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PROCESS FOR PRODUCING NEGATIVE TRANSPARENCIES

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U.S. Cl. 96—1 4 Claims

ABSTRACT OF THE DISCLOSURE

An electrophotographic process for producing negative transparencies, comprising the steps of: forming an electrostatic charge pattern on a photo-sensitive member containing an essentially transparent photoconductive insulating layer and a component capable of responding to treatment with an agent to convert the member from transparent to opaque; developing the electrostatic charge pattern with an essentially transparent barrier material not convertible to opaque when said member is treated with said agent; and treating the photosensitive member with said agent so that, through the coaction of the component and the agent, the areas of the member not developed with said barrier material are converted from transparent to opaque, but the areas of the member developed with barrier material are prevented from such conversion because of the barrier material, thereby forming a negative transparency.

This invention relates to a method for producing photographic transparencies or translucencies and, more particularly, to electrostatic and electrophotographic methods especially suited for producing negative photographic transparencies or translucencies from either a negative or positive original.

One problem of using electrophotography (herein defined to include both electrophotographic and electrostatic methods, i.e. electrostatic images formed with and without an exposure step) to produce negative transparencies of negative and positive originals is that greater field intensity, or sharp voltage contrast is present at the edges of an electrostatic image so that, when the electrostatic image is developed without a development electrode, the large image areas of continuous toning are highly developed at the edges and almost completely undeveloped in the central portions. Thus, negative transparencies or translucencies which have many large image areas are unusable when developed by, for example, the cascade technique without a development electrode.

Even when a development electrode or the effect of a development electrode is employed to develop large areas of continuous toning, large amounts of toner are needed to develop the large image areas and this presents what is termed a toner depletion problem. That is, the toner/carrier ratio rapidly decreases during development to a point where there is not sufficient toner on the carrier to completely develop the image areas. Thus, pinholes and, in some cases, undeveloped gaps result in the negative rendering it unsuitable.

An imaging process for producing negative transparencies of limited resolution is known in which a uniform layer of charged powder on the surface of a conductive transparent material is removed by the electrostatic fields of an electrostatic image on a photoconductor. The transfer of the powder occurs when the uniformly dusted transparent conductive plate is brought into contact with the electrostatic image and a D.C. potential is applied between the two surfaces. Depending on the magnitude of polarity of this potential, it is possible to transfer powder away from the pretoned surface in areas corresponding to either the charged or discharged areas of the photoconductor. Thus, while this process is capable of producing negative transparencies from positive originals, it is very cumbersome and results in low resolution transparencies. Further, it requires large amounts of toner, is susceptible to pinholes and uses a development electrode effect.

A process is known which does not use an electrode and which gives good resolution negatives. However, this process requires many additional steps after the formation of the electrophotographic image as will be seen by the following description.

The developed image of unpigment toner on a photoconductor is transferred to an expendable transparent material having a pressure sensitive adhesive coating. The adhesive properties of the coating are destroyed in the transferred image areas. The adhesive sheet is next placed into contact with a second expendable material having a thin releasable layer of high opacity coated on a transparent sheet. After contact has been established, the two layers are separated and the opaque layer is transferred to the sheet in the non-image areas and remains on the first adhesive sheet in the image areas. Thus, the first adhesive sheet becomes a negative transparency and the second adhesive sheet becomes a positive transparency. While this process provides high resolution negative transparencies and permits cascade toning, it should be readily apparent that the process requires a multitude of additional steps after the formation of the toner image on the photoconductor.

Accordingly, it is the primary object of the present invention to provide a new and improved electrophotographic process and materials for producing electrophotographic negative transparencies.

A more specific object of the present invention is to provide a new and improved process for producing electrophotographic negative transparencies in which large areas of continuous toning is not necessary.

A further object of the present invention is to provide a new and improved process for producing negative electrophotographic transparencies from the positive originals which requires essentially only one additional step beyond the steps of the electrophotographic process.

The foregoing and other objects are achieved by forming an electrostatic charge pattern on a photosensitive member containing an essentially transparent photoconductive insulating layer and component capable of responding to treatment with an agent to convert the member from transparent to opaque, developing the electrostatic charge pattern with a transparent or translucent barrier material not convertible to opaque when said member is treated with said agent so that, if the material was opaque, a positive transparency would result, and treating the transparent layer with said agent so that the areas of said member not developed with said barrier material are converted from transparent to opaque, but the areas of the member developed with the barrier material are prevented fom such conversion because of the barrier material, thereby forming a negative transparency.

Any electrophotographic process may be used in forming the electrostatic image. For example, the process disclosed in U.S. Patent 2,297,691 in which the photoconductive insulating layer is electrostatically charged in the dark and then the charged layer is exposed to a light image to form an electrostatic charge image. Alternatively, a persistent internal polarization or persistent photoconductivity mode of electrophotography such as described in U.S. Patent 2,845,348 and in copending application, Ser. No. 474,977, filed July 26, 1965 could be used. Further, the charge transfer process of U.S. Patent 2,937,943 in which the electrostatic image formed on the photoconductor is transferred to a dielectric sheet, i.e. a sheet having a resistivity of greater than 10^{10} ohm-cm. Also, processes in which the electrostatic charge pattern is formed on the dielectric sheet, such as those described in U.S. Patents 2,919,170, 3,001,848 and 3,001,849, may be used.

Inasmuch as the photoconductor must be transparent, it is desirable to use organic photoconductors and organic dielectrics because they provide a greater degree of transparency. Examples of organic photoconductors useful in the processes of the present invention are both the small molecule and the polymeric photoconductors listed in copending application, Ser. No. 474,977 and U.S. 3,232,755. In addition, if a conductive substrate is to be used, it also must be transparent and may be a layer of polyethylene terephthalate coated with a thin layer of aluminum or copper, or may be a layer of NESA glass. Alternatively, the photoconductive layer can be self-supporting or be carried on a non-conductive support if the dual corona charging technique of U.S. Patent 2,922,883 is employed.

A number of known electrophotographic development techniques may be used. For example, cascade development of U.S. Patent 2,618,551, liquid development of U.S. Patent 2,877,133 and magnetic brush development of U.S. Patent 2,874,063 are all suitable methods for developing the electrostatic image formed by one of the above electrophotographic processes.

In accordance with the present invention, the photosensitive member contains, in addition to the photoconductive insulating layer, a component uniformly dispersed in the photoconductive layer or uniformly dispersed throughout a separate layer and capable of responding to an agent for converting the layer in which the component is present from transparent to opaque. The separate layer is sufficiently insulating to support an electrostatic charge, i.e. having a resistivity greater than 10^{10} ohm-cm. In general, the process of the present invention comprises:

(a) Forming an electrostatic charge image on the photosensitive member containing the component,

(b) Developing the electrostatic charge image with a transparent or translucent barrier material so that, if the material was opaque, a positive transparency would result.

(c) Treating the photosensitive member with the agent so that, through the coaction of the component and agent, the member is converted from transparent to opaque in the areas of the member not covered by barrier material, the portions of member being covered by the barrier material remaining transparent because the agent is unable to reach and coact with component underlying the barrier material, thereby forming a negative transparency.

The following table, in general, shows the various photosensitive systems of the present invention and the relationship of the component and barrier material to the agent.

TABLE I

Component

(1) alkaline sensitive material, such as:
  (a) diazo compound (e.g. 2,5 - diethoxy - 4 - morpholino benzene diazonium fluoborate) and azo coupler (e.g. 2-hydroxy-3-naphtoyl-o-anisidine)
  (b) diazo compound (e.g. p-dimethylamino benzene diazonium fluoborate)
(2) light sensitive material, such as:
  (a) an aryl amine (e.g. diphenylamine) and halo substituted hydrocarbon (e.g. carbon tetrabromide)
  (b) triarylmethane - dye cyanides (e.g. 4,4',4'' - triamino-triphenyl acetonitrile)
  (c) diazo compound (e.g. p-dimethylamino benzene diazonium chloride zinc chloride)
(3) dye absorbing material, such as:
  (a) a material having polar functional groups (e.g. polyvinyl formal)

Agent

(1) alkaline material, such as:
  (a) dry gaseous material (e.g. ammonia and ammonia generating precursors)
  (b) semi-wet material (e.g. sodium carbonate-azo coupler solution)
(2) light, such as:
  (a) ultraviolet and visible light (e.g. 3000 A.–4800 A.)
  (b) ultraviolet light (e.g. 2400 A. to about 3500 A.)
  (c) ultraviolet light (e.g. 3000 A.–4000 A.)
(3) dye, such as:
  (a) cationic or anionic dye (e.g. Crystal Violet; tris-(4 - dimethylaminophenyl) - carbinol hydrochloride)

Barrier material

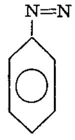
(1) transparent alkaline absorbing, but not sensitive material such as:
  (a) acidic compounds (e.g. stearic acid)
  (b) same as above
(2) non-light sensitive, but light absorbing material, such as:
  (a) ultraviolet and visible light absorber (e.g. 2,4,4'-trinitrodiphenylamine)
  (b) ultraviolet light absorber (e.g. 2,4 - dihydroxy benzophenone)
  (c) ultraviolet light absorber (e.g. 2,2' - dihydroxy-4,4'-dimethoxy benzophenone)
(3) non-dye absorbing material, such as:
  (a) a non-polar material having essentially no polar functional group or at least substantially less than the dye absorbing material (e.g. polystyrene)

In system (1) of Table I, the electrostatic image on the photosensitive member is developed with a barrier material comprising transparent alkaline absorbing or acidic material which serves as a barrier to an alkaline agent. A number of solid organic acids may be employed as the barrier material and, for example, phenylacetic, malonic, and glycolic carboxylic acids as well as saturated fatty acids with melting points above 43° C. (see Table 15.1 in Fieser and Fieser, Organic Chemistry, 3rd edition) are a few specific acids which may be used. The components of the photosensitive member is an alkaline sensitive substance such as a diazo compound which either is uniformly dispersed throughout the photoconductor layer or is dispersed in a layer overcoating the photoconductor.

Preferably an azo coupler is present with the diazo compound. With this system (1)(a) of Table I, the alkaline agent preferably is a gas, such as ammonia, and diffuses into the areas of the photosensitive member unprotected by the acidic barrier material to provide the necessary alkaline medium for a reaction between the diazo compound and the azo coupler to form the dye. In the areas of the photosensitive member covered with the alkaline absorbing or acidic barrier material, preferably stearic acid, the ammonia is absorbed and neutralized so that an alkaline medium is not present for dye formation under these barrier areas. Hence, they remain transparent and a negative transparency results.

Alternatively, system (1)(b) of Table I may be employed in which the azo coupler is present with the alkaline agent rather than the diazo compound. The alkaline agent now takes the form of a liquid solution and a semi-wet development step is necessary to form the dye in the areas not covered by the acidic barrier material. Preferably, the alkaline agent is sodium carbonate and the barrier material is the same as in the system (1)(a) as long as the solvent or solvents for the carbonate and azo coupler do not dissolve the barrier material. If desired, sodium phosphate or sodium acetate may be substituted for sodium carbonate.

Suitable diazo compounds for both systems (1)(a) and (1)(b) are, as shown by the following formula, unsaturated aromatic compounds bearing a diazo group attached to a carbon atom of an aromatic nucleus:



They can be substituted diazobenzenes, and un-, mono-, di-, and poly-substituted diazo-p-aminobenzenes and diazo-o-aminobenzenes. Also, diazo mercaptobenzenes may be used. Examples of such diazo compounds are 1-diazo-4-ethoxybenzene, 1-diazo-2,5-diethoxybenzene, 4-diazo-2,5-dimethoxy-diphenyl, 1-diazo-4-dimethylaminobenzene, 1-diazo-4-methylallylaminobenzene, 1-diazo-4-(1,3-oxazolidino)benzene, N,N′-bis (4-aminophenyl) piperazine, 9 - (p - diazophenyl) carbazole, 1 - diazo - 3 - methyl-4 - dimethylaminobenzene, 1 - diazo - 2,5 - diethoxy - 4-dimethylaminobenzene, 1 - diazo - 4 - ethylbenzyl - 3-ethoxyaminobenzene, 1 - diazo - 4 - morpholino - 2,5-diethoxyaminobenzene, N-4′ - amino - 3′ - ethoxyphenyl-(1′) - thiomorpholine and 1 - diazo - 4,5 - dimethyl -2-dimethylaminobenzene. For purposes of stability, the diazo compounds preferably are employed in the form of salt complexes with, for example, zinc chloride, cadmium chloride, tin chloride and boron trifluoride.

Suitable couplers are monohydric phenols, catechol and its derivatives, hydroquinone derivatives, trihydroxybenzenes, hydroxy diphenyl derivatives, naphthols, dioxynaphthalene derivatives, diketones, acetonitriles, cyanacetylamides, sulfonamides, alkylmalonamates, pyronones, hydroxy pyridones, 4-oxyquinolones, pyrazolones, and thiophene derivatives. Specific compounds within these classes are listed on pages 220–248 of Light Sensitive Systems by Jaromir Kosar.

The color of the resulting dye desired and, hence, the particular coupler selected. will depend on how the negative transparency is utilized. For example, if it is to serve as a master to expose an ultraviolet sensitive material with an ultraviolet light source then the dye should be yellow or sepia. If an incandescent light source is employed to expose a material sensitive to those wavelengths, through the negative master, the dye of the master should be blue or preferably black.

In system (2) of Table I, the barrier material deposited to develop the electrostatic image on the photosensitive member is a material which will absorb but not be sensitive to (i.e. become colored) the wavelengths of light serving as the agent, while the component of the photosensitive member is sensitive to such wavelengths of light and becomes colored when exposed. Again, the light sensitive material either can be disposed in a layer overcoating the photoconductive layer or be present in the photoconductive layer.

There are a number of light sensitive materials, as indicated by Table I, which are operable in the present invention. Namely, in system (2a) an aryl amine is the light sensitive material in conjunction with a halo substituted hydrocarbon. Any one of the aryl amine listed on page 362 of the above-cited Light Sensitive Systems book may be used, providing the resulting color is suitable for the application of the negative transparency. That is, the proper color will depend on whether it is employed as a master in a visible light or ultraviolet light systems as discussed under system (1). The halo substituted hydrocarbon preferably is carbon tetrabromide, but may be iodoform, n-bromosuccinimide, carbon tetrabromide, 2-chloroanthaquinone, tetrabromo - o - cresol, brominated polystyrene, tetrabromphenolphthalein, 1,2,3,4 - tetrabrombutane, 1,2,3,4 - tetrachlorobenzene, carbon tetrachloride, tetrachlortetrahydronaphthalene, 1 - chloro - 4-nitrobenzene, hexachloroethane. Also, several of these halogenated compounds may be utilized as a mixture in the photosensitive member.

The wavelength of light, to which the system (2a) of Table I is sensitive, is dependent not only on the aryl amine, whose sensitivity normally is in the ultraviolet portion of the spectrum, but also the halogenated compound and the complex formation between them. For instance, halogenated methane compounds in which at least one hydrogen has been replaced by iodine are sensitive in the spectral range from 5100 A. and 5500 A. whereas the spectral range of bromated compounds is 3900 A.–4000 A., and chlorinated derivatives are sensitive to radiation of 3000 A. Therefore, the usable portion of the spectrum ranges from 3000 A.–5000 A.

Accordingly, the barrier material or light absorbing material must be selected so as to match the wavelength sensitivity of the aryl amine-halo compound or must broadly absorb 3000 A.–5500 A. For example, if the photosensitive member is sensitive to wavelengths of light within the range of 3300 A. and 4200 A., then the barrier material may be one of the following light absorbers: 1,3-di-2-thienyl-2-propen-1-one, 2-naphthalenediazocarboxamide, phenylsalicylate, 2,4-dibenzoylresorcinol, 4,4′-oxalyldiresorcinol, butyl-3-umbelliferonecarboxylate, 2,3-bis - (3,4-methylenedioxyphenyl) - 5-penylpyrrole, 2,2′-dihydroxy-4,4′-dimethoxybenzophenone and 2,2′4′-trihydroxy - 4-methoxy-benzophenone. Other compounds which will absorb wavelengths of light within 3000 A.–5500 A. are: 2,4,6-trinitroanisole, 2,4,6-trinitrophenol, 4-nitro-N,N-diethylaniline, 2-nitrodiphenylamine, 4 - nitrodiphenylamine, 2,2′,4′ - trinitrodiphenylamine, 2,4,6-trinitrodiphenylamine, and 4-nitrocatechol.

In system (2)(b) of Table I, the component or light sensitive material of the photosensitive member is a trarylmethane-dye cyanide which again either is dispersed throughout the photoconductve layer or present in an overcoated layer. As in system (2)(a), the agent is light, more specifically ultraviolet light, and the barrier material is an ultraviolet light absorbing material. Examples of triarylmethane-dye cyanides useful as the component or light sensitive material are 4,4′,4″-triamino-triphenylacetonitrile, 4,4′,4″-triamino - 3-methyl-triphenylacetonitrile, Aurin cyanide, Ethyl Green cyanide, Xylene Blue VS cyanide, Light Green SF cyanide. Acid Violet 6B cyanide, Soluble Blue cyanide, 4,4′-bis-dimethylamino-2″-chloro-triphenylacetonitrile, Helvetia Green cyanide, Acid Fuchsine cyanide, N,N,N′,N′,N″,N″-hexa - 2-hydroxyethyl rosaniline cyanide, Acid Green 16-cyanide, Naphthalene Green V-cyanide. These dye cyanides are sensitive to wavelengths of light in the range 2400 A. to 3500 A.

Materials which absorb in the 2400 A.–3800 A. range and can serve as the barrier material: are phenylsalicylate, 4-tert-butyl phenylsalicylate, 5-chloro - 2-hydroxybenzophenone, 2,4 - dibenzoylresorcinol, 2 - hydroxy - 4-methoxy-benzophenone, 2,2′-dihydroxy - 4,4′-dimethoxybenzophenone, and 2(2′-hydroxy-5′-methylphenyl)benzotriazole.

In system (2)(c), the vesicular process, such as described initially in U.S. 2,750,292 and subsequent vesicular patents, is used to render opaque the areas of the photosensitive member not covered with barrier material. The member contains, in addition to the photoconductor, a gas generating material such as daizo compound of benzene or naphthalene. Examples of specific gas generating materials are p-diazodimethylaniline zinc chloride, p-diazodiethylaniline zinc chloride; p-diazodiphenylamine sulfate, p-diazoethylhydroxyethylaniline zinc chloride, 1-diazo-2-oxynaphthalene-4-sulfonate, 4-benzoylamino - 2,5-diethoxybenzene diazonium chloride, p-chlorobenzenesulfonate of 4-diazo-2-methoxy-1-cyclohexylaminobenzene, 7-dimethylamino - 8-methoxy-3-oxo-dihydro - 1,4-thiazine - 6-diazonium fluoroborate, 1-dimethylamino - 4-naphthalene diazonium fluoroborate, 3-oxo - 7-dialkylaminobenzothiazine diazonium borofluorides, 1-carbazido - 2:5-dihydroxybenzene, 2-amino - 1-carbazidobenzene, 2-carbazido - 1-naphthol, 1,4-dicarbazido - 2,3-dihydroxyfurane, 3- or 4-azidophthalic anhydride, diazo oxides, diazosulfonates, diazo quinonylsulfonamide, azides and quinone diazides, sodium 1:2-naphthoquinone - 2-diazide - 5-sulfonate. Also, the gas generating compositions of U.S. Patent 3,183,091 may be used.

Instead of a permanent transparent barrier material which absorbs the wavelengths of light necessary to decompose the component or sensitive compound, a commercial electrophotographic toner may be used to develop the electrostatic image and is removed after the necessary exposure to generate the gas in the photosensitive member. After such exposure, the toner may be removed and the photosensitive member heated to form the vesicular structure and render the exposed area opaque. Depending on the particular gas generating material, the heating step may range from 80° to 150° C.

In process (3) the agent is a dye and the component is the surface of the photosensitive member which is such that it readily absorbs the dye agent. Conversely, the barrier material does not absorb the dye and remains transparent. Usually, the dye absorption-non absorption depends whether the substance being dyed contains polar or non-polar functional groups. That is, the dye contains polar groups and is attracted to the substance to be dyed if it also contains polar groups. Therefore, the photoconductor, if it is a polymer, or the polymeric binder for the photoconductor, should contain polar groups whereas the barrier material should not. Accordingly, examples of polymeric binders are polyvinyl formal and polyvinyl butral while the examples of the barrier material are polystyrene and polyalkenes (polyethylene, polypropylene, etc.), In some cases, the photoconductor will be sufficiently polar so that the binder and the barrier material can be the same polymer.

Examples of dyes which are useful are di- and triphenylmethane dyes; such as Auramine O (C.I. 41000, Color Index, second edition), Malachite Green (C.I. 4200), Para Rosaniline (C.I. 42500), Methyl Violet (C.I. 42535), Aurine (C.I. 43800), and Victoria Blue (C.I. 44045); xanthene dyes; such as Rhodomine B (C.I. 45170); acridine dyes, such as Acridine Orange (C.I. 46005); and Thiazine dyes, such as Methylene Blue (C.I. 52015).

In the above processes (1–3), the barrier material can be formed into toner by grinding the material into fine particles and dispersing the particles with a carrier such as glass beads for cascade development, a dielectric liquid for liquid development and ferromagnetic particles for magnetic brush development. In addition, the toner particles can be dissolved in a solution and the solution dispersed in a dielectric liquid immiscible with the solution to form an emulsion type liquid toner for liquid development.

In some cases, the barrier material may not be fusable at low temperatures, i.e. between 60° C. and 120° C. or at least below the decomposition temperature of the component, or does not have the proper electrostatic properties, i.e. triboelectric property. In such cases, a solid solution is formed and consists of the barrier material and a material with a low melting point and/or the proper triboelectric property, for example, polystyrene, butyl methacrylate-styrene copolymer and polymethylmethacrylate. This solid solution then is ground to fine particles to serve as a toner.

The general nature of the invention having been set forth, the following examples are now presented as illustrations, but not limitations of the compositions used in the method for the present invention.

EXAMPLE I

A photosensitive composition was prepared by the addition of 0.04 gram of 3,5-dinitrobenzoic acid to 7% solution of polyvinyl carbazole in dichloroethane. To this was added 0.07 gram of 2,5-diethoxy-4-morpholino-benzene diazonium borofluoride and 0.07 gram of 2-hydroxy-3-naphthoyl-o-anisidine. The composition was coated on an aluminum coated polyethylene terephthalate substrate. After being given a positive electrostatic charge with a corona unit at 7500 volts and exposed through a positive master to 100 watt incandescent lamp at 12.5 inches for one second, the latent electrostatic image was developed by immersion into trichlorotrifluoroethane containing suspended finely powdered stearic acid. This resulted in a transparent film. To convert the areas of the film not containing stearic acid, the film was suspended in an ammonia atmosphere and, where the ammonia was able to diffuse into the film, i.e. the undeveloped stearic acid areas, these areas formed a blue color to provide a negative film of the positive original. To destroy the residual 2,5-diethoxy-4-morpholino-benzene diazonium borofluorate in the film, the film was given a short ultraviolet exposure.

EXAMPLE II

A photosensitive film was prepared by coating a polyvinyl carbazole photoconductive layer containing 0.25% Malachite Green oxalate and 4% 3,5-dinitrobenzoic acid on an aluminum coated polyethylene terephthalate substrate. On top of the photoconductive layer was coated a thin layer of polyvinyl pyrrolidone containing 10% of tris-[4-(2-hydroxyethyl)aminophenyl] acetonitrile trihydrochloride. The film was charged with positive corona of 7500 volts after heating for one minute at 100° C. The film was then exposed through a positive master to a 25 watt incandescent lamp at 30 centimeters for one second. To develop the electrostatic image, an ultraviolet light absorber consisting of finely powdered 2,2′-dihydroxy-4,4′-dimethoxy benzophenone and isomers, and glass beads were cascaded over the film containing the electrostatic image. After a few seconds of heating to melt the ultraviolet light absorber, the film was exposed to General Electric UA–2 mercury arc at 10 inches for five seconds to produce a negative image containing a dark blue background with light green image areas.

EXAMPLE III

A photosensitive film was prepared by dissolving 2 grams of 1,3,5-triphenylpyrazoline and 0.1 gram of 3,5-dinitrobenzoic acid in 10 ml. of 1,2-dichloroethane. To this was mixed a 20-gram solution of 10% polyvinyl formal in 60 parts of toluene and 40 parts of ethanol. The resulting mixture was coated on an aluminum coated polyethylene terephthalate substrate with a 5 mil gap on the doctor blade. The photosensitive film thus prepared was electrostatically charged with a corona unit at plus 7000 volts and exposed through a positive master to a 40 watt incandescent lamp at 12 inches for 5 seconds. The electrostatic charge pattern was developed by cascading a developer mixture of carrier with 1% of finely divided low melting polystyrene as toner over the electrostatic image. The polystyrene powder was attracted to the electrostatic image and was fused to the photosensitive film by heating at 150° C. for about five seconds. The background or undeveloped areas of the almost invisible image was converted to opaque by immersion of the film in a 3% solution Victoria Blue BO base in ethanol for 10 seconds. After immersion, the photoconductor was reheated for 5 seconds at 150° C. In the areas where the polystyrene was deposited the dye solution did not penetrate the film and remained transparent. In the areas not developed with styrene, the film was dyed a deep blue and resulted in a negative of the original positive image.

EXAMPLE IV

A solution of 0.76 gram of polyvinyl carbazole, 40 mg. of 3,5-dinitrobenzoic acid and 3 mg. of Malachite Green oxalate in 10 ml. of 1,2-dichloroethane was prepared. Using a polyethylene terephthalate substrate containing a transparent film of aluminum, the prepared solution was coated on the substrate using a 7 mil gap on the doctor blade. The photoconductor was overcoated with a solution obtained by mixing 10 ml. of 15% solution vinylidene chloride-acrylonitrile copolymer in 2-butanone and a solution of 0.3 g. of p-dimethylamino benzene diazonium chloride zinc chloride in 5 ml. acetonitrile. The overcoat was coated with 3 mil doctor blade gap. The thus prepared film was electrostatically charged with a positive 7000 volt corona unit and then exposed through a positive master to a 40 watt incandescent lamp at 12 inches for two seconds. The electrostatic charge image was developed with particles of 2,2′-dihydroxy-4,4′-dimethoxy benzophenone and fused. With the toner particles fused to the electrostatic image or the unexposed portions of the film, the film was exposed to a General Electric UA–2 mercury arc for 40 seconds. After this exposure, the film was heated by passing it through rollers at 115° C. In the areas where the film had been exposed to ultraviolet radiation of the mercury arc, a vesicular structure formed in the film. Thus, when the film was viewed with a projected light, a negative image of the positive original was obtained due to scattering of the light by the vesicular structure in the background areas.

We claim:

1. An electrophotographic process for producing negative transparencies comprising the steps of:

forming an electrostate charge pattern on a photosensitive member containing an essentially transparent conductive insulating layer and an alkaline sensitive material capable of responding to treatment with an alkaline material to convert the member from transparent to opaque;

developing the electrostatic charge pattern with an essential transparent alkaline absorbing but not alkaline sensitive material not convertible to opaque when said member is treated with said agent; and

treating the photosensitive member with said alkaline material so that, through the coaction of the alkaline sensitive material and the alkaline material, the areas of the member not developed with said alkaline absorbing material are converted from transparent to opaque, but the areas of the member developed with alkaline absorbing material are prevented from such conversion because of the alkaline absorbing material, thereby form a negative transparency.

2. The process of claim **1** wherein said alkaline sensitive material is a diazo compound and an azo coupler compound, said alkaline material is selected from the group consisting of ammonia and ammonia-generating precursors, and said alkaline absorbing material is an acidic compound.

3. The process of claim **2** wherein, after said treatment, said photosensitive member is uniformly exposed to light to destroy the residual diazo compound.

4. The process of claim **2** wherein said diazo compound is 2,5-diethoxy-4-morpholino-benzene diazonium borofluoride and said azo coupler is 2-hydroxy-3-naphthanol-o-anisidine, said alkaline material is ammonia, and said acidic barrier material is finely powdered stearic acid.

References Cited

UNITED STATES PATENTS

3,113,022	12/1963	Cassiers et al.	96—1.5
3,226,227	12/1965	Wolff	96—1.8
3,313,626	4/1967	Whitney	96—35 X
2,939,787	6/1960	Giaimo	96—1.3
3,038,799	6/1962	Metcalfe et al.	96—1.3
3,083,117	3/1963	Schmiedel et al.	117—17.5
3,104,169	9/1963	Metcalfe et al.	96—1
3,212,890	10/1965	Kimble et al.	96—1
3,236,639	2/1966	Tomanek	96—1
3,272,644	9/1966	Nelson	96—1 X

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U.S. Cl. X.R.

96—1.5, 67; 117—17.5, 37; 252—62.1; 355—17

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,510,297 Dated May 5, 1970

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

In the claims:

Column 9: line 26, "electrostate" should read --electrostatic--; line 28, "conductive" should read --photoconductive--.

Column 10: line 5, "form" should read --forming--.

SIGNED AND
SEALED

SEP 29 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents