United States Patent Office 3,704,124 Patented Nov. 28, 1972

3,704,124

DIAZO-CONTAINING MATERIAL EXHIBITS AN IMAGEWISE CHANGE IN TRIBOELECTRIC CHARGING PROPERTIES

Dale H. Conant, 32 Kings Court Way, Rochester, N.Y. 14617

No Drawing. Filed June 30, 1970, Ser. No. 51,352
Int. Cl. G03g 5/02, 13/14, 13/22
U.S. Cl. 96—1 R 12 Claims

ABSTRACT OF THE DISCLOSURE

Visible images corresponding to latent electrostatic charge images are produced on photographic layers incorporating a radiation-sensitive diazo material, such as a diazonium salt or a diazo resin, which exhibits a change in triboelectric series position upon exposure to activating rays, by means of a photographic process which includes (a) imagewise exposing the photographic layer to electromagnetic radiation capable of effecting an exposed imagewise change in triboelectric series position, (b) differentially triboelectrically charging the surface of the exposed photographic layer imagewise to form a latent electrostatic image thereon and (c) developing the latent electrostatic image by contacting the charged surface with a developer composition containing electrostatically attractable toner particles, to form a pattern of the toner particles on the charged surface corresponding to the non-exposed or the exposed regions. The inclusion of at least one surface active agent, such as alkali metal or ammonium alkyl sulfonate, alkali metal or ammonium sulfonated alkyl carboxylate esters, alkali metal or ammonium aryl sulfonates or alkylamines, in the photographic layer promotes not only ease of coating, but also an enhanced developed image density.

This invention relates to the electrophotographic production of images and particularly to the triboelectric production of electrostatic charge images and visible images corresponding to the electrostatic charge images.

The production of electrostatic charge images is well known. Typically, such images are produced by methods of electrophotography on elements utilizing a photoconductive, electrically-insulating layer superposed on and contiguous to an electrically-conducting support member. The photoconductive layer is first uniformly electrically charged, conventionally by a corona discharge apparatus, then imagewise exposed to light or other activating electromagnetic radiation which selectively dissipates the charge in illuminated areas through the conducting support or layer, leaving an unexposed imagewise latent electrostatic charge image on the photoconductive layer. This latent electrostatic charge image can be made visible according to well-known techniques of dry powder or liquid electrophotographic development by depositing charged electrostatically attractable toner particles having a polarity opposite to that of the electrostatic latent image.

With known electrostatic image-forming processes and using conventional photoconductive species and corona charging methods, there are certain disadvantages inherent in the image-forming operation. Generally, a high voltage power supply is required to charge the corona apparatus to the point wherein an adequate voltage potential can be impressed on the photoconductive layer. Due to the significant voltages involved, such apparatus offers a potentially dangerous electrical shock hazard. Additionally, the corona discharge and power supply apparatus can be expensive. Conventional apparatus utilized in the mechanized, imagewise exposure of photoconductive species often requires an intricate traveling optical system to secure the sharp formation of an exposure pattern either from

a traveling original to be copied or onto a traveling or rotating photoconductive element. Upon development, the image usually produced in electrophotographic image-forming processes is a boundary image (fringe development) wherein toner is deposited only at the edges of the charged portion of the photoconductive element. The effect of this phenomenon is to render the uniform development of solid areas exceedingly difficult or even impossible without additional specialized apparatus. Moreover, the latent electrostatic image formed on a photoconductive sheet is not generally a persistent charge image, and if the subsequent formation of identical copies is desired, each copy typically requires a recharging if the photoconductive element and a re-exposure of the charged surface to produce a latent electrostatic image prior to the toning step to prepare a visible image. Conventional electrophotographic systems are also positive working and form toner images corresponding to unexposed regions of the photoconductive surface. Negative-working systems are known, but these typically require additional specialized apparatus such as development electrodes and the like, and can involve delicate electrical calibration and adjustment to promote an adequate negative image forming operation.

Still another problem of many electrostatic image-forming processes is that the developed image is often of an optical density less than that which is desired for viewing purposes.

Accordingly, it is an object of the present invention to provide a novel electrophotographic image-forming process wherein high voltage corona discharge apparatus is not required to provide an electrostatic latent image.

Another object of this invention is to provide a new, improved electrophotographic image-forming process utilizing triboelectric charging means.

Still another object of the present invention is to provide a new, improved electrophotographic image-forming process wherein the electrostatic latent image which is formed is a persistent image from which subsequent identical copies can be prepared without the necessity for re-exposure or re-charging.

Still another object of the present invention is to provide a novel, improved electrophotographic image-forming process wherein, from an original to be copied, a uniformly solid area developed positive or negative image can be prepared without additional, specialized apparatus.

Still an additional object of the present invention is to provide a new, improved photographic image-forming process wherein photographic images are prepared by electrophotographic means on a photographic layer or element which is free from an electrically-conducting layer.

Yet another object of this invention is to provide a novel electrophotographic image-forming process wherein improved optical density is obtained in the developed image.

These and other objects of the present invention will become increasingly apparent from a reading of the following specification and appended claims.

The objects of this invention are accomplished with an improvement in a photographic image-forming process for the preparation of images by electrophotographic means on the surface of a photographic layer comprising a radiation-sensitive, phototriboelectrically alterable diazo material which exhibits a change in triboelectric series position upon exposure to electromagnetic radiation, which process comprises:

(a) imagewise exposing the photographic layer to electromagnetic radiation capable of effecting an imagewise change in triboelectric series position within the exposed regions of the radiation-sensitive diazo material,
(b) differentially triboelectrically charging the surface of the exposed layer imagewise to form a latent electrostatic image (electrostatic charge pattern) thereon, and

(c) developing the latent electrostatic image by contacting the charged surface with a developer composition containing electrostatically attractable toner particles to form a pattern of the toner particles on the charged surface corresponding to either the non-exposed or the exposed regions, the improvement comprising having in the photographic layer a surface active agent.

Surface active agents that are useful in carrying out the present photographic image-forming process include such surfactant materials as alkali metal (e.g. sodium, potassium, etc.) and ammonium alkyl sulfonates, aliphatic and aromatic sulfonates such as sulfonated esters of carboxylic acids and aryl sulfonates, as well as alkyl amines, preferably wherein the alkyl moiety has in excess of 8 carbon atoms, such as from about 8 to about 20 carbon atoms like octyl, tert-octyl, decyl, dodecyl, tetradecyl, pentadecyl, octadecyl, lauryl and the like. Generally, the aryl radicals are preferably of the benzene or naphthalene series, e.g., phenyl or naphthyl, either substituted or unsubstituted.

As used herein, the term alkyl sulfonate is generally inclusive of mono- or polysulfonated aliphatic sulfonates, e.g., an alkali metal or ammonium lauryl sulfonate that can include functional groupings additional to the alkyl and sulfonate moieties. The sulfonated esters of carboxylic acids include sulfonates derived from aliphatic organic acids, e.g., sulfonated alkyl carboxylate esters including dicarboxylates like sodium dioctylsulfosuccinate, for example. The term aryl sulfonate is meant to include mono- or polysulfonated derivatives of aromatic compounds, such as sodium isopropylnaphthalene sulfonate as well as disulfonates of bis aryl compounds like bis aryl ethers, sodium dodecyldiphenylether disulfonate for example. Advantageous alkylamines include those having in excess of about 8 carbon atoms in the alkyl moiety, e.g., dodecylamine.

Exemplary surface active agents of the types described herein include such surfactants as the alkali metal or ammonium sulfonates of compounds like

octadecane,
laurane,
decane,
dioctylsuccinate,
tert-octylbenzene,
isopropylnaphthalene,
tert-butylnaphthalene, and
dodecylidphenylether.

Additionally, the useful surface-active agents herein include alkylamines such as

octylamine,
dodecylamine,
tetradecylamine, and
tert-octylamine.

The term radiation-sensitive, as used herein, refer broadly to a responsiveness to electromagnetic radiation including such forms as, for example, X-rays, ultraviolet radiation, visible light, infrared rays, and any other wavelength of electromagnetic radiation suitable to initiate phototriboelectrical alteration of the sensitive materials described herein.

Also as used herein, the term alkyl radical describes branched or straight chain alkyl radicals having from 1 to about 18 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, tert-butyl, pentyl, hexyl, octyl, decyl, dodecyl, hexadecyl, octadecyl or the like alkyl radicals. The term aryl radical defines mono- or polycyclic aryl radicals having from six to about 14 atoms in the nucleus and preferably phenyl and naphthyl.

After exposing the photographic layer to activating, electromagnetic radiation, using either direct exposure (including contact exposure and other transmission exposures where activating rays pass in only one direction) or reflex exposure techniques, the exposed photographic layer can be differentially triboelectrically charged in an imagewise fashion by rubbing the surface of the layer with a material capable of inducing a latent electrostatic charge image onto either the exposed regions exclusively, the unexposed regions exclusively, or the exposed and non-exposed regions simultaneously, but differentiated in either polarity, magnitude of electrical potential (volts) or both between exposed and non-exposed regions. The designation latent electrostatic charge image defines an imagewise electrostatic charge pattern which is conventionally invisible to detection by the human eye but can be intensified to provide a corresponding visible image by suitable development techniques. The latent electrostatic image is conveniently developed to yield a visible image by contact with a developer composition including electrostatically-attractable toner particles having a polarity opposite to that of the electrostatic latent image intended for development. The toner particles adhere to the oppositely charged latent electrostatic image to define a corresponding visible image. Either the electrostatic latent image or the visible image can be transferred, if desired, according to techniques such as those which are described herein, and the ultimate visible image is typically stabilized or "fixed" by heat or solvent action to provide a durable reproduction of the exposed or unexposed image areas. The visible images produced according to the process of this invention are advantageous solid area developed, providing substantially uniform visual image density over expansive, solid image areas, as contradistinguished from line copy.

The photographic layers which are advantageous in carrying out the photographic image-forming process of this invention include generally those photographic layers utilizing a phototriboelectrically alterable diazo material as the radiation-sensitive component. The designation phototrielectrically alterable, as that term is utilized herein, designates the capabality of a material, upon exposure to activating electromagnetic radition, to undergo a change in triboelectric series position. Upon radiation, the exposed regions of layer including a phototriboelectrically alterable material exhibit a triboelectric series position which is different from that of the remaining, unexposed regions. The mechanism of alteration in triboelectric series position is not completely understood. It has been theorized, however, that variations in a material's molecular orientation, as well as in the electronic energy levels and ionization potentials associated with a particlar physical or chemical state, may effect its triboelectrification potential or level relative to other materials or other physical or chemical states of the same material.

A characteristic of electrochemical potential is expressed in the phenomenon that electrically neutral materials of unlike electrochemical potentials assume mutual electrostatic charges of opposite polarity on each other when brought into intimate contact, advantageously by rubbing. The magnitude of these charges is directly related to the disparity of electrochemical potential existing between the materials. This charging phenomenon is typically designated triboelectric charging or triboelectrification. Additionally, the relative electrochemical potential separation existing between a grouping of materials and the relative triboelectric charging characteristics associated with each relative to one or more additional members of the grouping can be conveniently ascertained by establishing a triboelectric series of the component materials.

A triboelectric series is an artificial reference framework that conveniently positions materials in a relative fashion according to their respective electrochemical potentials. The term triboelectric series, well established in the literature, is often interposed with the designation electrostatic series, and they are frequently used as equivalent expressions, as in Hackh's Chemical Dictionary, 4th ed., McGraw-Hill Inc. (1969), page 689. Determining a triboelectric series position of any material relative to

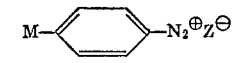
another is conveniently accomplished merely by contacting two materials, separating them and detecting the charge polarity of each with an electrometer or other suitable charge recording instrument. The series is then conventionally compiled in descending order from positive to negative such that a material higher in the series charges positively with respect to those lower in the series. Although each member of a triboelectric series is itself electrically neutral, when two members (their surfaces differing in electrochemical potential) are placed in intimate contact, such as by rubbing, an imbalance in surface potential is created at their contact interface, and electrons tend to flow from the member having a higher energy level to the member having a lower energy level, thereby seeking to equalize the noted surface potential imbalance. When the members are separated or removed from intimate contact, the charge transfer that has occurred between such members to equalize their varying surface potentials cannot undergo a reversal which is sufficiently rapid to reattain the original electrical neutrality of each member. The net effect is an electrostatic surface charge being present on each member, the charges being of equal magnitude but of opposite polarity. The member that is higher in the triboelectric series will have a positive polarity charge. Additionally, the magnitude of electrostatic charge potential is directly related to the degree of separation in triboelectric series position, with lower voltages being produced by mutual rubbing or contact of closely positioned members than by like interaction of members having a greater separation of position in the series.

The radiation-sensitive, phototriboelectrically alterable materials advantageous herein include those which, after exposure, can be differentially triboelectrically charged, imagewise, to provide an electrostatic latent image capable of intensification to a visible image. For desirable visible image density, phototriboelectric alteration produced in the radiation-sensitive materials described herein is advantageously sufficient to produce a potential difference of at least about 50 volts between exposed and non-exposed regions of a photographic layer after triboelectric charging. In calculating a voltage differential, if exposed and nonexposed regions are charged to voltages of positive polarity and negative polarity respectively, the potential difference is equal to their sum total, without regard to sign. As such, a polarity of 100 volts positive in exposed regions and of 100 volts negative in non-exposed regions provides a potential difference of 200 volts. Preferably, the electrostatic charge in regions intended for visible image development is at least about 50 electrostatic units (ESU)/cm.^{2}.

It is to be emphasized that the electrophotographic process of this invention is not one which relies on either photoconductivity, photoconductive media or any of the imaging techniques specific to photoconductography. Rather, the process described herein must operate under electrically insulating conditions or image formation is not obtained. The absence of imagewise conductivity is illustrated elsewhere herein by examples wherein either a negative or a positive imagewise reproduction of an original is developed merely by altering the polarity of electrostatically attractable toner particles in a developer composition. In effect, a single triboelectric charging step on the surface of an imagewise exposed photographic layer containing a radiation-sensitive, phototriboelectrically alterable material as described herein can effect a latent electrostatic image having dual polarity between exposed and non-exposed areas. Accordingly, positively charged toner particles can adhere to the negative polarity latent electrostatic image, and negatively charged toner particles can adhere to the positively charged latent electrostatic image. This same effect can be produced between areas of similar polarity but differing in charge potential. Were electrical conductivity to exist through the photographic layer, then visible image development would not occur.

Advantageous radiation-sensitive, phototriboelectrically alterable diazo materials which exhibit a change in triboelectric series position upon exposure to electromagnetic radiation include such chemical species as diazonium salts and diazo resins.

Useful diazonium salts include such diazonium salts as those having the formula



wherein M is either:

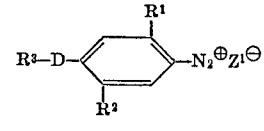
(1) a hydrogen atom,
(2) a halogen atom,
(3) an aryl radical,
(4) an amino radical including substituted amino radicals such as those having the formula



wherein R and R^0 are the same or different and can be a hydrogen atom, an aliphatic alkyl radical (aliphatic alkyl radicals are defined herein to include straight and branched chain alkyl radicals having from 1 to 8 carbon atoms such as methyl, ethyl, isopropyl, tert-butyl, n-amyl, octyl and the like) or an aryl radical such as phenyl or naphthyl, or
(5) an alkyl or aryl thioether radical, and
(6) Z$^\ominus$ is an anion.

These compounds can also be substituted on one or more of the nuclear benzene carbons with, for example, at least one of either a halogen atom, an aliphatic alkyl radical, an alkoxy radical (defined herein to include alkoxy radicals having from 1 to 8 carbon atoms such as methoxy, ethoxy, propoxy, isobutoxy, amyloxy, octoxy, etc.) and acyl radical, a carbamyl radical, a carboxyl radical or a nitro radical.

Particularly useful diazonium salts include p-aminobenzene diazonium salts having the formula wherein M is either an amino radical including substituted amino radical or a thioether radical as described above, and wherein the benzene nucleus is unsubstituted or substituted in at least one of the 2-position and the 5-position with either an aliphatic alkyl radical or an alkoxy radical. This class of useful diazonium salts can be represented by the formula:

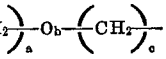


wherein:

(1) D is either a sulfur atom or a radical having the formula NR^4,
(2) R^3, when taken alone, is either a hydrogen atom when D is NR^4, or a lower alkyl radical (having 1 to 4 carbon atoms) a lower alkoxy radical (having 1 to 4 carbon atoms) an acyl radical having the formula



wherein T is either an aryl radical or an alkyl radical as described elsewhere herein, or a phenyl radical when D is either a sulfur atom or NR^4,
(3) R^4, when taken alone, is either a hydrogen atom, a lower alkyl radical or a lower alkoxy radical,
(4) R^3 and R^4, when taken together, complete a divalent radical having the formula:

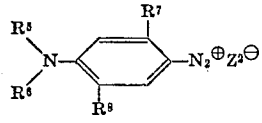


wherein b is an integer having a value of 0 or 1, each of a and c is a positive integer, and the sum of a, b and c has a value of 5.

(5) R^1 and R^2 are each either a hydrogen atom, a halogen atom, a lower alkyl radical (preferably methyl or ethyl) or a lower alkoxy radical (preferably methoxy or ethoxy), and

(6) $Z^{1\ominus}$ is an anion.

Preferred p-aminobenzene diazonium salts include substituted aminobenzene diazonium salts having the formula:



wherein:

(1) each of R^5 and R^6, when taken alone, is a lower alkyl radical,

(2) R^5 and R^6, when taken together, are the number of carbon and hetero oxygen atoms necessary to complete a morpholino radical,

(3) each of R^7 and R^8 is a hydrogen atom, a halogen atom, a lower alkyl radical or a lower alkoxy radical, and

(4) $Z^{2\ominus}$ is either a chlorozincate anion, a fluoroborate anion, a sulfate anion, a phosphate anion, a cadmium chloride anion, or a chlorostannate anion. The diazonium salts can exist in the double salt form, e.g., the zinc chloride double salt.

The most preferred benzene diazonium salts are the fluoroborate salts wherein:

(1) R^7 and R^8 are lower alkoxy radicals when R^5 and R^6 complete a morpholino radical, and

(2) R^7 and R^8 are each a hydrogen atom when R^5 and R^6 are each a lower alkyl radical.

Illustrative of the subject diazonium salts are such compounds as the salts of

1-diazo-2,5-dimethoxybenzene;
1-diazo-2,5-diethoxybenzene;
1-diazo-4-chloro-2,5-diethoxybenzene;
4-diazo-2,5-dimethoxybiphenyl;
4-diazo-2,5,4'-triethoxybiphenyl;
1-diazo-4-dimethylaminobenzene;
1-diazo-4-(diethoxyamino)benzene;
1-diazo-4-[bis(hydroxypropyl)amino]benzene;
1-diazo-4-(N-methyl-N-allylamino)-benzene;
1-diazo-4-(diamylamino)benzene;
1-diazo-4-(oxazolidino)-benzene;
1-diazo-4-(cyclohexylamino)benzene;
1-diazo-4-(9-carbazolyl)benzene;
1-diazo-4-(dihydroxyethylamino)-3-methylbenzene;
1-diazo-4-dimethylamino-3-methylbenzene;
1-diazo-2-methyl-4-(N-methyl-N-hydroxypropylamino) benzene;
1-diazo-4-dimethylamino-3-ethoxybenzene;
1-diazo-4-diethylamino-3-chlorobenzene;
1-diazo-2-carboxy-4-dimethyl-aminobenzene;
1-diazo-3-(2-hydroxyethoxy)-4-pyrrolidinobenzene;
1-diazo-2,5-diethoxy-4-acetoxyaminobenzene;
1-diazo-4-methylamino-3-ethoxy-6-chlorobenzene;
1-diazo-2,5-dichloro-4-benzylaminobenzene;
1-diazo-4-phenylaminobenzene;
1-diazo-4-morpholinobenzene;
1-diazo-4-morpholino-3-methoxybenzene;
1-diazo-4-morpholino-2,5-dimethoxybenzene;
1-diazo-4-morpholino-2-ethoxy-5-methoxybenzene;
1-diazo-4-morpholino-2,5-dibutoxybenzene;
1-diazo-2,5-diethoxy-4-benzoylaminobenzene;
1-diazo-2,5-dibutoxy-4-benzoylaminobenzene;
1-diazo-4-ethylmercapto-2,5-diethoxybenzene;
1-diazo-4-tolylmercapto-2,5-diethoxybenzene

and the like, as well as mixtures thereof.

Radiation-sensitive diazo resins which are advantageous as phototriboelectrically alterable materials include resinous, monomeric and polymeric compounds wherein a diazonium salt moiety is substituted on a resinous monomer or polymer. Conventionally a diazonium salt having a suitably reactive functional group is reacted with a resin to prepare a composite diazo resin. Alternatively, a diazonium substituted diol or diamine can be condensed with an active reagent to prepare additional polymeric diazo resins.

Especially advantageous diazo resins are formed from p-aminobenzene diazonium salts, including p-phenylaminobenzene diazonium compounds the amino group a p-phenyl group of which is substituted with organic radicals functionally capable of entering into an addition polymerization, polyesterification, condensation or other resin-producing reaction, or capable of reacting with a preformed polymer.

The placement of various groups on the anilino (amino) nitrogen or phenyl group can result in the preparation of polyesters, polyethers, polymethanes, polyacetals, polycarbonates, etc., by direct polymerization or condensation with functionally proper preformed polymers. Exemplary such polymeric diazo resins include those condensation products formed from an active carbonyl compound, such as an aldehyde like formaldehyde or an acid anhydride, and a diazonium compound such as 4-diazo-1,1'-diphenylamine. Additional diazo resins include amide salts formed by reacting an amino substituted diazonium salt with a monomeric or polymeric resin having reactive acid sites. Other resinous substances useful for preparing diazo resins include hydroxylated chemical compounds such as cellulose, gelatin, polyvinyl alcohol and the like.

Preferred diazo resins include the aldehyde condensation products, such as, e.g., the condensation product of formaldehyde compound, e.g., formaldehyde and paraformaldehyde) and a diazonium salt such as 4-diazo-1,1'-diphenylamine zinc chloride (4-phenylaminobenzenediazonium chlorozincate). Such aldehyde condensate diazo resins are described in detail in U.S. Patent 2,714,066, and are available commercially, e.g., Diazo Resin No. 4, a diazonium sulfate-zinc chloride double salt supplied by Fairmount Chemical Co. Additional advantageous diazo resins include such compounds as the fluorophosphate salt of p-diazodiphenylamine-formaldehyde condensate, the phosphate salt of p-diazodiphenylamine-acetone condensate and the like.

Photographic layers useful in the subject process are advantageously self-supporting layers where the radiation-sensitive material, for example, the diazo resin, is itself a film-forming material. In this case, the aid of an underlying support material to maintain the dimensional integrity of the photographic layer is not required. In the event that the radiation-sensitive phototriboelectrically alterable material is not a film-forming species, i.e., a diazonium salt, or not sufficiently film-forming to maintain a self-supporting layer, it can be substantially uniformly dissolved or dispersed in a film-forming resinous matrix vehicle to provide a composite sensitive material which is capable of forming a self-supporting photographic layer. Suitable resinous matrices include, for example, materials such as hydrophilic colloids like gelatin or polyvinyl alcohol. Especially advantageous are electrically insulating, substantially hydrophobic and film-forming resinous vehicles such as those including styrene-butadiene copolymers; silicone resins; styrene-alkyd resins; silicone-alkyd resins; soya-alkyd resins; poly(vinyl chloride); poly(vinylidene chloride); vinylidene chloride-acrylonitrile copolymers; poly(vinyl acetate); vinyl acetate-vinyl chloride copolymers; poly(vinyl acetals), such as poly(vinyl butyral); polyacrylic and methacrylic esters, such as poly(methylmethacrylate), poly(n-butylmethacrylate), poly-(isobutyl methacrylate), etc.; polystyrene; nitrated poly-styrene; polymethylstyrene; isobutylene polymers; polyesters, such as poly(ethylene-alkaryloxyalkylene terephthalate); phenolformaldehyde

resins; ketone resins; polyamide; poly-carbonates; polythiocarbonates; poly(ethylenegycolcobishydroxyphenyl propane terephthalate); etc. Methods of making resins of this type have been described in the prior art, for example, styrene-alkyd resins can be prepared according to the method described in U.S. Pats. 2,361,019 and 2,258,-423. Suitable resins of the type contemplated for use in the photographic layers described herein are sold under such trade names as Vitel PE–101, Cymac, Piccopale 100, Saran F–220 and Lexan 105. Other types of binders which can be used in these layers include such materials as paraffin, mineral waxes, etc. When a resinous matrix vehicle is employed, the radiation-sensitive material is typically present, in the composite coating composition, in an amount of from about 1 to about 50 parts by weight per 100 parts by weight of resin binder. More widely varying ratios can be utilized for particular formulations or coating operations according to conventional practice.

For purposes of convenience, or where the photographic layer is insufficiently dimensionally stable to form its own self-supporting layer, such layers can be coated onto an electrically insulating support material to prepare a composite photographic element. The designation electrically insulating refers to support materials having an electrically insulating surface on which the photographic layers described herein can be coated. It is desirable that the electrically insulating support members have a surface resistivity in excess of about 10^{10} ohms per square as measured by VanderPauw technique, described in Philips Research Report, 13, 1–9 (1958). Preferred insulating supports exhibit a surface resitivity of at least about 10^{12} ohms per square. Advantageous support materials include, generally in the form of a flexible film, a wide variety of compositions such as cellulosic materials like cellulose nitrate, cellulose acetate, cellulose acetate butyrate, cellulose butyrate, etc., as well as a variety of additional resinous materials including polystyrene resins, polycarbonate resins and polyester resins, such as poly(ethylene terephthalate). Additional advantageous supports include either rigid or flexible materials such as glass, metal (when overcoated with a suitable insulating layer such as one of an electrically insulating resin like those described elsewhere herein) and paper including paper coated with alpha-olefin polymers such as those containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

Preparing a photographic layer or photographic element of the sort mentioned herein is conveniently accomplished by coating a phototriboelectrically alterable material, e.g., a diazonium salt or diazo resin, in combination with a surface active agent such as those described herein, from a solvent medium onto a receptive surface of electrically insulating support material. The surface active agent is generally included in a concentration of from about 5 to about 300 (p.p.m.) parts per million based on the weight of the coating solution, with from 10 to about 300 (p.p.m.) being preferred for most formulations. As noted herein, the coating formulation can also contain a resinous matrix if desired. Coating can be effected by a variety of techniques, with such means as doctor blade coating, brushing, whirl coating, flow coating and extrusion hopper coating being desirable. Where a self-supporting photographic layer is prepared, the receptive surface is typically one which exhibits low adhesion for the photographic material, for example a highly polished metal surface such as chronium or an organic surface having high natural lubricity like a polyhalogenated alkane e.g., poly(tetrafluoroethylene). After the layer has obtained sufficient dimensional stability, e.g., after chilling or solvent extraction, it is usually physically stripped from the underlying receptive coating surface. With photographic elements incorporating an electrically insulating support material, the coated layer is merely allowed to dry in situ on the support, providing a composite radiation sensitive photographic element.

The thickness of the coated photographic layers is widely variable in accordance with conventional practice. When present on an underlying electrically insulating support material, the thickness of the layer, as coated, need only be sufficient to form a continuous film that covers any surface irregularities in the support. Typical thicknesses range from about .001 mil to about 3 mils, although more widely varying thicknesses can be utilized if desired for any reason since phototriboelectric alterability of the radiation-sensitive materials described herein is substantially independent of coating thickness variations. When the photographic layers are coated without a support and exist as self-supporting layers, then coating thickness is advantageously sufficiently thick to maintain a dimensionally stable layer. Such a thickness is variable and depends in a large part on the stability characteristics associated with the diazo resin or matrix vehicle, if present. Generally, thicknesses of from about 1 mil to about 5 mils are employed, although more extensive thickness variations can be utilized for particular coating formulations if desired.

Prior to image formation, the photographic layers and elements of the types described herein which are useful in preparing images according to the process of this invention are advantageously maintained under dark conditions or under illumination which does not produce phototriboelectric alteration in the radiation sensitive component. Typically, yellow light is acceptable since many diazonium salts and diazo resins are inherently sensitive to ultraviolet and other actinic rays.

The preparation of latent electrostatic images and of subsequent visible images corresponding to the latent electrostatic images is accomplished by sequentially (a) exposing, (b) differentially triboelectrically charging imagewise and (c) contacting the charged surface with a developer composition. Additionally, transfer of either electrostatic or visible toner image and stabilization of the visible toner image can be effected by convenient techniques.

Exposing a photographic layer such as those described herein can be carried out by imagewise irradiating the sensitive material with a source of electromagnetic radiation. The radiation is desirably of a wavelength, e.g., ultraviolet or actinic rays, such that triboelectric alteration, i.e., a change in triboelectric series position, is produced in exposed areas. The exposing step can be a direct transmission exposure e.g., contact exposure, wherein the photographic layer or element is exposed to activating radiation, conventionally through a photographic transparency or other material permitting an imagewise pattern of the exposing rays to impinge upon the sensitive-material.

Alternatively, the exposure can be accomplished by reflex exposing techniques wherein the image bearing surface of an original to be copied is first contacted against the radiation-sensitive surface of the photographic layer or element, after which exposing rays are then sequentially directed through the element and the original, and thereafter in the reverse direction as a reflection, to effect an exposed imagewise change in triboelectric series position in the photographic layer. In this fashion, offset copies of an original can be prepared. Offset copies are often designated wrong-reading or lateral reading copies. With either a transfer step or using the offset image as a printing master, right-reading copies can be obtained. Where the radiation-sensitive materials are carried in a self-supporting layer, either a right-reading image or an offset image can be obtained merely by triboelectrically charging and developing a visible image on the proper surface of the layer which is imagewise struck by exposing rays. This is possible since either surface of the imagewise exposed photographic layer, in the absence of a contiguous support material, can be charged and developed to prepare a visible image. Reflex exposing techniques can

be advantageously, but offset and direct, right-reading images are thus obtainable with direct exposures.

As described elsewhere herein, imagewise exposure of the above-described photographic layers and elements to activating electromagnetic radiation causes triboelectric alteration, a shifting in triboelectric series position, in radiation-struck areas of the sensitive material. Exposed and unexposed regions remain electrically insulating, but each exhibits distinct triboelectric charging characteristics which can be used to advantage in the formation of latent electrostatic images and corresponding visible images.

A variety of charging techniques can be used to form a latent electrostatic image, (electrostatic charge pattern) including various corona charging methods. Especially advantageous, however, are charging operations which utilize either the frictional charging or contact charging phenomena conventionally designated triboelectrification. These triboelectric charging methods advantageously provide an imagewise differential charging which significantly heightens the image-forming flexibility of the photographic elements and layers useful herein. A detailed summary of the mechanisms of triboelectric contact electrifications is presented in U.S. patent application Ser. No. 730,624, filed May 20, 1968, and presently copending herewith, now U.S. Patent 3,579,330. Contact electrification utilizes the charge transfer which occurs when two materials, differing in triboelectric series position, are intimately contacted and separated to form a latent electrostatic image corresponding to the areas in which the contacting surfaces exhibit a relative dissimilarity electrochemical potential. This disparity in electrochemical potential is conveniently expressed as a difference in triboelectric series position.

Frictional triboelectric charging is conveniently accomplished by frictionally contacting the imagewise exposed photographic layer or element with a material which has a triboelectric series position, i.e., an electrochemical potential, which is different from that of at least one of either the exposed or the non-exposed regions of the photographic material. In this fashion, since electrical charge transfer occurs between materials differing in triboelectric series position, a latent electrostatic charge image is formed on the photographic layer or element in those areas which possess a triboelectric series position different from that of the frictionally contacted material. The magnitude of charge buildup is generally directly related to the amount of triboelectric series separation existing between a rubbing material and the rubbed photographic material. Additionally, where the rubbing material is separated in the triboelectric series, i.e., exhibits a different triboelectric series position, from both the exposed and non-exposed regions of the rubbed phototriboelectrically alterable material, then a distinct latent electrostatic charge image is established in each of the exposed and non-exposed regions. If the triboelectric series position of the rubbing material is either above or below both exposed and non-exposed regions, then the electrostatic charge image in each region will be of a similar polarity but of a lower potential (voltage) in the region which is triboelectrically closer to the rubbing material. If, however, the triboelectric series position of the rubbing material intervenes those of the exposed and non-exposed regions, then the polarity of electrostatic charge image in each area of the photographic material will be of opposite sign, and the magnitude of potential in each will be related to the amount of its separation in the triboelectric series from the triboelectric series position of the rubbing material. With this charging phenomenon, it is possible to form two distinct electrostatic charge images either simultaneously or at different times, by differentially triboelectrically charging the photographic layer or element imagewise.

The triboelectric charging operation is conveniently accomplished by frictionally contacting the photographic surface with a rubbing material. Advantageous rubbing materials include generally any material that has a triboelectric series position different from that of at least one of the exposed or non-exposed regions of the photographic material. Especially advantageous rubbing materials include flexible materials which contain multiple filamentary projections that facilitate contact between the rubbing material and rubbed surface, such as animal fur, cotton cloth or additional natural fibers such as wool, etc., as well as linen, cellulosic materials and other synthetic fibers in woven or other physical form, such as numerous resinous fibers including polyamides, polyesters and additional polymeric species like polyvinyl compounds, poly-alpha-olefins, etc. The physical chemical composition of the ultimate rubbing material is secondary, e.g., smooth surfaced rubber and glass are useful. Of primary significance is its triboelectric series position relative to either the exposed regions of the photographic material, the unexposed regions or both. Triboelectric charging of the photographic surface by frictional contact with a rubbing material can be accomplished by a variety of techniques. As an example, the rubbing material can be hand held and drawn across the photographic surface. Alternatively, it can be maintained in a holding apparatus adapted to produce the desired frictional contact. In another aspect, it can be formed into a cylinder, for example by being wrapped about a cylindrical support or core, and then rotated to provide a smooth, continuous triboelectric charging operation.

As an alternative, the imagewise exposed photographic layers described herein can be conveniently chraged by cascade means. With such a technique, imagewise differential triboelectric charging is accomplished simultaneously with visible image development. A developer composition, such as those described in detail hereinbelow, containing carrier particles is "cascaded" poured or otherwise permitted to flow across the photographic surface such that there is mutual frictional contact between the photographic surface and the surfaces of numerous carrier particles. These carrier particles, as the rubbing materials described hereinabove, exhibit a triboelectric series position different from at least one of the exposed and non-exposed regions of the photographic layer and cause a latent electrostatic charge image to be formed in at least one of the noted regions of the photographic layer. The cascade charging phenomenon is analogous to the previously described triboelectrification by rubbing; it differs only in the particular technique used to effect frictional contact and is likewise a triboelectric charging means. Cascade development promotes uniform solid area development.

Subsequent to the production of an imagewise latent electrostatic image or images on the surface of the photographic material, this electrostatic charge pattern can either be developed to form a visible image in situ, or it can be transferred to a receiver surface and developed thereon. Transfer of an electrostatic image is accomplished merely by contacting the charged, electrostatic-image-bearing surface of the photographic layer or element with an electrically insulating receiver surface. Such contact is advantageously effected while maintaining each contacting surface stationary with respect to each other in order to prevent blurring, spreading or other distortion of the latent electrostatic image. Suitable receiver sheets for accepting a latent electrostatic image include those having an electrically insulating surface, i.e., having a surface resistivity of at least about 10^{10} ohms per square. Certain paper materials, either coated with a hydrophobic resin layer or having a low moisture content, are extremely useful and readily available. Additionally, the receiver sheet is preferably possessed of a smooth surface to facilitate uniform contact with the charged photographic surface, thereby promoting effective transfer of the latent electrostatic image.

After a latent electrostatic image has been formed, either in situ on a photographic surface or on a receiver

sheet subsequent to transfer, it can be intensified or developed to provide a visible image corresponding to the latent electrostatic image. Developing the latent electrostatic image is conveniently accomplished by contacting the electrostatic image-bearing surface with a developer composition containing electrostatically attractable toning or marking particles. These toner particles are then drawn to the charged surface to form a pattern corresponding to a charge pattern, which itself corresponds to either the non-exposed or the exposed regions. This pattern of toner particles can then be stabilized or fixed to render the visible image substantially permanent.

Developer compositions useful in the image-forming process of this invention include both dry developers and liquid developers. Dry developer compositions conventionally incorporate a particulate carrier vehicle and toner particles. The range of carrier vehicles which are desirable is extensive and includes various non-magnetic particles such as glass beads, crystals of inorganic salts such as sodium or potassium chloride, hard resin particles, metal, particles, etc. Additionally, magnetic carrier particles can be used. Suitable magnetic carrier materials are particles of ferromagnetic materials such as iron, cobalt, nickel and alloys thereof. Other magnetic carriers that can be used are resin particles coated with a thin, continuous layer of a ferromagnetic material as disclosed in Miller, U.S. application Ser. No. 699,030, filed Jan. 19, 1968, now abandoned, and entitled Metal Shell Carrier Particles. Still other useful magnetic carriers are ferromagnetic particles overcoated with a thin, continuous layer of a film-forming, alkali-soluble carboxylated polymer as disclosed in Miller, U.S. application Ser. No. 702,201, filed Feb. 1, 1968 and entitled Scum Retardant Carrier Particles and Compositions Thereof, now U.S. Pat. 3,547,822.

Toners useful with a carrier vehicle such as those described herein, to produce a composite, dry powder electrostatic developer composition, can be selected from a wide variety of materials to give desired physical properties to the developed image and proper triboelectric relationship to match the carrier particles used. Generally, any of the toner powders known in the art are suitable for mixing with the carrier particles to form a developer composition. Toners are generally prepared by finely grinding a resinous material and mixing the resultant, finely ground resin with a coloring material such as a pigment or a dye. The resin, or mixture in the event that a colorant is added is then typically ground additionally, for example in a ball mill, and then heated so that the resin flows and encases the coloring material. The mass is cooled, broken into small chunks and finely ground again. After this procedure, the toner powder particles usually range in diameter from about 0.5 to about 25 microns, with an average size of about 2 to about 15 microns. Optionally, where initial particle sizes are desirable, additional grinding is not performed. Other methods of toner preparation are also useful, and these methods are well known to those skilled in that art.

The resin material used in preparing the toner can be selected from a wide variety of materials, including natural resins, modified natural resins and synthetic resins. Exemplary useful natural resins are balsam resins, colophony and shellac. Examplary suitable modified natural resins are colophony-modified phenol resins and other resins listed below with a large proportion of colophony. Suitable synthetic resins include the extensive variety of synthetic resins known to be useful for toner purposes, for example, polymers, such as vinyl polymers including polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl acetals, polyvinyl ether and polyacrylic and polymethacrylic esters; polystyrene and substituted polystyrenes or polycondensates, e.g., polyesters, such as phthalate resin, terephthalic and isophthalic polyesters, maleinate resin and colophony-mixed esters of higher alcohols; phenol-formaldehyde resins, including colophony-modified phenol-formaldehyde condensates, aldehyde resins, ketone resins, polyamides and polyadducts, e.g., polyurethanes. Moreover, polyolefins, such as various polyethylenes, polypropylenes, polyisobutylenes and chlorinated rubber are suitable. Additional resinous toner materials which are useful are disclosed in the following U.S. Patents: 2,917,460; Re. 25,136; 2,788,288; 2,638,416; 2,618,552 and 2,659,670.

As noted above, color material can be incorporated into toners to render electrostatic images toned therewith more distinct or visible. The coloring material additives useful in suitable toners are preferably dyestuffs and colored pigments. These materials serve to color the toner and thus render it more visible. In addition, they sometimes affect, in known manner, the polarity of the toner. In principle, virtually all of the compounds mentioned in the Color Index, vol. I and II, second edition, 1956, can be used as colorants would be such materials as Nigrosin Sipirit soluble (C.I. 50415), Hansa Yellow G (C.I. 11680), Chromogen Black ETOO (C.I. 14645), Rhodamine B (C.I. 45170, Solvent Black 3 (C.I 26150), Fuchsine N (C.I. 42510), C.I. Basic Blue 9 (C.I. 52015), etc. Another useful class of colorants are nigrosine salts such as nigrosine salts of mono and difunctional organic acids having from 2 to about 26 carbon atoms such as chloroacetic acid, stearic acid, sebacic acid, lauric acid, azelaic acid, adipic acid, abietic acid, docosanoic acid and the like. Nigrosine salts of this type are disclosed in copending application Ser. No. 770,122, filed Oct. 23, 1968, in the name of James R. Olson and entitled Uniform Polarity Resin Electrostatic Toners. In addition to the resin and colorant, dry toners can also contain such additional desirable components as are known in the art.

In toners for dry developers, colorant materials are typically included in an amount of from about 1 part to about 10 parts by weight per 100 parts by weight of the resin binder. Composite dry developers generally include from about 1 part to about 10 parts by weight of toner particles and other addenda per 100 parts by weight of the entire developer, i.e., from about 90 to about 99 parts by weight of carrier vehicle.

Latent electrostatic images can also be developed using liquid developer compostions, these typically including a dyed or pigmented resin dispersed in an electrically insulating carrier liquid. Typical liquid developers are prepared by grinding or ball milling at least one pigment with a suitable polymer solution and diluting this concentrate with an insulating carrier liquid. Alternatively, a dye can be dispersed or dissolved in the polymer solution in lieu of or in addition to the pigment. The resultant developer is in the form of a carrier liquid having dispersed therein toner particles comprised of the pigments or dyes or both as a colorant and a suitable resinous material. Advantageous pigments include inorganic materials such as structural forms of carbon like graphite, carbon black, lamp black, bone black, charcoal, etc., as well as additional materials including cadmium sulphide, titanium dioxide, zinc oxide, iron oxide, aluminum powder and bronze powder. Suitable dyestuff colorants include organic dyes such as:

	C.I.
Crystal violet	42,555
Malachite green	42,000
Methylene blue	52,015
Victoria blue	42,595 and 44,045
Carmine red	75,470
Nigrosine C 140 powder	50,420
Chloramine Black Ex (dark)	30,235
Rayon Black C (double conc)	35,255

In addition to the pigment or dyestuff colorants which are dispersed in the carrier liquid, a resinous material can be used if desired to facilitate binding of the colorant to the surface to be developed. Suitable resinous materials used in the present developers appear to form a coating

around each colorant particle and thus also facilitate dispersion of the colorants in the carrier liquid. Useful resins can be selected from a wide variety of substances. The following are illustrative of suitable materials; rosins, including hydrogenated rosins and esters of hydrogenated rosins, alkyl methacrylate copolymers having from 2 to 5 carbon atoms in each alkyl moiety, such as isobutyl methacrylate and normal butyl methacrylate copolymers, etc.; phenolic resins including modified phenolic resins such as phenol formaldehyde resins; pentaerythritol phthalate; coumaroneindene resins; ester gum resins; vegetable oil polyamides; alkyd resins, including modified alkyds such as soya oil-modified and linseed oil modified alkyds, phthalic, maleic and styrenated alkyds, etc.; and the like.

In addition, the electrostatic charge polarity of the toner particles present in liquid developers can be enhanced or altered by the addition of suitable charge control agents if so desired. A variety of materials can be used as charge control agents. Illustrative of suitable charge agents are the polyoxyethylated alkyl surfactants such as polyoxyethylated alkylamine, polyoxyethylene palmitate, polyoxyethylene stearate, etc. Other useful materials are magnesium and heavier metal soaps of fatty and aromatic acids as described in Beyer U.S. Pat. No. 3,417,019. Useful metal soaps include cobalt naphthenate, magnesium naphenate and maganese naphthenate, zinc resinate, calcium naphthenate, zinc lionleate, aluminum resinate, isopropyltitanium stearate, aluminum stearate, and others many of which are also described in U.S. Pat. No. 3,259,581. Typically, the amount of such materials used is less than about 2% by weight based on the weight of toner. In certain instances, the resinous binder per se can function as the charge control agent as can the colorant.

Suitable developer compositions can be prepared simply by grinding the pigments to the appropriate size and dispersing the pigment powder in a carrier liquid without the addition of a resinous binder and/or charge control agent. A developer which does not contain a binder material would produce developed images which were not fixed. Accordingly, it would be necessary to overcoat such images by spraying with a lacquer composition in order to hold the pigment particles in place. The pigment or pigment-binder particles generally have an average particle size of from about 0.5 to about 5μ, with preferred materials in the range of from about 0.1 to about 1 micron. Typical developer compositions contain the present pigments or other colorant in a concentration of from about 0.01 to about 1.0 gram per liter. When a resin binder is used, the pigment (colorant) to binder weight ratio can vary from about 1:30 to about 2:1.

Carrier liquids which can be used to form such developers can be selected from a wide variety of materials. Preferably, the liquid has a low dielectric constant and a very high electrical resistance such that it will not disturb or destroy the electrostatic latent image. In general, useful carrier liquids should have a dielectric constant of less than about 3, should have a volume resistivity of greater than about 10^{10} ohm-cm. and should be stable under a variety of conditions. Suitable carrier liquids include halogenated hydrocarbon solvents, for example, fluorinated lower alkanes, such as trichloromonofluoromethane, trichlorotrifluoroethane, etc., having a typical boiling range of from about 2° C. to about 55° C. Other hydrocarbon solvents are useful such as isoparaffinic hydrocarbons having a boiling range of from about 145° C. to about 185° C. such as Isopar G (Humble Oil & Refining Co.) or cyclohydrocarbons having a major aromatic component and also having a boiling range of from about 145° C. to about 185° C., such as Solvesso 100 (Humble Oil & Refining Co.). Additional useful carrier liquids include polysiloxanes, odorless mineral spirits, octane, cyclohexane, etc. Conventionally, the amount of toner dispersed in a carrier vehicle to provide a composite developer varies from about .1 g. to about 10 g. of toner per liter of carrier liquid.

Contacting the charged surface with the developer composition can be accomplished with a variety of development techniques. With dry developers, it is convenient to cascade the developer over the charged surface by, for example, pouring or otherwise directing the developer composition onto the charged surface. As previously mentioned, where the triboelectric series position of the carrier particles is suitably separated from that of at least one of the exposed or non-exposed regions, then latent electrostatic image formation and visible image development can occur simultaneously, thus eliminating the need for a separate charging operation. Alternatively, when ferromagnetic carrier materials are utilized, dry developers can be applied to a previously electrostatically charged surface by magnetic brush techniques. An example of apparatus suited for magnetic brush development is that type which is described in U.S. Pat. No. 3,003,462, which apparatus often comprises a non-magnetic, rotatably mounted cylinder having fixed magnetic means mounted inside. The cylinder is arranged to rotate so that part of the surface is immersed in or otherwise contacted with a supply of developer mix. The granular mass comprising the developer mix is magnetically attracted to the surface of the cylinder. As the developer mix comes within the influence of the field generated by the magnetic means within the cylinder, the particles thereof arrange themselves in bristle-like formations of developer mix tend to conform to the lines of magnetic flux, standing erect in the vicinity of the poles and lying substantially flat when said mix is outside the environment of the magnetic poles. Within one revolution the continually rotating tube picks up developer mix from a supply source and returns part or all of this material to the supply. This mode of operation assures that fresh mix is always available to the copy sheet surface at its point of contact with the brush. In a typical rotational cycle, the roller performs the successive steps of developer-mix pickup, brush formation, brush contact with the electrostatically charged surface, brush collapse and finally mix release. Still additional advantageous develeopmnt techniques, e.g., powder cloud development and other aerosol techniques, are well known by those skilled in this art. Powder cloud development includes fluidized bed development techniques, e.g., those described in U.S. Pat. 3,008,826. When fluidized bed development is employed, concomitant charging and development can be effected, as with cascade development.

When liquid developers are utilized, development is conveniently effected by a wide range of techniques including immersion of the charged surface into the developer, flowing the liquid developer across the charged surface, spraying the developer onto the charged surface, etc. When spray aerosol techniques are used, the toner particle charge can be intensified by passage of the aerosol by or through a charged point source or grid.

Unfixed toner images can be transferred to a receiver surface by, for example, contact transfer means. Additionally, by sequentially repeating the developing and transfer steps at least once, multiple copies can be prepared without necessitating either re-exposure or recharging.

Conventionally, after visible image development, the resultant toner image is fixed or stabilized to render it resistant to smudging or other degradation caused by physical contact, solvent action or the like. Fixation can be accomplished by a number of techniques in accordance with usual practice. When binderless toners are used, a film-forming, adherent layer is typically applied over the toner image to bind it to the underlying substrate. Advantageous materials include film-forming, thermoplastic resins or lacquers such as described hereinabove. When a binder component is present in the toner, fixation can easily by accomplished by heating or solvent treatment means. Upon heating, a thermoplastic binder can be

melted or suitably softened such that the toner particles fuse to form a continuous film which adheres tightly to the underlying surface. Alternatively, the oner image can be treated with a solvent treatment means. Upon heating, a thermoplastic binder can be melted or suitably softened such that the toner particles fuse to form a continuous film which adheres tightly to the underlying surface. Alternatively, the toner image can be treated with a solvent or solvent vapors which produce a solvent effect upon the resinous binder. Upon resolidification, the resin binder forms a solid film which also tightly adheres to the supporting surface.

With the phototriboelectrically alterable materials described herein, both exposed and non-exposed regions remain electrically insulating and can be simultaneously or sequentially electrostatically charged and developed, by techniques surh as those described elsewhere herein, to provide separate images of, for example, varying colors. Also, when an imagewise exposed photographic layer as described herein is triboeletcrically charged such that opposite polarity eletcrostatic latent charge images are produced in exposed and non-exposed regions respectively, either a negative or a positive copy of the original can be obtained from a single imagewise exposure, merely by developing the charged surface with a developer composition whose toner particles exhibit a polarity opposite to that of the image region intended for development. Additionally, if the imagewise exposed and developed photographic layers and element of the types herein described are not subsequently overall exposed to activating rays, then additional, add-on images can be prepared in previously unexposed and exposed areas by using a suitable combination of the exposing, charging and development techniques prevously mentioned.

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

EXAMPLE 1

A light-sensitive element, coated over polyethylene coated paper support is prepared as follows: a light-sensitive diazo resin, the condensation product of paraformaldehyde and 4-diazo-1,1'-diphenylamine sulfate-zinc chloride double salt (75 mg.) is dissolved in 25 ml. of distilled water, after which 25 ml. denatured ethyl alcohol and 100 ml. methanol are added to the aqueous solution. This composite solution is flow coated onto polyethylene coated paper support and dried. A second element is prepared in like fashion, except that the added ethyl alcohol and methyl alcohol contain 150 mg. of a surfactant, sodium dioctyl sulfosuccinate. An electrostatic latent image is then formed on each of the two elements as follows: the light-sensitive element is exposed through a negative appearing line copy original, to the light of two 300 watt photoflood lamps for 30 seconds and at a distance of 10 inches from the center of each lamp (the lamps being themselves separated by 10 inches between centers). The exposed surface is then differentially triboelectrically charged imagewise by rubbing with a nylon plush cloth. The exposed areas are found to be charged to a negative potential and the unexposed areas to a positive polarity, since the nylon plush rubbing material, in the triboelectric series, lies between the triboelectric series positions of the exposed and non-exposed regions. A portion of the charged surface of each element is then developed with a dry electrostatic developer composition, having positive polarity toner particles. The developer composition is of the type described above and is composed of iron carrier particles admixed with toner particles of a polystyrene resin dyed with nigrosine base (the free base of C.I. 50,415) as a colorant. Development is accomplished by magnetic brush techniques and toner patricles are deposited in the negatively charged, exposed regions. A second portion of each element is developed in a similar fashion, but using a developer composition having negatively charged toner particles which are deposited in the positively charged unexposed regions. The developer composition is of the type described above and is composed of iron carrier particles admixed with toner particles of a polystyrene resin pigmented with carbon black as a colorant. Each toner image is then fixed by treatment with trichloroethylene vapors which exert a solvent effect upon the toner particles and permanently fuse them to the underlying support surface. In this fashion, either a postive copy or a negative copy of the original negative line transparency can be prepared merely by using an electrostatic developer having toner particles of a polarity suitable to effect deposition in the desired image region. The toner image present on the portions of the second element (containing a surfactant) are of a higher quality, exhibiting increased maximum density, decreased minimum density and cleaner background areas than the control element not containing a surfactant.

EXAMPLE 2

Five photographic elements are prepared as in Example 1 except that in lieu of the second element are prepared four similar elements (2–5) having the following surfactants in equal amounts.

Element:

(2) sodium isopropylnaphthalene sulfonate,
(3) sodium dodecyl diphenylether disulfonate,
(4) sodium lauryl sulfonate, and
(5) dodecylamine

These elements are exposed and charged as in Example 1. Development of a portion of each element is then obtained by flowing a liquid developer composition, containing negatively charged toner particles, across the charged surface. The developer composition is of the type described hereinabove and is composed of an n-pentane carrier liquid having dispersed therein droplets of linseed oil pigmented with carbon black as a colorant. Toner particles are deposited in unexposed regions to prepare a positive copy of the original line transparency. Image stabilization (fixing) is obtained by the application of heat. The preparation of a negative copy is conveniently accomplished on the remaining portion of each element by using a liquid electrostatic developer composition having positively charged toner particles which are deposited in the exposed image regions. The liquid developer comopsition is of the type described hereinabove and is composed of cyclohexane carrier liquid having dispersed therein toner particles of an alkyd resin dyed with phthalocyanine blue as a colorant. Fixation of the resultant visible image is accomplished by heating. The images of the elements containing a surfactant exhibit improved quality commensurate with that of Element 2 of Example 1.

The enhanced image effects described above in Examples 1 and 2 are not produced by all surface active agents. The following materials, when coated in similar photographic layers and at like concentrations, produced inferior images when compared to a control image.

(a) condensed naphthylene sulfonate,
(b) alkyl phenoxy polyglicidol,
(c) lauryl diethyl amine oxide,
(d) ethanolated alkylguanidine amine complex,
(e) polyethylene alkylamine,
(f) N-cetyl-ethyl-morpholinium ethosulfate,
(g) lauryl pyridinium p-toluene sulfonate,
(h) 1-methyl-1-alkylamidoethyl-2-alkylimidozolinium, methosulfate, and
(i) alkyl dimethylamine oxide.

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.

I claim:

1. In a photographic image-forming process for the

preparation of images by electrophotographic means on the surface of a photographic element comprising an electrically insulating support having coated on a surface thereof a photographic layer comprising a phototriboelectrically alterable material consisting essentially of a diazo material including a diazonium salt moiety, which material exhibits a change in triboelectric series position upon exposure to electromagnetic radiation which process comprises:

(a) imagewise exposing said photographic layer to electromagnetic radiation capable of effecting an exposed imagewise change in triboelectric series position within the exposed regions of said diazo material,

(b) differentially, triboelectrically charging the surface of said exposed layer imagewise to form a latent electrostatic image thereon, and

(c) contacting said charged surface with a developer composition containing electrostatically attractable toner particles to form a pattern of said toner particles thereon corresponding to the nonexposed or the exposed regions,

the improvement comprising having in said photographic layer sodium dioctyl sulfosuccinate.

2. A photographic image-forming process as described in claim **1** wherein the radiation-sensitive diazo material is selected from the group consisting of a diazonium salt and a diazo resin.

3. A photographic image-forming process as described in claim **2** wherein the diazonium salt is a p-aminobenzene-diazonium salt.

4. A photographic image-forming process as described in claim **3** wherein the diazo resin is selected from the group consisting of diazo resins containing a p-aminobenzene diazonium moiety.

5. A photographic image-forming process as described in claim **1** wherein the radiation-sensitive diazo material is dispersed in an electrically insulating resin.

6. A photographic image-forming process as described in claim **1** wherein said exposing step is accomplished by reflex exposure.

7. In a photographic image-forming process for the preparation of images by electrophotographic means on the light-sensitive surface of a photographic element comprising an electrically insulating support having coated on a surface thereof a photographic layer comprising an electrically insulating resin having dispersed therein a radiation-sensitive phototriboelectrically alterable material consisting essentially of a diazo material including a diazonium salt moiety, which material exhibits a change in triboelectric series position upon exposure to electromagnetic radiation, said radiation-sensitive diazo material being selected from the group consisting of light-senistive diazonium salts and light-sensitive diazo resins, which process comprises:

(a) imagewise exposing said photographic layer to electromagnetic radiation capable of effecting an exposed imagewise change in triboelectric series position within the exposed regions of said diazo material,

(b) differentially triboelectrically charging the surface of said exposed layer imagewise to form a latent electrostatic image thereon, and

(c) contacting said charged surface with a developer composition containing electrostatically attractable toner particles to form a pattern of said toner particles thereof corresponding to the non-exposed or the exposed regions,

the improvement comprising having in said photographic layer sodium dioctyl sulfosuccinate.

8. A photographic image-forming process as described in claim **7** wherein the diazonium salt is a p-amino-benzene diazonium salt.

9. A photographic image-forming process as described in claim **8** wherein the diazonium salt is p-diethylaminobenzenediazonium chlorozincate.

10. A photographic image-forming process as described in claim **7** wherein the diazo resin is the condensation product of an active carbonyl compound and a p-aminobenzenediazonium salt.

11. A photographic image-forming process as described in claim **10** wherein the diazo resin is the condensation product of a formaldehyde compound and a p-aminobenzenediazonium salt.

12. A photographic image-forming process as described in claim **11** wherein the diazo resin is selected from the group consisting of the condensation product of formaldehyde and 4-diazo-1,1'-diphenylamine sulfate-zinc chloride and the condensation product of paraformaldehyde and 4-diazo-1,1-diphenylamine sulfate-zinc chloride.

References Cited

UNITED STATES PATENTS

3,518,081	6/1970	Bickmore et al.	96—1
2,996,381	8/1961	Oster et al.	96—49
3,360,371	12/1967	Munder et al.	117—34 X
2,316,234	4/1943	Flett	252—353 X
3,206,599	9/1965	Gold	250—65.2
3,128,198	4/1964	Dulmage	117—17.5
3,206,600	9/1965	Gold	250—65.2
3,286,025	11/1966	Ingersoll	96—1 X

FOREIGN PATENTS

1,105,112	3/1968	Great Britain	96—49
1,103,864	2/1968	Great Britain	96—49

GEORGE F. LESMES, Primary Examiner

R. E. MARTIN, JR., Assistant Examiner

U.S. Cl. X.R.

96—1.4, 1.5, 49, 75, 91; 117—17.5; 250—65.2

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,704,124 Dated November 28, 1972

Inventor(s) Dale H. Conant

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

Column 4, line 36, "trielectrically" should read ---triboelectrically---;

Column 4, line 40, insert ---a--- before "layer";

Column 17, line 32, substitute ---or--- for "and"

Column 19, line 52, (Claim 7), "senistive" should read ---sensitive---.

Signed and sealed this 12th day of June 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents