May 31, 1966 D. L. SMITH ETAL 3,253,913

PROCESS FOR COLOR ELECTROPHOTOGRAPHY

Filed Oct. 13, 1960 2 Sheets-Sheet 1

Fig. 1

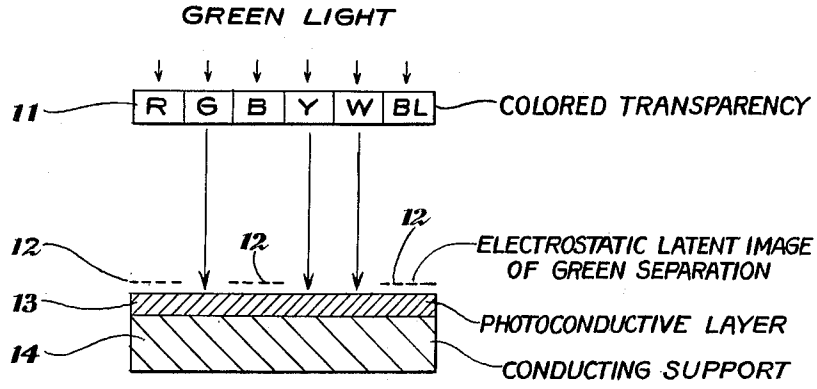
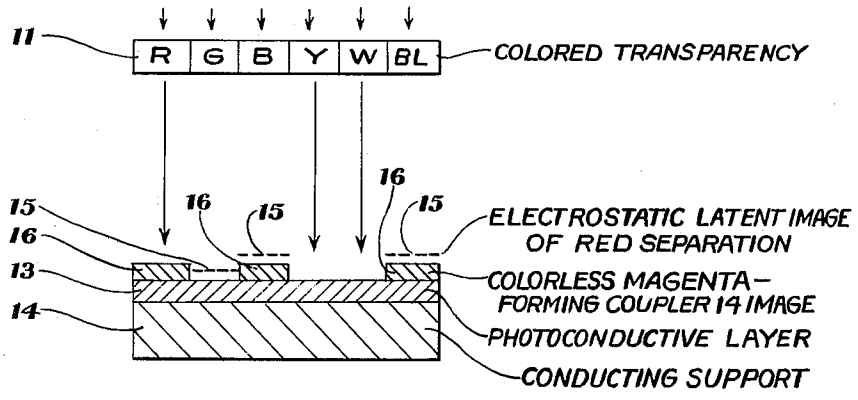


Fig. 2



Dale L. Smith
John R. Thirtle
INVENTORS

BY R. Frank Smith
Ray Carter Livermore
ATTORNEY & AGENT

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Fig. 3

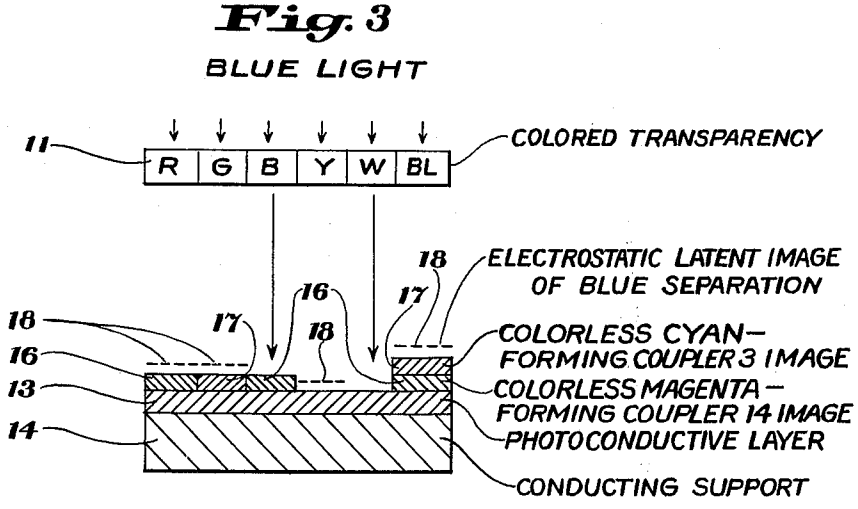
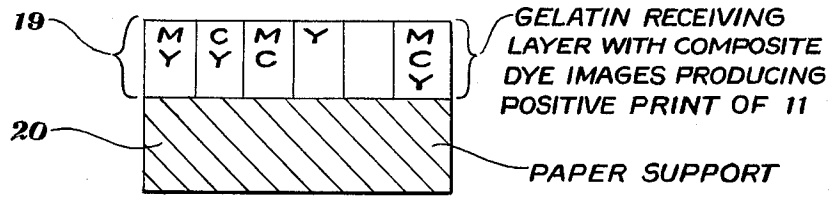


Fig. 4



Dale L. Smith
John R. Thirtle
INVENTORS

BY R. Frank Smith
Ray Carter Livermore
ATTORNEY & AGENT

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PROCESS FOR COLOR ELECTROPHOTOGRAPHY

Dale L. Smith and John R. Thirtle, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

Filed Oct. 13, 1960, Ser. No. 62,415
7 Claims. (Cl. 96—1)

This invention relates to electrophotography and particularly to a novel electrophotographic process for producing color pictures.

Electrophotographic methods for reproducing images are well known. In one of these processes known as xerography, a photoconductive layer coated on a conductive support is given a uniform electric charge, and exposed to a pattern of activating radiation which creates a corresponding electrostatic latent image on the surface of the photoconductive layer by dissipating the charge of the layer in the areas receiving the activating radiation in accordance with the amount of activating radiation. This electrostatic latent image is then converted into a visible image by depositing on it an opaque electroscopic material by electrostatic attraction. This image is then fixed by any of the known methods such as applying heat and/or pressure.

Finely divided opaque materials such as talcum powder, carbon black, other pigments and dyes are commonly used as electroscopic material to convert the latent image into a visible image. These materials, for use, are given an electric charge to aid in their deposition on the electrostatic latent image. The polarity of the charge carried by the electroscopic material relative to the charge of the electrostatic latent image is one factor in determining whether a negative or positive image is obtained; thus a positively charged electroscopic material will be attracted to a negatively charged electrostatic image to produce a positive toner image of the electrostatic image. Electroscopic materials sometimes referred to as xerographic developers are deposited on the electrostatic latent image by various methods, as a finely divided material either in the dry or liquid state dispersed in air as a cloud, coated on another slightly more coarsely divided material such as on the iron particles of a "magnetic brush" called a carrier from which the electroscopic powder is transferred to the electrostatic latent image, or the finely divided powder may be dispersed in a liquid carrier having a high electrical resistivity and applied by roller application or dipping known as liquid immersion development.

In another of these processes described in Jarvis U.S. application 598,017, now abandoned, a photoconductive layer is exposed to a pattern of activating radiation before and/or during a corona charging operation and while continuing to charge the layer, it is subjected to an aerosol of charged particles or droplets of colorant which accumulate in the areas that have been exposed to radiation. This process is differentiated from a xerographic process in that a continuous flow of electric current passes through the photoconducting layer in those areas exposed to activating radiation.

In these processes the making of a color print usually requires at least three separate exposures and three development cycles. Such prints can result from exposure to a selected region of the spectrum followed by deposition of an appropriate dye by one of the mentioned methods. This procedure is repeated two more times depositing thereby three dyes, for example, cyan, magenta, and yellow needed for adequate color rendition. A major deficiency of such a process is that dyes normally used are imperfect, and the undesirable absorption of dyes already deposited as the first, and first and second

color images affect the subsequent exposures of the second and third images adversely and degrade the color fidelity of the final three-color print.

A further disadvantage of electrophotographic processes using colored materials for developing the electrostatic latent image formed by the process into a color image is that great care must be taken in handling the highly colored electroscopic materials to insure that they not escape from the confines of the processing equipment and soil the hands and clothing of the operator or contaminate copy work already completed.

It is therefore an object of our invention to provide electrophotographic processes in which a colorless color-forming image is formed electrically and subsequently converted into a color image.

Another object is to provide a class of colorless, color-forming materials for use in electrophotographic processes for producing color prints.

Another object is to provide an electrophotographic process for making multicolor prints in which colorless, color-forming coupler images are made electrically in sequence one on top of the other, corresponding appropriately to the color separation images of a multicolor original and then subsequently converting the colorless images into the corresponding dye images by simply treating the layer bearing the combined colorless images with a solution of a primary aromatic amine in the presence of an oxidizing agent.

A further object is to provide an electrophotographic process for making color prints in which a charged photoconductive layer is exposed to blue light passed through an image in a color positive material, a charged electroscopic, colorless yellow-dye-forming coupler is deposited on the electrostatic image produced by the blue-light exposure, the photoconductive layer is recharged, exposed to green light through the same color positive image, a charged electroscopic, colorless, magenta-dye-forming coupler is deposited on the electrostatic image produced on the photoconductive layer by the green-light exposure, the process repeated with red light and a charged electroscopic, colorless, cyan-dye-forming coupler and subsequently the colorless coupler images on the surface of the photoconductive layer are converted to a positive color reproduction comprising the yellow, magenta, and cyan dye images by treating the layer with a solution of a primary aromatic amine in the presence of an oxidizing agent.

A further object is to provide an electrophotographic process for making color prints in which a charged photoconductive layer is exposed to one primary color separation image of a multicolor original, the electrostatic latent image formed is contacted with a dispersion of a charged, colorless, complementary-color-forming coupler and an oxidizing agent in an organic liquid carrier to produce a colorless image of these materials, the photoconductive layer is recharged and the process repeated to form a colorless, complementary-color-forming image of the electrostatic latent image produced by exposure to a second primary color separation of the original in register with the first, the photoconductive layer is recharged and the process repeated to form in register with the other two images a colorless complementary-color-forming image produced by exposure to a third primary color separation of the original and subsequently treating the three colorless images with a solution of a primary aromatic amine to produce the color reproduction of the original. This process will operate with either negative or positive multicolor originals.

A further object is to provide the process of the preceding object in which an electric charge control agent is added to the dispersion of coupler and oxidizing

agent in liquid carrier used to form one, two, or all three of the colorless color-forming images to enhance the uniformity of the image deposits.

Another object is to provide an electrophotographic process for making a color print in which a blue image of a color negative is projected onto a photoconductive surface, the conducting latent image formed is exposed to a cloud consisting of a finely divided and dispersed colorless, yellow-dye-forming coupler charged in a corona field maintained near the image bearing photoconductive layer and without moving the projected image or copy material, the process is repeated with green light and a cloud of a finely divided and dispersed colorless, magenta-dye-former followed by red-light exposure and a cloud of a finely divided and dispersed colorless, cyan-dye-former, then the three registered superimposed colorless, dye-forming images are treated with a solution of a primary aromatic amine and an oxidizing agent to produce a multicolor print. Alternatively, the colorless images can be transferred to a receiving sheet and then converted into their colored form.

Another object is to provide a process as described above in which the clouds of finely divided and dispersed material are made of the respective colorless, color-forming couplers and also include an oxidizing agent and in which the three colorless, color-foming coupler images containing the oxidizing agent are converted into three-color images by treating with a solution of a primary aromatic amine.

Other objects will become apparent from the following specification and claims.

These and other objects are accomplished by using the process of our invention.

According to the electrophotographic processes of our invention a colorless image is produced electrically on a charged photoconductive layer that has been exposed imagewise to an activating radiation and the colorless image is subsequently converted into a colored image.

The word colorless is used throughout this specification and the claims to describe an image or material which when deposited on the photoconductive layer in the thickness used to form an image, absorbs less than 30 percent of the incident radiation at any wave length in the range 430 to 670 mμ. In most instances the absorbence will be distinctly less than this. In no instance will the colorless materials per se have sufficient absorption to produce a useable image.

It is usually preferable to use colorless materials which have substantially no absorption of the activating radiation so that a colorless image on a photoconductive surface will have no effect at all on the exposure of a second image over the first. However, in some instances it may be advantageous to use materials which have a small amount of absorption for masking purposes.

In one of the electrophotographic processes of our invention, an electrostatic latent image is produced on the surface of a charged photoconductor by exposing the charged photoconductor to a light image; the electrostatic latent image is then treated with an electroscopic colorless, color-forming material to produce the corresponding colorless, color-forming image which is then subsequently converted into the corresponding color image by reacting the colorless, color-forming image with at least one other material. This process may be used to create single color images or multicolored images by repeating the process described for each of the color separation component images of a multicolor picture to produce the corresponding colorless images which are then converted by a chemical reaction into the three differently colored images.

Application of the electroscopic, colorless, color-forming materials to the electrostatic latent image is accomplished by various methods. For example, the finely divided electroscopic material may be applied to the electrostatic latent image by powder cloud methods in which the powder is carried as a dispersion in air or gas that is passed over the electrostatic image. These particles are charged to aid in the efficiency of their deposition and the formation of better images. The electroscopic material may be applied as a member of a two-component system in which the powder material is coated on glass beads or other slightly larger size particles of another material which is cascaded across the photoconductive surface bearing the electrostatic latent image to deposit the colorless, color-forming material in an imagewise manner. The electroscopic material is also deposited on the electrostatic latent image by uniformly spreading a thin layer of the electroscopic material on another surface which is then brought close to or in contact with the electrostatic latent image on the surface of the photoconductive layer. Deposition in this case may be aided by creating a strong electric field which moves the electroscopic material from the carrying sheet to the image-bearing layer.

The coupler may be applied to the electrostatic latent image on a photoconductive layer as a charged finely divided dispersion of the coupler in an organic liquid carrier, having a high electrical resistivity and other special properties which are defined later in the specification. The dispersion may also contain an oxidizing agent, and/or an electric charge control agent used to enhance the formation of a uniform image deposit. The dispersion is applied to the electrostatic latent image bearing photoconductive layer by immersing the layer in a suitable tray or tank of the dispersion, by roller application, or by any other method that is well known in the art. Roller application in which the dispersion supplied to a trough is transferred to the image bearing layer by one or a series of rollers has been used advantageously.

In another one of the electrophotographic processes of our invention, a photoconductive layer is exposed to a pattern of activating radiation before and/or during a corona charging operation and while continuing to charge the layer, it is subjected to an aerosol of charged colorless, color-forming coupler particles or droplets of the colorless, color-forming coupler dispersed in or dissolved in an organic liquid, the coupler particles are thus built up as images in the areas that have been exposed to activating radiation. The aerosols may be produced by any of the well known methods used to make aerosols and may be applied by methods described in the prior art such as in Jarvis U.S. application 598,017, filed July 16, 1956.

The electrophotographic element used in our process may be any of those which have been described in the prior art. The electrophotographic element consists of a conductive material such as a metal plate, e.g., brass, aluminum, zinc, etc., paper, etc., or a nonconductive material such as glass, etc., which is made conductive by a thin coating of a metal foil such as aluminum foil, etc., other materials such as tin oxide, carbon, etc., over which is coated a photoconductive layer. The photoconductive layer may comprise a thin layer of an organic compound such as anthracene, anthraquinone, etc, or other substances such as sulfur, selenium, tellurium in vitreous form or it may consist of a phosphor such as cadmium sulfide, arsenic sulfide, zinc cadmium sulfide, zinc cadmium selenide, zinc oxide, and various mixtures of these which are coated in a continuous layer or as discrete particles in a resinous binder. Various resins may be used as a binder such as polyvinyl resins, e.g., the polystyrenes, the polyvinyl acetates, polyvinyl chlorides, etc., the silicone resins, cellulose esters and cellulose ethers, and the acrylic resins. These resins must be transparent to the radiation that will be used in exposing the element and must have good electrical insulating properties.

If the photoconductive layer is inherently sensitive to light of short wave length such as ultraviolet, it may be

given sensitization to light in the visible parts of the spectrum by methods described in the prior art.

An electrophotographic element which can be used to advantage consists of a dispersion of zinc oxide in a resinous binder that is coated on a conducting support.

The photoconductive layer of the electrophotographic element is normally charged to a surface potential of 100 volts or more before exposure to a radiant image in order to produce a good quality latent image upon exposure.

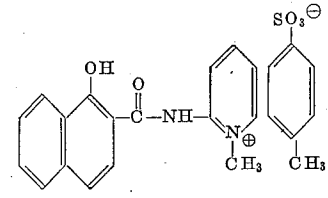
Any colorless, color-forming material can be used in the processes of our invention providing that it can be reduced to a sufficiently small particle size in the dry state or can be put into a liquid and dispersed as an aerosol and providing that it will form a color image of good quality by a subsequent reaction with another material. For example, the colorless leuco forms of suitable dyestuffs may be used and subsequently converted into a colored form by reacting with an oxidizing agent. Dye intermediates in the form of diazonium compounds may be used to form the colorless image which is then reacted with another intermediate that has a chemical group which reacts with the diazonium compound to produce a color dye. Among the preferred colorless, color-forming materials used advantageously in our process are colorless coupler compounds well known in the photographic art. Thus the phenolic and naphtholic coupler compounds well known in the art of color photography have been used as an electroscopic material to form a colorless image which is then reacted with an oxidized primary aromatic amine to form a cyan dye image. Similarly, the well known pyrazolone magenta color formers, and benzoyl acetanilide yellow forming couplers have been used to advantage in the preparation of magenta and yellow dye images, respectively. Among the color-forming couplers which we have found advantageous in our process are the following representative couplers.

Coupler	Name
1	1-Hydroxy-N-(2-N-methylpyridinium)-2-naphthamide p-toluenesulfonate.
2	1-Hydroxy-N-[3-(N,N,N-trimethylaminopropyl)]-2-naphthamide iodine.
3	2,4-Dichloro-5-(p-toluene sulfonamino)-1-naphthol.
4	1-Hydroxy-N-[2-methoxy-5-(3,5-dicarboxyphenyl)-carbamylphenyl]-2-naphthamide.
5	1-Hydroxy-2-cetylnaphthamide.
6	1-Hydroxy-4'-(2,4-di-tert-amylphenoxy)-2-naphthanilide.
7	5-Methyl-2-(3,5-disulfobenzamido)phenol barium salt.
8	2-(2,4-Di-tert-amylphenoxy)-acetamino-4,6-dichloro-5-methylphenol.
9	1-[p-(p'-Tert-butylphenoxy)-phenyl]-3-[α-(p-tert-butylphenoxy)propionylamino]-5-pyrazolone.
10	1-(2',4',6'-Trichlorophenyl)-3-[3''-(2''',4'''-di-tert-amylphenoxyacetamido)-benzamido]-5-pyrazolone.
11	1-Phenyl-3-(m-nitrobenzoylamino)-5-pyrazolone.
12	1-Phenyl-3-(3,5-disulfobenzamido)-5-pyrazolone dipotassium salt.
13	1-(3,5-Dicarboxyphenyl)-3-amino-5-pyrazolone.
14	3-Methyl-1-phenyl-5-pyrazolone.
15	3-Hexadecyl-1-phenyl-5-pyrazolone.
16	2-Cyanoacetylcoumarone.
17	N-(p-Benzoylacetaminobenzenesulphonyl)-N-(γ-phenylpropyl)-p-toluidine.
18	α-{3-[α-(2,4-Di-tert-amylphenyoxy)acetamido²benzoyl}-2-methoxyacetanilide.
19	4-(p-Toluenesulfonamino)-ω-benzoylacetanilide.
20	2-Methoxybenzoylacetanilide.
21	Benzoylacetanilide.

Some of the couplers which are useful in our invention are of the diffusing type while others are of the nondiffusing type. For example, cyan-forming couplers **1**, **2**, **3**, **4**, and **7** illustrate the diffusing type while couplers **5**, **6**, and **8** illustrate the nondiffusing type cyan couplers. Couplers **19**, **20**, and **21** illustrate the diffusing yellow type coupler while coupler **18** represents the nondiffusing type. Couplers **11**, **12**, **13**, **14**, and **16** illustrate diffusing type magenta couplers and couplers **9**, **10**, and **15** illustrate nondiffusing couplers.

Most of the couplers of our invention have been described earlier in the prior art. The p-toluene sulfonate salt of coupler **2** is described in Whitmore et al. U.S. 2,940,849. Coupler **3** is described in Vittum et al. U.S. 2,362,598. Coupler **5** was prepared by condensing α-hydroxynaphthoic acid chloride with hexadecylamine. Coupler **6** was prepared as described in column 6, lines 47 through 53, of Glass et al. U.S. 2,521,908. Coupler **7** is the barium salt of the parent of Coupler XIX of Whitmore et al. U.S. Serial No. 734,141, filed May 9, 1958, now abandoned. Coupler **8** was prepared as described in columns 3 and 4 of Graham U.S. 2,725,291. Coupler **9** is described as Example 47 in Porter et al. U.S. 2,369,489. Coupler **10** is described as coupler **7** in Loria et al. U.S. 2,600,788. Coupler **11** is described as coupler **17** in Porter et al. U.S. 2,369,489. Coupler **12** is described in Whitmore et al. U.S. Serial No. 734,141, filed May 9, 1958. Coupler **14** is the parent coupler of coupler (**2**) described in column 4 of Jelley et al. U.S. 2,434,272. Coupler **15** was prepared in a manner similar to that used for coupler **14**. Coupler **16** is the parent coupler for coupler (**4**) in column 2 of Jelley et al. U.S. 2,434,272. Coupler **17** is described as coupler **47** in Weissberger U.S. 2,298,443. Coupler **18** is described as coupler IV in McCrossen et al. U.S. 2,875,057. Coupler **19** is described in Vittum et al. U.S. 2,71,238. Coupler **20** is described as coupler **1** in Weissberger U.S. 2,407,210.

Coupler, **1**, 1 - hydroxy - N-(2-N-methylpyridinium)-2-naphthamide p-toluenesulfonate, has the structure:



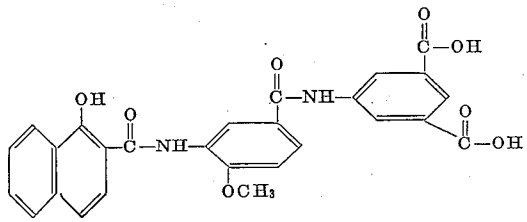
and was prepared as follows.

A mixture of 9.4 g. of 2-aminopyridine, and 26.4 g. of phenyl 1-hydroxy-2-naphthoate was dissolved in 100 ml. of ethanol. The mixture was placed in an oil bath and the ethanol distilled off. After the ethanol had distilled off, the temperature of the oil bath was slowly raised to 180° C. then dropped to 160° C. The phenol which formed was distilled off using an aspirator. The yellow residue was cooled and recrystallized from methanol containing a small amount of water. This material was recrystallized from ethanol containing a small amount of water to give 15 g. of 1-hydroxy-N-(2-pyridyl)-2-naphthamide having a melting point of 129–130° C.

Five g. of 1-hydroxy-N-(2-pyridyl)-2-naphthamide was dissolved in a solution of 50 ml. dry dioxane and 20 ml. of methyl p-toluenesulfonate. The mixture was heated overnight on a steam bath. A portion of the reaction mixture was washed with petroleum ether, ether, and then methanol. The product solidified. Some of these crystals was added to the main batch of the reaction mixture causing the product, coupler **1**, to crystallize out. It was filtered off, washed with ether, recrystallized from absolute ethanol, washed with ether and dried. It had a melting point of 178–179.5° C.

Analysis for	C	H	N	S
Calculated	63.9	4.9	6.2	7.1
Found	63.7	4.8	7.2	6.1

Coupler 4, 1 - hydroxy - N - [2 - methoxy - 5 - (3,5-dicarboxyphenyl]-2-napththamide, has structure:

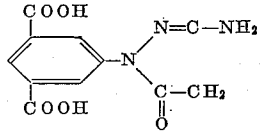


and was prepared as follows.

A mixture of 39.4 g. of 3-nitroanisic acid, 120 ml. of thionyl chloride, and a couple of drops of pyridine was heated to reflux. When the reaction was complete, the excess thionyl chloride was removed with an aspirator. The residue was washed with 30 ml. of benzene and then added to a mixture of 41.8 g. of dimethyl 5-aminoisophthalate, 350 ml. of dry acetonitrile, and 24.2 g. of N,N-dimethylaniline. The mixture was refluxed for 30 minutes and then allowed to stand overnight. The solid 2-nitro-4-[(3,5 - dicarbomethoxy) - phenylcarbamyl]anisole was filtered and dried. Ten g. of this compound was reduced in 400 ml. of glacial acetic acid over Raney nicked at a pressure of 35 p.s.i. of hydrogen. The reduction was started at the boiling temperature of glacial acetic acid and no further heat was applied during the reaction. The total up-take of hydrogen was 6 p.s.i. The catalyst was filtered off and the filtrate was concentrated to a volume of about 50 ml. under reduced pressure. The solution was drowned out in water, cooled, filtered, and then the 2 - amino - 4 - [(3,5 - dicarbomethoxy)phenylcarbamyl]anisole was dried.

A mixture of 5 g. of this compound and 3.7 g. of phenyl 1-hydroxy-2-naphthoate was ground up in a mortar, then heated in an oil bath at 180° C. for one hour at aspirator pressure. Phenol distilled off as it was formed. The brown colored melt solidified. The mixture was cooled, the solid broken up, and slurried with 50 ml. of refluxing ethanol. The gray solid 1-hydroxy-N - [2 - methoxy - 5 - (3,5 - dicarbomethoxyphenyl)-carbamylphenyl]-2-naphthamide was filtered and dried. This compound (6.7 g.) was taken up in a mixture of 50 ml. absolute ethanol and 20 ml. of 2.5 N sodium hydroxide. This solution was boiled for 30 minutes, treated with Norite decolorizing charcoal and filtered. The filtrate, from which a solid tended to separate, was acidified with concentrated HCl. The solid was filtered, washed well with ethanol and dried. The product was coupler 4. It decomposed on heating above 200° C. so no melting point could be obtained.

Coupler 13, 1-(3,5-dicarboxyphenyl)-3-amino - 5-pyrazolone, having the structure:



was prepared by the following procedure.

A flask was fitted with a stirrer and a reflux condenser and charged with 62.7 g. of dimethyl 5-aminoisophthalate and 100 ml. of 95% ethanol. A solution of 26.4 g. of sodium hydroxide and 200 ml. of water was added to the stirred suspension. The resultant solution was heated on a steam bath for one hour. The slight amount of insoluble material was separated by filtration and 50 ml. of glacial acetic acid was added to the hot filtrate. The resulting suspension was stirred and heated on a steam bath for 30 minutes to make the product more granular. The hot suspension was filtered and the solid product was pressed down well on the funnel and was washed successively with 50 ml. portions of water, ethanol, and ether. 56.2 g. of 5-aminoisophthalic acid was obtained.

A flask fitted with a stirrer, thermometer, and a dropping funnel was surrounded by a cooling bath. It was charged with 200 ml. of water, 150 ml. of concentrated hydrochloric acid, and 56.2 g. of 5-aminoisophthalic acid. The 5-aminoisophthalic acid seemed to go into solution and reprecipitated as the hydrochloride salt. The resulting suspension was stirred and cooled to 0° to 5° C. A solution of 21 g. of sodium nitrite in 50 ml. of water was added to the reaction mixture until nitrous acid was no longer taken up. The resulting slurry was stirred for an additional hour after completion of the addition. The temperature of the reaction mixture was kept at 0° to 5° C. during the entire diazotization. The diazotization mixture never became homogeneous. The suspension of diazonum salt prepared in this manner was used as follows.

A flask fitted with a stirrer was charged with 180 g. of anhydrous sodium sulfite and 870 ml. of water. This mixture was stirred and cooled to 5° C. At this point a hydrate of the sodium sulfite began to separate out. One hundred g. of ice was added and this was followed by the suspension of diazonium salt prepared above which was added in a single portion. The resulting orange-colored solution was warmed to 60° to 70° C. during a period of 30 minutes and held at this temperature for an additional 30 minutes. The color of the reaction went from orange to yellow. Forty-one ml. of concentrated hydrochloric acid was slowly added. On completion of the addition, the reaction mixture was warmed to 90° to 95° C. and held at that temperature for two hours. The mixture was cooled to 50° C., an additional 300 ml. of concentrated hydrochloric acid was added, and the mixture allowed to cool to room temperature and stand overnight. The solid which had separated was collected by filtration and washed with a 100 ml. portion of the 1:1 mixture of concentrated hydrochloric acid and water, followed by 100 ml. of ethanol and then 100 ml. of ether. The tan-colored solid which was obtained was dried and then dissolved in a solution of 48 g. of sodium hydroxide in 600 ml. of water. The resulting solution was filtered. The filtrate was warmed to 70° C. and acidified with 100 ml. of glacial acetic acid. The hot suspension was filtered and the tan-colored product was pressed down well on the funnel. It was washed successively with 200 ml. of water, 100 ml. of ethanol, and 100 ml. of water. 37.6 g. of 5-hydrazinoisophthalic acid was obtained.

A flask was charged with a solution of 37.6 g. of 5-hydrazinoisophthalic acid in 380 ml. of 1 N aqueous sodium hydroxide. This solution was cooled to 10° C. and a solution of 33.5 g. of ethyl β-ethoxy-β-iminopropionate in 380 ml. of ethanol which had also been cooled to 10° C. was added in a single portion. The resulting mixture was stirred until it was homogeneous and was then held at 5° C. for two days. The solid which had separated was collected by filtration and washed on the funnel with a 100 ml. portion of a 1:1 mixture of ethanol and water followed by 100 ml. of ethanol and then 100 ml. of ether. This material was recrystallized from a mixture of 400 ml. of 95% ethanol and 300 ml. of water. The resulting solid was collected by filtration and dissolved in 300 ml. of water. This solution was warmed to 50° C. and 60 ml. of glacial acetic acid was added. The resulting suspension was warmed on the steam bath for 15 minutes and the solid was collected by filtration. The product, coupler 13, was washed on the funnel successively with 100 ml. portions of water, 95% ethanol, and ether. 28.5 g. of material which did not melt below 310° C. was obtained.

The coupler particles used in the electroscopic dispersions have a particle size in the range of from 1 to 200 microns in diameter. The coarser size particles being satisfactory for reproductions of line drawings and the 1 micron size particles used for producing images have a very high resolving power and a high grade of tone quality. For the liquid development process the colorless,

color-forming couplers are dispersed in a liquid carrier with a ball mill, a Waring Blendor mixer, or ultrasonic equipment designed for making very fine dispersions.

The liquid carrier used in making these dispersions must not dissolve the coupler when liquid immersion development is employed. In order that the coupler particles dispersed in the liquid carrier be allowed to achieve and retain the necessary electrical charge and in order that the dispersion not destroy the charge on the photoconductive plate, the liquid carrier must be an insulating material with a high electrical resistivity. The carrier should have a low dielectric constant. Compounds that are used advantageously as liquid carriers for our process include compounds such as the paraffin hydrocarbons which are cyclic and acyclic and do not dissolve the couplers. Typical examples illustrating these are cyclohexane, n-pentane, isooctane, hexane, etc. Other compounds which are useful include halogenated compounds such as the chlorofluoromethanes and the corresponding ethanes. Particularly useful examples of these are trichlorotrifluoroethane sold under the trade name "Freon 113," tetrachlorodifluoroethane sold under the trade name of "Freon 112," etc. Various mixtures of these compounds can be used to advantage as liquid carriers. All the carrier liquids used have a viscosity in the range of 0.1 to 10 centipoises. The preferred carriers have a viscosity of about 1 centipoise.

The liquid used in making aerosols must be compatible with the coupler, but no harm is done if the coupler is soluble in the liquid. The liquid should have high electrical resistivity but its dielectric constant is not important. Thus a large range of organic liquids, not useable in the liquid immersion development, are suitable for making aerosols.

In liquid immersion development electrical charge control agents are advantageously added to certain of our coupler dispersions in a liquid carrier which have a tendency to form coupler and dye images of nonuniform or inadequate density. Addition of a charge control agent to such dispersions results in the formation of greatly improved to excellent image reproductions of the original image. Electrical charge control agents we have found particularly valuable are the liquid carrier soluble metal soaps sometimes called the curd soaps. Included in this class of soaps are the cobalt, manganese, lead, aluminum, calcium, chromium, copper, and zinc salts of naphthenic acids, and the aluminum, antimony, barium, bismuth, calcium, chromium, cobalt, copper, iron, lead, magnesium, strontium, tin and zinc salts of palmitic, stearic, and oleic acids.

Oxidizing agents are used in our process to oxidize primary aromatic amines which in turn react with the colorless, color-forming images to create the colored dye images. The oxidizing agent may be dispersed with the coupler in the liquid carrier so that it is deposited with the coupler on the electrostatic image and treatment of this colorless image with a solution of a primary aromatic amine will convert it into a dye image. Instead of adding the oxidizing agent to the dispersion it may be incorporated in the receiving sheet to which the coupler image is transferred so that treatment with the primary aromatic amine solution will produce the dye image, or the oxidizing agent need not be incorporated in either the image or receiving sheet but applied to the coupler-image-bearing layer as a solution just before or after treatment of the image with the primary aromatic amine solution.

The oxidizing agents used in the invention must have sufficient oxidizing potential to oxidize the primary aromatic amine used and must not form a colored reduction product. In addition to this oxidizing agents that are to be dispersed with the coupler in the liquid carrier must be insoluble in the liquid carrier. Among the suitable inorganic oxidizing agents used are potassium persulfate, sodium persulfate, potassium percholate, sodium percholate, potassium periodate, sodium periodate, potassium ferricyanide, sodium ferricyanide, etc., and organic oxidizing agents such as certain quinones which are insoluble in the liquid carrier, etc.

Any prior art primary aromatic amines used in photographic color developers can be used to color develop our coupler images. Included among these are the p-phenylene diamines, the p-aminophenols having at least one primary amino group, 2-amino-5-diethylaminotoluene, N - ethyl - N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate or sesquisulfate monohydrate, N-ethyl - N - β-methanesulfonamidoethyl-4-aminoaniline, 4 - (N-ethyl-N-β-hydroxyethyl)aminoanline, 4-amino-N, N-diethylaniline, etc. Concentrations of 0.1 to 10 g./l. are used.

Dyes formed from some of the couplers are somewhat water-soluble and therefore do not adhere to the hydrophobic resin binder surface of the photoconductive layer very well. Better adhesion of these dyes formed can be accomplished in one or more of the following ways: If the photoconductor is a dispersion of zinc oxide in a resinous binder, its surface may be treated to make it water receptive; by using a binder which would act as a mordant; by incorporating a tacky binder in the dispersion a little of which would be carried to the surface by the coupler; by dispersing gelatin or polyvinyl acetate particles impregnated with a coupler into a carrier liquid; or coating the coupler-image-bearing surface with gelatin prior to color development. To decrease or eliminate scattering, it is desirable to so constitute the coupler dispersions that the index of refraction of the deposited material is the same as the index of refraction of the photoconductive layer on which it is deposited.

We have found it advantageous to transfer the colorless coupler images from the photoconductive surface onto a receiving sheet before converting the coupler image into the corresponding colored dye image. Receiving sheets that are most advantageously used for receiving the diffusing type coupler compounds are coated with a gelatin layer whereas the receiving sheets used to receive non-diffusing type coupler images are coated with a dispersion of a coupler solvent in gelatin or in any of the materials commonly used as a gelatin substitute. Any of the prior art coupler solvents may be used. Among those which we have found useful are the coupler solvents of Jelley et al. U.S. 2,322,027. Examples of these are solvents such as p-sec. amylbenzoic acid, n-hexylphenylcarbinol, acetyl n-butyl aniline, N-n-amylphthalimide, ethyl N,N-di-n-butyl carbamate, tetrahydrofurfuryl benzoate, benzophenone, hydroquinone dimethyl ether, tricrysyl phosphate, etc.

The following examples will illustrate in greater detail the use of our process but are not to be considered as limiting our invention.

Example 1

An electrostatic latent image of negative polarity was obtained on a zinc oxide xerographic coating by standard methods. This coating was then treated with a dispersion of a few milligrams of coupler 5 with 50 ml. of cyclohexane prepared in a Waring Blendor mixer. This dispersion containing charged coupler particles suspended in an insulating liquid was roller applicated onto the electrostatic latent image on the photoconductive surface. The coupler particles suspended in the liquid carrier were repelled to and deposited on the electrostatic latent image bearing surface at charged areas or at charge discontinuities. The coupler image was then converted to a dye image by immersing it first in a solution of the color developer N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate, and then in a solution of potassium persulfate. A cyan dye image was formed.

Example 2

Another sample of the coupler image formed in Example 1 was transferred to a moistened gelatin layer containing a dispersion of tri-o-cresyl phosphate coated

on a receiving paper by squeezing its gelatin surface onto the coupler image, then separating the receiving layer bearing the coupler image and treating it with the color developer solution and oxidizing solution used in Example 1. A cyan dye image resulted.

Example 3

Similarly, images were made using couplers **6** and **8** and converted into the corresponding cyan dye images according to the methods used in Examples 1 and 2. In each case solid area dye deposits were obtained.

Example 4

The processes of Examples 1 and 2 were repeated using coupler **9** to produce good solid area magneta dye images on the photoconductive surface and on the receving sheet, respectively.

Example 5

The process of Example 1 was repeated using colorless magenta-forming coupler **12** to produce a good solid area magenta image having a good dye deposit.

Example 6

Another sample of the magneta-forming coupler image made using coupler **12** by the method of Example 5 was transferred to a separate moistened gelatin coated receiving sheet then treated with a color developer solution, followed by the oxidizing solution of Example 1. A good solid area magneta dye image was obtained having a good magenta dye deposit.

Example 7

The process of Example 1 was repeated using coupler **18** which gave a very sharp, clear image with a good solid area yellow dye deposit.

Another sample of the coupler image was transferred to a moistened gelatin layer containing incorporated di-n-butyl phthalate coated on a sheet of paper then processed as in Example 2 to give a yellow dye image having the same desirable characteristics as was obtained above.

Example 8

Coupler **20** was used in the process described in Example 1 to produce excellent solid area heavy yellow dye images.

Another sample of the coupler image was transferred to a moistened gelatin coated receiving sheet and subsequently converted into the corresponding dye image by treating with the primary aromatic amine solution and oxidizing solution used in Example 1.

Example 9

The magenta dye image was created using coupler **14** and the process of Example 1. The resulting dye image showed heavier densities about the edge of the image with a nonuniform dye density in the inner portions of the image areas.

This process was repeated using a dispersion of coupler **14** in cyclohexane to which had been added cobalt naphthenate. The dye image resulting on this sample had a good solid area devolpment with a good uniform dye deposit.

Similarly, greatly improved images were obtained by adding cobalt naphthenate to dispersions containing cyan-forming couplers **1**, **2**, **3**, **4**, and **7**; magenta-forming couplers **10**, **11**, and **16**; and yellow-forming couplers **17** and **19**. These particular couplers were found to produce the edge type of image development shown by coupler **14** when no charge control agent was used in their respective dispersions.

The following examples will illustrate how two-color images were formed using the process of our invention.

Example 10

A piece of zinc oxide coated paper was charged and exposed in a stepwise manner and developed with a xerographic developer containing magenta-forming coupler **14**, potassium persulfate, and the charge control agent cobalt naphthenate, all dispersed in cyclohexane. The sample was then recharged, exposed in a stepwise manner to a pattern (the steps of which ran perpendicular to those of the first original image) and developed with a similar xerographic developer containing yellow-forming coupler **21** and potassium persulfate in cyclohexane. One coupler image was thus deposited on top of the other coupler image. The combination was transferred by squeegeeing a damp gelatin coated receiving paper into contact with the image. The composite image removed on the receiving sheet was then developed with a color-forming developer solution of N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate, rinsed and blotted.

The resulting print showed in areas of overlap an image having the color resulting from the two dyes.

Example 11

Two-color prints were obtained by the process of Example 10 in which coupler **13** and then coupler **16** were substituted for coupler **14**. No charge control agent was used or needed in the dispersion containing coupler **13**.

The following example illustrates how our process was used to prepare a three-color positive image of a three-color positive transparency.

Example 12

A three-color print was prepared using a positive three-color transparency as the original. An 8 by 10 sheet of panchromatically sensitized zinc oxide-resin xerographic paper was charged by bringing it close to a corona wire at 9,000 volts negative potential and exposed to a projected image of the transparency through a green filter. The resulting green separation exposure was developed with a xerographic developer containing the magenta-dye-forming coupler **14** (3-methyl-1-phenyl-5-pyrazolone), an oxidizing agent, e.g., potassium persulfate and cobalt naphthenate as a control agent, which has the property of influencing the coupler to deposit more uniformly in large image areas.

Maintaining print register, the sample was recharged and exposed through a red separation filter, and the resulting red separation exposure was developed with a xerographic developer containing the cyan-dye-forming coupler **3** (2,4-dichloro-5-(p-toluenesulfonamido)-1-naphthol), the oxidizer, and the control agent. This step was repeated using a blue filter to obtain a blue separation exposure which was developed with a similar developer containing the yellow-dye-forming coupler **21** (benzoyl-acetanilide) and oxidizer.

The combination of coupler images was transferred by squeegeeing a damp gelatin coated paper receiver into contact with the image. The receiver bearing the composite coupler image was then developed with a color-forming developer solution containing 2-amino-5-diethylaminotoluene hydrochloride developing agent.

The accompanying drawings, FIGS. 1, 2, 3, and 4, showing greatly enlarged cross-sectional views of an original multicolor transparency, an electrophotographic element, and a multicolor print, will serve to further explain the use of our process in Example 12 to produce a positive multicolored print of a multicolor transparency.

FIG. 1 shows the projection printing of a colored transparency **11** having red (R), green (G), blue (B), yellow (Y), white (W), and black (Bl) tablets with green light onto the charged photoconductive surface **13** to produce the electrostatic latent image **12** of the red, blue, and black tablets.

FIG. 2 shows the projection printing of the red light component of the transparency **11** upon the charged photoconductive surface layer **13** bearing the colorless, magenta-forming image **16** that was formed by treating the electrostatic latent image **12** produced in FIG. 1 with a dispersion of coupler **14** in cyclohexane with an oxidiz-

ing agent and charge control agent, to produce the electrostatic latent images **15** of the green, blue, and black tablets.

FIG. 3 shows the projection printing of the blue light component of the transparency **11** upon the charged photoconductive surface layer **13** to produce electrostatic latent images **18** of the red, green, yellow, and black tablets (of transparency **11**) on top of colorless, color-forming images **16** and **17**.

FIG. 4 shows an enlarged cross-sectional view of the multicolor positive print comprising the composite of the yellow, magenta, and cyan dye images produced in the gelatin layer **19** of the receiving sheet produced by color developing the composite colorless, color-forming images that were transferred from the photoconductive surface of FIG. 3 after the blue separation electrostatic latent image was converted to a colorless, yellow-forming coupler image by contacting it with a dispersion of coupler **21** in cyclohexane with an oxidizing agent.

The novel color electrophotographic process of our invention provides a valuable method for making color prints by a simple nonsilver process without undue contrast and saturation problems. The process is characterized by using colorless, color-forming electroscopic materials as xerographic developers for converting the electrostatic latent image formed on an image exposed photoconductive surface to a colorless, color-forming image which is subsequently converted into the corresponding colored dye image. The use of a colorless electroscopic material is very advantageous over the use of the conventional prior art highly colored electroscopic materials used to make color prints by electrophotographic methods. The primary advantage from the use of colorless electroscopic materials is in the making of multicolored prints where the colorless electroscopic materials make it possible to form a colorless image corresponding to one color component of the color original and then expose the light-sensitive surface to the second component of the color original without having the unwanted color absorption and decreased light intensity that would be created by conventional colored electroscopic materials. The advantage is even greater in exposing for the third color component of the color original since it is no longer necessary to expose through two colored images as would be necessary in the piror art method. These advantages make possible much more accurate reproduction of colors than was possible with the prior art process. In addition to these advantages, colorless electroscopic materials are very advantageous over the conventional highly colored electroscopic material which created staining problems on operator's person and clothing as well as on the room where the processing equipment was located whenever leakage or spillage of the prior art electroscopic material occurred.

The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. An electrophotographic process for producing a color print on the hydrophobic surface of a photoconductive layer comprising the steps of giving the photoconductive layer a uniform charge, exposing the said charged photoconductive layer to the blue light component of a multicolor picture to produce a corresponding electrostatic latent image on the photoconductive layer, depositing a charged electroscopic colorless, yellow-dye-forming coupler on the electrostatic image bearing photoconductive layer, recharging the photoconductive layer exposing the said charged photoconductive layer to the green light portion of the said multicolor picture to produce a corresponding electrostatic latent image on the photoconductive layer which bears the said colorless, yellow-dye-forming image, depositing a charged electroscopic colorless, magneta-dye-forming coupler on the electrostatic latent image bearing photoconductive surface to produce the corresponding colorless, magenta-dye-forming image over the said colorless, yellow-dye-forming image, recharging the photoconductive layer, exposing it to the red light portion of said multicolor picture to produce the corresponding electrostatic latent image on the photoconductive layer which bears the said colorless, yellow- and magenta-dye-forming images, depositing on the electrostatic latent image bearing photoconductive layer a charged electroscopic colorless, cyan-dye-forming coupler, treating the said photoconductive layer bearing the three colorless, color-forming coupler images with a solution of a primary aromatic amine color developing agent in the presence of an oxidizing agent to produce the color print comprising the yellow, magenta, and cyan dye images in register.

2. An electrophotographic process for producing a color print on the hydrophobic surface of a photoconductive layer comprising the steps of giving the photoconductive layer a uniform charge, exposing the said charged photoconductive layer to the blue light component of a multicolor picture to produce a corresponding electrostatic latent image on the photoconductive layer, depositing a charged electroscopic disperson of a colorless, yellow-dye-forming coupler in an organic liquid carrier having a high electrical resistivity to produce the corresponding colorless, yellow-dye-forming coupler image, recharging the photoconductive layer, exposing the said charged photoconductive layer to the green light portion of the said multicolor picture to produce a corresponding electrostatic latent image on the photoconducting layer in register with the said colorless, yellow-dye-forming coupler image it bears, depositing a charged electroscopic dispersion of a colorless, magenta-dye-forming coupler in an organic liquid carrier having a high electrical resistivity to produce the corresponding colorless, magenta-dye-forming coupler image over said colorless, yellow-dye-forming coupler image, recharging the photoconductive layer, exposing it to the red light portion of said multi-color picture to produce a corresponding electrostatic latent image on the photoconducting layer in register with the yellow-forming and magenta-forming images, depositing a charged electroscopic dispersion of a colorless, cyan-dye-forming coupler in an organic liquid carrier having a high electrical resistivity, to produce the corresponding colorless, cyan-dye-forming image over the said colorless, yellow- and magenta-dye-forming coupler images, transferring the three colorless, color-forming coupler images from the photoconductive layer to the moistened surface of a receiving sheet and subsequently treating the said receiving sheet with a solution of a primary aromatic amine color developing agent in the presence of an oxidizing agent to produce a color print comprising the registered yellow, magenta and cyan dye images.

3. An electrophotographic process for producing a color print on the hydrophobic surface of a photoconductive layer comprising the steps of giving the zinc oxide-resin photoconductive layer of an electrophotographic element a uniform charge, exposing the said charged photoconductive layer to the green light component of a multicolor picture to produce a corresponding electrostatic latent image on the photoconducting layer, depositing on the said electrostatic latent image a charged electroscopic dispersion of colorless, magenta-dye-forming coupler 3-methyl-1-phenyl-5-pyrazolone, an oxidizing agent and a control agent in an organic liquid carrier having a high electrical resistivity to produce the corresponding colorless, magenta-forming image, recharging the photoconductive layer, exposing it to the red light component of the said multicolor picture to produce in register with the said magenta-forming image an electrostatic latent image, depositing on said electrostatic latent image a charged electroscopic dispersion of colorless, cyan-dye-

former 2,4 - dichloro - 5-(p-toluenesulfonamido) - 1-naphthol, an oxidizing agent and a control agent in an organic liquid carrier having a high electrical resistivity to produce the corresponding cyan-forming image over the said magenta-forming image, recharging the photoconductive layer, exposing it to the blue-light component of the said multicolor picture to produce in register with the said magenta-forming and cyan-forming images an electrostatic latent image, depositing on said electrostatic latent image a charged electroscopic dispersion of colorless, yellow-forming coupler benzoylacetanilide and an oxidizing agent in an organic liquid carrier having a high electrical resistivity to produce the corresponding yellow-forming image over the said cyan-forming and magenta-forming images, transferring the said three colorless, color-forming images from the photoconductive layer to the moistened surface of a receiving sheet and subsequently treating said images on receiving sheet with a solution of a primary aromatic amine color developing agent to produce the color print comprising the registered magenta, cyan, and yellow dye images.

4. The process of claim 3 in which the photoconductive layer comprises a dispersion of zinc oxide in a resinous binder selected from the class consisting of polystyrene, polyvinyl acetate, polyvinyl chloride, silicone resins, cellulose esters, cellulose ethers, and acrylic resins.

5. An electrophotographic process for making a color print on the hydrophobic surface of a photoconductive layer comprising the steps of negatively charging a zinc oxide photoconductive layer, exposing said charged photoconductive layer to the green light component of a multicolor picture to create the corresponding electrostatic latent image, depositing on said electrostatic latent image bearing photoconductive layer, a charged electroscopic dispersion of colorless, magenta-forming coupler 3-methyl-1-phenyl-5-pyrazolone, $K_2S_2O_8$, and a charge control agent in cyclohexane to produce the corresponding magenta-forming image, recharging the said photoconductive layer negatively, exposing it to the blue light component of the said multicolor picture to create the corresponding electrostatic latent image on the photoconductive layer in register with the magenta-forming image, depositing on said electrostatic latent image bearing photoconductive surface a charged electroscopic dispersion of colorless, yellow-forming coupler benzoylacetanilide and $K_2S_2O_8$ in cyclohexane, to produce a yellow-forming image over the magenta-forming image, transferring the resulting colorless images from the photoconductive layer to a damp gelatin coated paper by squeegeeing said damp gelatin coating against the photoconductive layer, separating from the photoconductive layer the gelatin coated paper bearing the colorless magenta-forming and yellow-forming images and treating the said images on the gelatin coated paper with a primary aromatic amine color developing agent solution to form a magenta and yellow reproduction of the said multicolor picture.

6. An electrophotographic process for producing a color print on the hydrophobic surface of a photoconductive layer comprising the steps of giving the photoconductive layer a uniform charge, exposing the said charged photoconductive layer to a first primary color component of a multicolor picture to produce a corresponding electrostatic latent image on the photoconductive layer, depositing charged electroscopic colorless dye-forming coupler capable of forming the color complementary to said first primary color component to produce the corresponding colorless image, recharging the photoconductive layer, re-exposing the charged photoconductive layer to a second primary color component of the said multicolor picture in register with the first exposure, depositing charged electroscopic colorless dye-forming coupler capable of forming the color complementary to said second primary color component to produce the corresponding colorless image, recharging the photoconductive layer, re-exposing the charged photoconductive layer to a third primary color component of the said multicolor picture to produce a corresponding electrostatic latent image in register with the first and second colorless images on the photoconductive layer, depositing charged electrostatic colorless dye-forming coupler capable of forming the color complementary to said third primary color component and subsequently treating the three composite colorless images with a primary aromatic amine color developing agent in the presence of an oxidizing agent.

7. An electrophotographic process for producing from a multicolor original a two color print on the hydrophobic surface of a photoconductive layer comprising the steps of:

(1) giving the photoconductive layer a uniform charge,
(2) exposing the said charged photoconductive layer to one color separation image of said multicolor original to produce a corresponding electrostatic latent image on the said photoconductive layer,
(3) depositing a charged colorless, first color-forming coupler compound on the said electrostatic latent image to create a corresponding colorless, first color-forming coupler image,
(4) giving the said photoconductive layer with its colorless, first-color forming coupler image a uniform charge,
(5) exposing said charged photoconductive layer with its colorless, first color-forming coupler image to a second color separation image of said multicolor original to produce a corresponding electrostatic latent image on the said photoconductive layer,
(6) depositing a charged colorless, second color-forming coupler on the said electrostatic latent image produced in step (5) to create a corresponding colorless, second color-forming coupler image, and
(7) treating the two colorless, color-forming coupler images with a solution of an oxidized primary aromatic amine color developing agent which is capable of reacting with said coupler images to form two corresponding dye images forming the two color print.

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NORMAN G. TORCHIN, *Primary Examiner.*

PHILIP E. MANGAN, *Examiner.*

G. H. BJORGE, A. LIBERMAN, *Assistant Examiners.*