopolymer, such as poly(acrylic acid), or a copolymer with one or more ethylenically unsaturated copolymerizable hydrocarbon monomers or their esters, such as styrene, the alkyl acrylates and methacrylates or their esters, and the alkyl vinyl ethers. Polymers in which the alpha-beta ethylenically unsaturated carboxylic acid is present in the acid form or in which it is present in the form of the anhydride or partial alkyl ester can be employed.

As specific examples of the many suitable polymers of an alpha-beta ethylenically unsaturated carboxylic acid or its anhydride or partial alkyl ester which can be used as a component of the aforesaid blends, the following are illustrative:

1. poly(acrylic acid)

2. poly(methacrylic acid)
3. copolymer of acrylic acid and styrene
4. copolymer of acrylic acid and methyl acrylate
5. copolymer of acrylic acid and ethyl acrylate
6. copolymer of acrylic acid and propyl acrylate
7. copolymer of acrylic acid and butyl acrylate
8. copolymer of methacrylic acid and methyl methacrylate
9. copolymer of vinyl methyl ether and maleic anhydride
10. copolymer of vinyl ethyl ether and maleic anhydride
11. copolymer of vinyl methyl ether and maleic anhydride partially converted to the free acid form
12. methyl half ester of copolymer of vinyl methyl ether and maleic anhydride
13. copolymer of maleic anhydride and styrene
14. copolymer of maleic anhydride and methyl acrylate
15. copolymer of maleic anhydride and methyl methacrylate
16. poly(itaconic acid)
17. poly(crotonic acid)
18. poly(citraconic acid)
19. poly(fumaric acid)
20. methyl half ester of copolymer of vinyl methyl ether and itaconic anhydride
21. copolymer of itaconic acid and styrene
22. copolymer of crotonic acid and styrene
23. copolymer of vinyl acetate and acetoacetoxyethyl methacrylate
24. copolymer of vinyl acetate and vinyl-2-pyrrolidone, and the like.

The proportions of the two polymers in the polymer blends used to form the overcoat layers of this invention should be such that the ratio of the vinyl acetate polymer to the polymer of the alpha-beta ethylenically unsaturated carboxylic acid or its anhydride or partial alkyl ester is in the range from about 0.1 to 1 to about 10 to 1 on a weight basis. Preferred proportions are such as to provide a ratio in the range from about 0.2 to 1 to about 3 to 1.

The cross-linking agent for the polymeric material can be any of the well-known substances widely used for this purpose. Exemplary of suitable materials are diepoxy reactive modifiers, such as 1,4-butanedioldiglycidyl ether, melamine hardeners, such as hexamethoxymethylmelamine, and dialdehydes, such as glyoxal, which are reactive with polymers containing active methylene groups. Formaldehyde and bis(vinylsulfonyl) compounds are also useful for hardening copolymers containing active methylene groups. Particularly useful bis(vinylsulfonyl) compounds are those disclosed in Burness et al., U.S. Patents Nos. 3,490,911 issued Jan. 20, 1970, and 3,539,644 issued Nov. 10, 1970.

The concentration of the cross-linking agent may be varied within rather wide limits. For example, it may be present in an amount of from about 0.01 to about 10 percent by weight based on the weight of the cross-linkable polymer. A preferred range is between about 0.25 and about 5 percent by weight on the same basis.

In applying the photoconductive insulating layer to the support, or in applying the overcoat layer on the photoconductive insulating layer, any of several different coating techniques can be employed. For example, spray coating, dip coating, swirl coating, extrusion hop-

per coating, air knife coating and other well known coating procedures can be utilized. The copolymers, or polymer blends, used to form the overcoat layer, as hereinbefore described, are readily applied from solutions in an organic solvent. The solvent chosen should be such that application of the overcoat layer will not harm the photoconductive layer, for example, the solvent used should not dissolve the hydrophobic resin used as the binder in the photoconductive layer. Of course, the solvent chosen must be capable of dissolving the vinyl acetate polymer and the polymer of the alpha-beta ethylenically unsaturated carboxylic acid or its anhydride or partial alkyl ester when a polymer blend is used, as well as the cross-linking agent. Examples of suitable solvents for forming the overcoat layer are lower alkanols such as methanol or ethanol, ketones, such as acetone or methyl ethyl ketone, and esters such as ethyl acetate or ethyl propionate. It is an important advantage of this invention that the copolymer or polymer blends used for the overcoat layer can be dissolved in readily available, low cost solvents that will not adversely affect the underlying photoconductive layer.

The overcoat layers of this invention which may include a filler (e.g., clay, silica, titanium dioxide) preferably have a thickness in the range of from about 0.07 to about 10 microns, and more preferably from about 0.1 to about 5 microns. Other layers making up the electrophotographic element can have thicknesses selected in accordance with conventional practice in the art of electrophotography.

The overcoated electrophotographic elements of this invention are especially advantageous for the preparation of lithographic printing plates. To prepare a lithographic printing plate, a hydrophobic powder image is formed on the surface of the overcoat layer by conventional electrophotographic procedures. Ordinarily, this will involve the steps of charging the element uniformly, exposing to an image, developing with an oleophilic toner, and fusing the toned image by application of heat. All of these steps are very well known in the art and need not be discussed in detail herein. The imaging process can be employed in the positive-to-positive mode or a biasing electrode, maintained at the same polarity as the initial charge on the element, can be used to obtain a reversal or negative-to-positive imaging process.

Thereafter, in accordance with this invention, no special treatment of any kind is needed prior to placing the element on a conventional lithographic printing press for making printed copies therefrom.

The invention is further illustrated by the following examples of its practice. In each of these examples, the electrophotographic element to be overcoated in accordance with the invention can be prepared by coating a conductive support with a suitable photoconductive composition. The conductive support comprises a poly(ethylene terephthalate) film base optionally bearing an adhesion layer on which is coated a layer of nickel, by vacuum evaporation, for example. Over the nickel layer is coated a photoconductive layer comprising a triarylmethane photoconductor in a polycarbonate binder and sensitized with a pyrylium dye of the type hereinbefore disclosed. Thereafter, the overcoat layer is applied as described in each of the examples which follow.

After the application of the overcoat layer, a lithographic printing plate is prepared by charging the element in the dark to approximately 600 volts (negative), exposing to an image with light from a 3,000°K source, and developing the resultant electrostatic charge pattern with a powder developer comprising pigmented particles of a carbonate polymer having an inherent viscosity of about 0.15. Thereafter, the powder developer or toner is fused to the photoconductive element by heating the element to approximately 130°C. for about 30 seconds. No special hydrophilizing step or treatment is required.

In each of the examples, the lithographic plate is tested by using it on a press (A.B. Dick Offset Duplicator, Model 350) to prepare prints on paper. It is observed that the image areas of the plate bearing the fused toner attracted printer's ink (A.B. Dick Offset Ink 3-1010 C), while the remainder of the surface repels the ink in the presence of a fountain solution (A.B. Dick Offset Fountain Concentrate 4-115 diluted from 62.5 milliliters to 1 liter with distilled water).

The following examples are included for a further understanding of the invention.

Example 1 — Overcoats of a Blend of Poly(vinyl acetate) and Poly(acrylic acid) with a Diglycidyl Ether Hardener

A coating composition consisting of a 4 percent by weight solution in methanol of a blend of 3 parts by weight poly(vinyl acetate) to 7 parts by weight poly(acrylic acid) is prepared. Just prior to coating onto the photoconductive layer of the electrophotographic element just described, 0.5 percent by weight based on the weight of poly(acrylic acid) of 1,4-butanedioldiglycidyl ether (Araldite RD2, Ciba Corp.) is added to the solution. The coating composition is then coated onto the photoconductive layer in an amount to provide an overcoat layer of approximately 1 micron dry thickness. The overcoated element is then heated at about 120°C for about 5 minutes to dry the overcoat and promote cross-linking of the overcoat layer. A lithographic printing plate is prepared as described hereinabove which has an excellent resistance to scumming in that essentially no ink buildup occurs in the background areas after 50 prints are prepared. A press run on a lithographic press results in 250 high quality prints on paper. A printing plate made in a similar manner but without the diglycidyl ether cross-linking agent in the overcoat composition shows gradual erosion of the edges of the toned image areas, with a corresponding reduction in press run to about 50 prints of good quality. Omission of the poly(vinyl acetate) from the overcoating solution results in poor adhesion of the overcoat to the photoconductive layer and very low quality prints.

Example 2

A lithographic printing plate (A) is made according to the procedure of Example 1. A second element (B) is prepared in which the photoconductive insulating layer is overcoated with an ammoniacal solution containing 1 percent by weight of poly(acrylic acid) and 2 percent by weight of zinc acetate. A third element (C), similar to B, is prepared in which the overcoating solution contains a surfactant, Strodex Super V8 (the potassium salt of complex organic phosphate esters, made by Dexter Chemical Corp.). In a fourth element (D), prepared similarly to C, the zinc acetate is omitted from the overcoating solution. The resultant elements

are then treated according to the following procedure. Element A receives no further treatment before being placed on the press. In preparing Element B, it is observed that the ammoniacal solution does not wet the surface of the photoconductive layer, and dries in small droplets on the surface; thus, the resultant element is not usable as a printing plate. Element C, in which the surfactant is used to avoid the formation of the droplets observed in preparing Element B, accepts the overcoating solution, but upon heating to 120°C for 3 minutes, it is found that the overcoat is readily softened and removable from the element by swabbing with a soft cloth moistened with a conventional fountain solution. Element C thus would not stand up under press conditions. Element D, after being overcoated, is dried for 3 minutes at 120°C, the surface swabbed with a 1 percent aqueous zinc chloride solution, and heated for a further 3 minutes at 120°C, after which it is swabbed with fountain solution similar to Element C. Element D also shows poor resistance to fountain solution attack. Furthermore, an electrophotographically prepared toner image on Element D has very poor resolution, attributable to excessive surface conductivity produced by the zinc chloride. It is, therefore, concluded that both the poly(vinyl acetate) and the poly(acrylic acid) are necessary, together with an organic hardener, such as 1,4-butanedioldiglycidyl ether, to produce a satisfactory printing plate which needs no special hydrophilizing step.

Example 3 — Overcoat of a Blend of Poly(vinyl acetate) and Poly(acrylic acid) with Melamine Hardener

The procedure of Example 1 is followed using as the overcoat a blend of 6 parts by weight of poly(acrylic acid) with 4 parts of poly(vinyl acetate) together with 0.83 percent by weight of the poly(acrylic acid) of a melamine hardener, hexamethoxymethylmelamine, (Cymel 300, American Cyanamid Co.). When coated as in Example 1, charged, exposed and toned to form a lithographic printing plate and placed on a press, over 200 prints of good quality are obtained. A printing plate prepared similarly but without the hardener shows the same erosion of the edges of toned areas observed in the plate containing no hardener in Example 1.

Example 4 — Overcoat of a Blend of Poly(vinyl acetate) and a Poly(acrylic acid-2-acetoacetoxyethyl methacrylate) Copolymer

The procedure of example 1 is followed by using as the polymer mixture a blend of 6 parts by weight of a 90/10 copolymer of acrylic acid with 2-acetoacetoxyethyl methacrylate and 4 parts by weight of poly(vinyl acetate) together with 5 percent by weight of ethanediol hardener based on the weight of the copolymer. In a control element, the ethanediol is omitted. When coated as in the previous examples, charged, exposed and toned to form a lithographic printing plate and placed on a press, the element of the invention yields over 200 prints of good quality. The control element shows erosion of the edges of toned areas after approximately 100 prints are made. Similar results are obtained using a bis(vinylsulfonyl) hardener, a polymeric aldehyde, or formaldehyde in place of the glyoxal or ethanediol hardener.

Example 5 — Overcoat of a Blend of Poly(vinyl acetate) and Methyl Acrylate/Acrylic Acid Copolymer

Following the procedure of Example 1, an overcoat is prepared from a blend of 1 part by weight of poly(vi-

nyl acetate to 3 parts by weight of a copolymer consisting of three parts by weight methyl acrylate to 7 parts by weight acrylic acid, together with 0.2 percent by weight of butanediol diglycidyl ether, based on the weight of the methyl acrylate/acrylic acid copolymer. In a control element, the hardener is omitted. When used on a lithographic press as in the previous examples, the element prepared according to the invention shows good press life, while the control element shows severe wear after less than 50 prints are produced.

Example 6 — Overcoat of a Blend of Poly(vinyl acetate) and Butyl Acrylate/Acrylic Acid Copolymer

An overcoat is prepared according to the procedure of Example 1 from a blend of 1 part by weight of poly(vinyl acetate) and 3 parts by weight of a copolymer consisting of 2 parts by weight of butyl acrylate to 8 parts by weight of acrylic, together with 0.2 percent by weight of butanediol diglycidyl ether, based on the weight of the butyl acrylate/acrylic acid copolymer. The element thus prepared and a control element, in which the hardener is omitted, are both used as printing masters. Again, the element of the invention shows good press life, while the control element fails much earlier.

Example 7 — Overcoat of a Blend of Poly(vinyl acetate) and a Partial Methyl Ester of Vinyl Methyl Ether/Maleic Anhydride Copolymer

A colymer of vinyl methyl ether and maleic anhydride is refluxed in methanol for about 3 hours to convert a portion of it from the anhydride to the methyl ester form. An overcoat is prepared from a blend of 4 parts by weight of the resultant copolymer with 1 part by weight of poly(vinyl acetate), together with 0.2 percent by weight of a hardener, butanediol diglycidyl ether. Additional overcoat compositions are prepared, consisting in one case of one part of poly(vinyl acetate) to 9 parts of the copolymer, and in the other case of 3 parts of poly(vinyl acetate) to 7 parts of the copolymer, together with hardener in each case. Each of the resultant elements and control elements prepared identically but containing no hardener are made into printing masters as in Example 1 and press runs made from each. The elements of the invention show extended press life, while the control elements show deterioration of image quality after a relatively short press run. Similar results are obtained using a copolymer of vinyl acetate and crontonic acid in place of the poly(vinyl acetate).

Example 8 — Overcoat Containing a Blend of Poly(vinyl acetate) and a Vinyl Methyl Ether/Maleic Anhydride Copolymer Partially Converted to the Free Acid Form

A copolymer of vinyl methyl ether and maleic anhydride is refluxed in a mixture of 97 parts by weight of acetone and 3 parts by weight of water for 100 hours to convert a portion of it from the anhydride to the free acid form. An overcoat is prepared from a blend of 1 part by weight of poly(vinyl acetate) and 4 parts by weight of the copolymer, which contains, in addition, 0.5 percent by weight of a hardener, butanediol diglycidyl ether. A second overcoat composition contains only the copolymer blend and no hardener. Elements prepared as previously described, each bearing one of the overcoat compositions, are charged, exposed and toned in the manner already set forth, to form printing plates. Again, the element of the invention shows

longer press life than the control when prints are made from each on a lithographic printing press.

Example 9 — Overcoat of a Blend of Poly(vinyl acetate) and Methyl Methacrylate/Methacrylic Acid Copolymer

An overcoat for an electrophotographic element is prepared according to the procedure of Example 1 from a blend of poly(vinyl acetate) and a copolymer consisting of 1 part by weight of methyl methacrylate to 1 part by weight of methacrylic acid, the blend having 8 parts by weight of copolymer to 1 part by weight of the poly(vinyl acetate), together with 0.1 percent by weight of butanediol diglycidyl ether hardener based on the weight of the copolymer. The element of the invention and a control element containing no hardener are both placed on a lithographic press and prints made therefrom. The element of the invention, containing the hardener, shows greatly increased press life over the element containing no hardener.

Example 10 — Overcoat Containing a Blend of Vinyl Acetate/Vinyl Pyrrolidone Copolymer and Poly(acrylic acid)

An overcoat for an electrophotographic element is prepared from a blend of 1 part by weight of poly(acrylic acid) and 1 part by weight of a copolymer of 7 parts by weight of vinyl acetate to 3 parts by weight of vinyl pyrrolidone, together with 0.01 percent by weight of a hardener, butanediol diglycidyl ether. The resultant element, when charged, exposed and toned, is placed on a press as in the previous examples. A control element is prepared identically but without the hardener in the overcoat composition. As in the previous examples, the element prepared according to the invention shows much longer press life than the control, showing the importance of the hardener in making a durable printing master.

The invention has been described in detail with particular reference to certain 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. An electrophotographic element comprising (1) an electrically conductive support, (2) an organic photoconductive insulating layer on one side of said support and (3) a hydrophilic overcoat layer on said photoconductive layer, said overcoat layer consisting essentially of a crosslinkable polymer blend and an organic crosslinking agent therefor, said polymer blend comprising (a) a vinyl acetate polymer and (b) a polymer of a member selected from the group consisting of an alpha-beta ethylenically unsaturated carboxylic acid, (i) an anhydride thereof, (ii) a partial alkyl ester thereof and (iii) an alkyl ester thereof containing an active methylene group, the ratio of component (a) to component (b) in said blend on a weight basis being in the range from about 0.1 to 1 to about 10 to 1, the crosslinking agent being present in an amount within the range of from about 0.01 to less than 10 percent by weight based on the weight of the crosslinkable polymer.

2. An electrophotographic element as described in claim 1 wherein the overcoat layer consists of a blend in which the ratio of component (a) to component (b) is in the range from about 0.2 to 1 to about 3 to 1.

3. An electrophotographic element as described in claim 1 wherein said crosslinking agent is present in an

amount of about 0.025 to about 5 percent by weight of the polymer.

4. An electrophotographic element as described in claim 1 wherein said electrically conductive support comprises a polymeric film coated with a conductive coating.

5. An electrophotographic element as described in claim 1 wherein the crosslinkable polymer blend in said overcoat layer consists essentially of a blend of polyvinyl acetate and polyacrylic acid.

6. An electrophotographic element as described in claim 1 wherein the crosslinkable polymer blend in said overcoat layer consists essentially of a blend of polyvinyl acetate and a copolymer of vinyl methyl ether and maleic anhydride or partial esters thereof.

7. An electrophotographic element as described in claim 1 wherein the crosslinkable polymer blend in said overcoat layer consists essentially of a blend of polyvinyl acetate and a copolymer of methyl acrylate and acrylic acid.

8. An electrophotographic element as described in claim 1 wherein the crosslinkable polymer blend in said overcoat layer consists essentially of a blend of polyvinyl acetate and a copolymer of butyl acrylate and acrylic acid.

9. An electrophotographic element as described in claim 1 wherein the crosslinkable polymer blend in said overcoat layer consists essentially of a blend of polyvinyl acetate and a copolymer of methyl methacrylate and methacrylic acid.

10. An electrophotographic element as described in claim 1 wherein the crosslinkable polymer blend in said overcoat layer consists essentially of a blend of polyacrylic acid and a copolymer of vinyl acetate and vinyl pyrrolidone.

11. An electrophotographic element as described in claim 1 wherein the crosslinkable polymer blend in said overcoat layer consists essentially of a blend of a copolymer of vinyl acetate and crotonic acid and a copolymer of vinyl methyl ether and maleic anhydride or partial esters thereof.

12. An electrophotographic element as described in claim 1 wherein the crosslinkable polymer blend consists essentially of a blend of poly(vinyl acetate) and a copolymer of acrylic acid and 2-acetoacetoxyethyl methacrylate.

13. An electrophotographic element comprising (1)

an electrically conductive support, (2) an organic photoconductive insulating layer on one side of said support and (3) a hydrophilic overcoat layer on said photoconductive layer, said overcoat layer consisting essentially of a crosslinkable polymer blend and an organic crosslinking agent therefor, said polymer blend comprising (a) a vinyl acetate polymer and (b) a polymer of a member selected from the group consisting of an alpha-beta ethylenically unsaturated carboxylic acid, (i) an anhydride thereof and (ii) a partial alkyl ester thereof, the ratio of component (a) to component (b) in said blend on a weight basis being in the range from about 0.1 to 1 to about 10 to 1, the crosslinking agent being present in an amount within the range of from about 0.01 to less than 10 percent by weight based on the weight of the crosslinkable polymer.

14. An electrophotographic element as described in claim 13 wherein said crosslinking agent is butanedioldiglycidyl ether.

15. An electrophotographic element as described in claim 13 wherein said crosslinking agent is hexamethoxymethyl melamine.

16. An electrophotographic element comprising (1) an electrically conductive support, (2) an organic photoconductive insulating layer on one side of said support and (3) a hydrophilic overcoat layer on said photoconductive layer, said overcoat layer consisting essentially of a crosslinkable polymer blend and an organic crosslinking agent therefor, said polymer blend comprising (a) a vinyl acetate polymer and (b) a polymer of a member selected from the group consisting of an alkyl ester of an alpha-beta ethylenically unsaturated carboxylic acid containing an active methylene group, the ratio of component (a) to component (b) in said blend on a weight basis being in the range from about 0.1 to 1 to about 10 to 1, the crosslinking agent being present in an amount within the range of from about 0.01 to less than 10 percent by weight based on the weight of the crosslinking polymer.

17. An electrophotographic element as described in claim 16 wherein said crosslinking agent is glyoxal.

18. An electrophotographic element as described in claim 16 wherein said crosslinking agent is selected from the group consisting of a bis(vinylsulfonyl) compound, a polymeric aldehyde, formaldehyde and glyoxal.

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