

[54] **COLOR ELECTROPHOTOGRAPHIC IMAGING PROCESS UTILIZING SPECIFIC CARRIER-TONER COMBINATIONS**

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[*] Notice: The portion of the term of this
patent subsequent to Apr. 16, 1991,
has been disclaimed.

[22] Filed: **Dec. 17, 1973**

[21] Appl. No.: **425,481**

[52] U.S. Cl. **96/1.2**; 96/1 SD; 117/17.5;
252/62.1 P

[51] Int. Cl.² **G03G 13/01**

[58] Field of Search 96/1.2, 1 SD; 117/17.5;
252/62.1 P

[56]

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[57]

ABSTRACT

A color electrophotographic imaging process is disclosed employing uniquely distinct developer materials. Specific cyan, yellow, and magenta developers which uniquely cooperate to form true color images in an electrophotographic process are described. The electrophotographic processes employing these developers are also disclosed.

8 Claims, No Drawings

COLOR ELECTROPHOTOGRAPHIC IMAGING PROCESS UTILIZING SPECIFIC CARRIER-TONER COMBINATIONS

BACKGROUND OF THE INVENTION

This invention relates to color electrophotography and more specifically concerns specific developers employed in a color electrophotographic process.

Color electrophotography with multiple development techniques is capable of producing color reproductions employing multiple sequencing of electrophotographic charging, exposing, and developing steps with color toners. A suitable photoconductor such as substantially panchromatic zinc oxide photoconductive paper, electrofax paper, for example, is electrostatically charged uniformly in the dark then exposed through a green filter to an imagewise projection of a color image to form an electrostatic latent image on the photoconductor. The electrostatic latent image is then developed with the complementary magenta colored toner to form a magenta-colored image corresponding to said electrostatic latent image and transferred in register to an image receiving member. A zinc oxide photoconductive paper is then again electrostatically charged uniformly in the dark and then exposed through a red filter to an imagewise projection of a color image in register with said magenta developed image to form a second electrostatic latent image which second image is developed with the complementary cyan-colored toner and likewise transferred in register. Similarly, zinc oxide photoconductive paper is again electrostatically uniformly charged in the dark and then exposed through a blue filter to an imagewise projection of a color image in register with said magenta and cyan-developed images to form a third electrostatic latent image which is then developed with the complementary yellow toner and again transferred in register.

This conventional electrophotographic process with superimposed development to obtain images of cyan, magenta, and yellow, respectively, is capable of producing multicolor images by employing toners of different colors. The sequence of exposures through color filters in this multiple development process may be performed in any suitable sequence other than the green, red, and blue sequence recited above. In any event, after the desired number of exposures and developments and transfers in register, the finished image is itself fused to provide a permanent reproduction of the original.

Each developer employed comprises ordinarily a toner or a resin colorant mixture in combination with a carrier. It is a function of the toner carrier combination or developer package in a given development system, for example cascade, to assume a triboelectric relationship such that the toner will be carried with the carrier during the development cycle by electrostatic attraction and then selectively deposited chargewise on the electrostatic latent image which has a greater affinity for the toner electrostatically than does the carrier particle. In addition to the very significant triboelectric properties that a developer must possess and maintain during the development cycle, the toner must possess the appropriate color and continue to function under machine conditions which expose the developer to impaction and humidity among other undesirable factors. It is, therefore, critical that a specific toner which com-

prises a colorant and a resin be combined with a specific carrier of the appropriate size relation to the toner particle so that the appropriate color is exhibited and the appropriate triboelectric relationship is maintained to achieve successful development. Under continuous electrophotographic imaging, it has been found that with regard to one developer package great difficulty is realized in maintaining the proper triboelectric relationship so that proper development is achieved. With the advent of a three-color system, the complexities of producing suitable cyan, magenta, and yellow developers which will cooperate in a color electrophotographic continuous imaging process, as above described, are further exaggerated. It is apparent that any one of a number of variables in any one of the developers could cause incomplete, improper, or inadequate developments so that the color balance is thereby shifted resulting in a completely unacceptable color print.

It is, therefore, an object of this invention to provide an electrophotographic color system devoid of the above noted deficiencies.

It is a further object of this invention to provide a unique combination of developer materials which surprisingly produce sharp true reproductions in the color electrophotographic imaging process.

Still another object of this invention is to provide a novel magenta developer for use in a color electrophotographic imaging process.

Yet another object of this invention is to provide a novel color electrophotographic imaging process.

Yet again another object of this invention is to provide a trichromatic electrophotographic imaging process of the registration type.

These and other objects of the instant invention are obtained generally speaking by providing a three-developer package including a magenta toner which may be a 2,9-dimethyl substituted quinacridone toner, an anthraquinone dye identified in the Colour Index as CI60710, CI Disperse Red 15, or a diazo dye identified in the Colour Index as CI26050, CI Solvent Red 19, each combined with a nickel berry carrier; a cyan toner which may be a copper tetra-4-(octadecylsulfonamido) phthalocyanine, an X-copper phthalocyanine pigment listed in the Colour Index as CI74160, CI Pigment Blue 15, or an indanthrene blue identified in the Colour Index as CI69810, Special Blue X-2137 each combined with a methyl terpolymer coated steel shot carrier; and a yellow toner which may be a diarylide yellow 3,3-dichlorobenzidine aceto-acetanilide, a monoazo dye identified in the Colour Index as CI12700, CI Solvent Yellow 16, or a nitrophenylaminesulfonamide identified in the Colour Index as Foron Yellow SE-GLF, CI Disperse Yellow 33 each combined with a methyl terpolymer coated steel shot carrier.

In conventional electrophotographic imaging processes, commonly referred to as xerographic imaging processes or xerography, there are numerous known carrier materials from which to select in providing a developer, i.e., a toner and a carrier combination. However, in color electrophotographic imaging the selection of appropriate carrier material is not just a matter of choice. For example, steel shot may be employed with the cyan and yellow toner materials disclosed above; however, steel shot is found to be inoperable with the magenta toner therefore necessitating the discovery of an appropriate carrier, namely nickel berry, to perform this function. Further, the selection of a

toner material of the appropriate color and triboelectric properties is in itself far more than a matter of choice. A colorant and resin combination must be selected such that the color, of course, is the appropriate hue, but more significantly that the toner possesses the appropriate triboelectric properties which will enable it to function in an electrophotographic automatic imaging mode. Few, if any, of these toner materials are known other than those disclosed above. It, therefore, becomes even a more demanding and crucial operation to develop the appropriate combination of toner and carrier so that they will develop and maintain the appropriate triboelectric relationship further complicated by employing these color developers in combination in an electrophotographic imaging process.

The above mentioned developers perform surprisingly well in combination yielding color-xerographic prints of originals in an automatic imaging mode which are clear and true. When employed in an electrophotographic imaging mode, these three developers, or the developer package as it is termed, proves to have a highly acceptable performance life in an automatic electrophotographic imaging apparatus. There is no degradation of the triboelectric properties of the developers nor unacceptable imaging due to impaction and other problems associated with prior art developers.

The carrier employed with both the cyan and yellow toners is a methyl terpolymer coated steel shot. The steel shot carrier is about 100 microns in diameter as compared to the cyan and yellow toner particle sizes which are about 16 microns. The magenta toner, on the other hand, is combined with a nickel berry carrier having a size of about 100 microns as compared to the magenta toner which has a size of about 16 microns.

The developer package thus provided is usually disposed in three separate developer housings in an automatic color electrophotographic imaging machine. A photoconductive member is then charged, selectively exposed to the light of one of the primary colors and then developed with the developer, i.e., the complement to that primary color. The image thus formed is then transferred to an image receiving member. In two successive operations the process is again repeated to provide images employing the other two primary colors, developing in each case with the complement of the respective primary colors, and then transferring both images in registration to the image receiving member after which the final image is fixed normally by fusing.

The cyan, yellow, and magenta colorants may be combined with any suitable electrophotographic resin. The selected colorant may be combined with any typical resin including: thermoplastics including olefin polymers such as polyethylene and polypropylene; polymers derived from dienes such as polybutadiene, polyisobutylene, and polychloroprene; vinyl and vinylidene polymers such as polystyrene, styrene butylmethacrylate copolymers, styrene-acrylonitrile copolymers, acrylonitrile-butadienestyrene terpolymers, polymethylmethacrylate, polyacrylates, polyvinyl alcohol, polyvinylchloride polyvinylcarbazole, polyvinylethers, and polyvinyl ketones, fluorocarbon polymers such as polytetrafluoroethylene and polyvinylidene fluoride; heterochain thermoplastics such as polyamides, polyester, polyurethanes, polypeptides, casein, polyglycols, polysulfides, and polycarbonates; and cellulosic co-

polymers such as regenerated cellulose, cellulose acetate and cellulose nitrate.

Any suitable inorganic or organic photoconductor may be used in the process of the present invention.

- 5 Typical inorganic photoconductor materials are: sulfur, selenium, zinc sulfide, zinc oxide, zinc cadmium sulfide, zinc magnesium oxide, cadmium selenide, zinc silicate, calcium-strontium sulfide, cadmium sulfide, indium trisulfide, gallium triselenide, arsenic disulfide, arsenic trisulfide, arsenic triselenide, antimony trisulfide, cadmium sulfo-selenide and mixtures thereof. Typical organic photoconductors are: triphenylamine; 2,4-bis (4,4'-diethyl-aminophenyl)-1,3,4-oxadiazol; N-isopropylcarbazole triphenylpyrrol; 4,5-diphenylimidazolidinone; 4,5-diphenylimidazolidinethione; 4,5-bis-(4'-amino-phenyl)-imidazolidinone; 1,5-dicyanonaphthalene 1,4-dicyanonaphthalene; aminophthalodinitrile; nitrophthalodinitrile; 1,2,5,6-tetraaza-N-isopropylcarbazole triphenylpyrrol; 4,5-diphenylimidazolidinone; 4,5-diphenylimidazolidinethione; 4,5-bis-(4'-amino-phenyl)-imidazolidinone; 1,5-dicyanonaphthalene; 1,4-dicyanonaphthalene; aminophthalodinitrile; nitrophthalodinitrile; 1,2,5,6-tetraazacyclooctatetranene (2,4,6,8); 2-mercapto-benzthiazole; 2-phenyl-4-diphenylidene-oxazolone; 6-hydroxy-2,3-di(p-methoxyphenyl)-benzofurane; 4-dimethyl-amino benzylidene-benzhydrazide; 3-benzylidene-amino-carbazole; polyvinyl carbazole; (2-nitrobenzylidene)-p-bromo-aniline; 2,3-diphenyl quinazoline; 1,2,4-triazine; 1,5-diphenyl-3-methyl-pyrazoline; 2-(4'-dimethylaminophenyl)-benzoxazole; 3-amino-carbazole; phthalocyanines; trinitrofluoronone polyvinylcarbazole; charge transfer complexes and mixtures thereof.
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Any suitable method of charging may be employed in the system of the instant invention. Typical charging methods include corona, charge deposition resulting from air breakdown in the gap commonly referred to as TESI or charging in vacuo with an electron gun.

Any suitable method of exposure may be employed in the system of the instant invention. Typical methods of exposure include: reflex, contact, holographic techniques, non-lens slit scanning systems, and optical projection systems involving lens imaging of opaque-reflection subjects as well as transparent film originals.

Any suitable method of development may be employed in the system of the instant invention. Typical development systems include: cascade development, magnetic brush development, powder cloud development, and liquid development.

Any suitable method of fixing may be employed in the process of the instant invention. Typical methods of fixing include: heat-pressure fusing, radiant fusing, combination radiant, conductive and convection fusing, cold pressure fixing, flash fusing, solvent fusing, and combination heat, pressure solvent fusing.

- 55 The developer compositions of the present invention may be prepared by any well-known developer mixing combination technique. Generally speaking, satisfactory results are obtained when about one part toner is used with about 10 to 200 parts by weight of carrier prepared by blending and milling the components and thereafter micropulverizing the resulting mixture. Alternatively, the toner particles may be formed by spray drying, suspension polymerization, hot melt atomizing, or precipitation of a solution of the toner composition.
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When the toner mixture of this invention is employed in the cascade development process, the toner should have an average particle diameter of less than about 30 microns and preferably between about 5 and about 20 microns for optimum results. For use in powder cloud development methods, particle diameters of slightly less than about 5 microns are preferred.

As previously stated, the cyan and yellow toners must be combined with methyl terpolymer coated steel bead carriers while the magenta toner must be combined with the nickel berry carrier in order to provide the highly effective color imaging system of the present invention.

EXAMPLE I

Cyan, magenta, and yellow toners are prepared which are respectively designated as copper tetra-4-(octadecylsulfonamido phthalocyanine pigment available from GAF Corporation under the designation of Heliogen Blue OS, a 2,9-dimethylquinacridone pigment identified in the Colour Index as Pigment Red 122 available from American Hoechst Corporation under the designation Hostaperm Pink E, and 3,3-dichlorobenzindene aceto-acetanilide pigment identified in the Colour Index as Pigment Yellow 12 available from Hercules, Inc., under the designation Amazon Yellow X-2485. Each colorant is dispersed in a 65/35 styrene to n-butylmethacrylate copolymer. Five parts of each colorant are placed in 95 parts of beads of the toner copolymer resin together to form a homogenous mixture. The pigments employed have a particle size essentially less than one micron with occasional agglomerates up to about five microns. The toner copolymeric resin beads that are employed are about one-sixteenth inch in diameter. The mixture is then fed into a twin-screw extruder operating at a temperature of about 150°C. The extruder softens the copolymer resin, disperses the pigment throughout the molten resin, and extrudes the mixture as a strand of about one-fourth inch in diameter. The strand is cooled by immersion in a cold water bath and cut to about ¼ inch length pellets. The pellets are continuously ground in a controlled pressurized air-jet mill to yield toner particles of about 16 microns in size. The cyan and yellow toners produced as above are combined with a steel carrier particle coated with a terpolymer material prepared as disclosed in Example XIII of U.S. Pat. No. 3,526,533. The steel carrier has a particle diameter of about 100 microns. The cyan toner is blended with the carrier to yield a developer containing about 2% toner concentration by weight. The yellow toner is blended with the carrier to yield a developer containing about 3% toner by weight.

The magenta toner is blended with an uncoated nickel berry carrier bead to yield a developer containing about 4% toner concentration by weight. The nickel berry carrier bead employed has a spheroidal shape with a rough pebbly surface and a particle size of about 100 microns and is available from the British Metal Corporation (Canada) Ltd. under the designation Sheritt Nickel Powder, C-Grade. Both the steel and nickel berry carriers employed are magnetic. The developers thus produced are disposed in magnetic brush developer housings which are positioned around a selenium photoconductor. The photoreceptor is charged to a positive potential of +1000 volts and exposed to a color image through a blue filter. The latent

electrostatic charge remaining on the photoreceptor is developed with the yellow developer by engaging the developer housing into development configuration with the photoreceptor. The image on the photoreceptor is transferred to a receiver sheet in register. The photoreceptor is cleaned of the residual yellow toner and the cycle above is repeated by exposing through a green filter and developing the resulting electrostatic latent image with a magenta developer. This image is then transferred in register to the same receiver sheet containing the yellow separation image. The process is repeated a third time except that the red filter is used for exposure and the image developed with the cyan developer. The resulting image is transferred in register to a receiver sheet containing both the yellow and magenta toner images. The receiver sheet containing the cyan, magenta, and yellow toner separation images in register is then heat fused to adhesively fix and fuse the images to the substrate. The above process is repeated for 75,000 cycles thereby producing 25,000 color prints of good contrast, color, and quality.

EXAMPLE II

The developers in the xerographic three-color print process procedure described in Example I are again repeated with the exception that the magenta developer is substituted for one that is 3% by weight of magenta toner blended with a nickel carrier coated with a terpolymer composition of Example XIII of U.S. Pat. No. 3,526,533. Excellent three-color prints are produced through the initial 100 copies after which the magenta print quality deteriorates rapidly due to the excessive toner background deposits and eventual image reversal occurs by the 500th print. The cyan and yellow developers continue to produce good single-color print quality although the three-color prints are unacceptable.

EXAMPLE III

The xerographic three-color print process employing the developers enumerated in Example I is again repeated with the exception that the magenta developer is replaced by one having 3% by weight of magenta toner in combination with a steel carrier coated with the terpolymer composition used for cyan and yellow developers. Three-color prints produced are unacceptable from the initial start-up due to excessive magenta toner deposits on the print and by the 200th copy image reversal occurs. The individual cyan and yellow single-color prints show magenta contamination and are also unacceptable.

EXAMPLE IV

The xerographic three-color print process employing the developers enumerated in Example I is repeated with the exception that the cyan and yellow toners are combined with the uncoated nickel carrier used for the magenta developer of Example I. Excellent three-color prints are produced through the initial 500 copies after which the print quality deteriorates because of cyan and yellow carrier bead adhesion to the photoreceptor surface. This results in deletion of solid area toner coverage, poor line definition, inefficient cleaning, and difficulty in maintaining image density as well as damage to the photoreceptor surface. Carrier bead adhesion is attributed to the high triboelectric charge of the cyan and yellow toners with the nickel berry carrier. The

magenta developer is found to produce single-color copies of good quality.

EXAMPLE V

The xerographic three-color print process employing the developers of Example I is again repeated with the exception that the cyan and yellow developers are combined with the uncoated steel carrier. It is found that good three-color prints are produced through the initial 250 copies after which cyan and yellow print quality deteriorates rapidly and image reversal occurs by the 300th print. As a result, it is found that although the magenta developer continues to produce good single color-print quality, the three-color prints are unacceptable.

EXAMPLE VI

The procedure as outlined in Example I is again performed with the exception that the cyan, magenta, and yellow toners are prepared which are respectively designated as copper phthalocyanine pigment identified in the Colour Index as CI74160, CI Pigment Blue 15; anthraquinone dye identified in the Colour Index as CI60710, CI Disperse Red 15; and monoazo dye identified in the Colour Index as CI12700, CI Solvent Yellow 16.

EXAMPLE VII

The procedure as outlined in Example I is again performed with the exception that the cyan, magenta, and yellow toners are prepared which are respectively designated as indanthrene blue identified in the Colour Index as CI69810, Special Blue X-2137; disazo dye identified in the Colour Index as CI26050, CI Solvent Red 19; and nitrophenylaminesulfonamide identified in the Colour Index as Foron Yellow SE-GLF, CI Disperse Yellow 33.

EXAMPLES VIII-XI

The procedures as outlined in Examples II-V are again performed with the developers of Example VI with similar results obtained.

EXAMPLES XII-XV

The procedures as outlined in Examples II-V are again performed with the developers of Example VII with similar results obtained.

In the above examples, i.e., II-V, VIII-XI, and XII-XV, it is clearly seen that when the toner compositions employed in the developers of the instant invention are combined with carriers other than the metal terpolymer coated steel carrier for the yellow and cyan toners and an uncoated nickel berry carrier for the magenta toner, unsatisfactory results are obtained.

Although the present examples were specific in terms of conditions and materials used, any of the above listed typical materials may be substituted when suitable in the above examples with similar results. In addition to the steps used to carry out the process of the present invention, other steps or modifications may be used if desirable. In addition, other materials may be incorporated in the system of the present invention which will enhance, synergize, or otherwise desirably affect the properties of the systems for their present use.

Anyone skilled in the art will have other modifications occur to him based on the teachings of the present

invention. These modifications are intended to be encompassed within the scope of this invention.

What is claimed is:

1. A color electrophotographic imaging process comprising charging a photoconductive member, exposing said photoconductive member to an original to be reproduced through a filter of one color thereby selectively discharging said photoconductive member, developing the electrostatic image formed thereby with a developer of a complementary color, said developer being one member of the group consisting of copper phthalocyanine pigment identified in the Colour Index as CI74160, CI Pigment Blue 15, cyan toner and a methyl terpolymer coated steel carrier; anthraquinone dye identified in the Colour Index as CI60710, CI Disperse Red 15, magenta toner and a nickel berry carrier; and monoazo dye identified in the Colour Index as CI12700, CI Solvent Yellow 16, yellow toner and a methyl terpolymer coated steel carrier; charging said photoconductor for a second time and selectively exposing said photoconductor to the same image through a filter of another primary color, developing the latent electrostatic image formed thereby with a developer of a complementary color, said developer being another member selected from the group consisting of copper phthalocyanine pigment identified in the Colour Index as CI74160, CI Pigment Blue 15, cyan toner and a methyl terpolymer coated steel carrier; anthraquinone dye identified in the Colour Index as CI60710, CI Disperse Red 15, magenta toner and a nickel berry carrier; and monoazo dye identified in the Colour Index as CI12700, CI Solvent Yellow 16, yellow toner and a methyl terpolymer coated steel carrier; charging said photoconductive member for a third time, exposing said photoconductor to the same image through a filter of the remaining primary color and developing the latent electrostatic image with a complementary developer, said developer being the remaining developer of the group consisting of copper phthalocyanine pigment identified in the Colour Index as CI74160, CI Pigment Blue 15, cyan toner and a methyl terpolymer coated steel carrier; anthraquinone dye identified in the Colour Index as CI60710, CI Disperse Red 15, magenta toner and a nickel berry carrier; and monoazo dye identified in the Colour Index as CI12700, CI Solvent Yellow 16, yellow toner and a methyl terpolymer coated steel carrier.

2. The process as defined in claim 1 wherein said cyan toner is applied first, said magenta toner is applied second, and said yellow toner is applied third.

3. The process as defined in claim 1 wherein said magenta toner is applied first, said yellow toner is applied second, and said cyan toner is applied third.

4. The process as defined in claim 1 wherein said yellow toner is applied first, said cyan toner is applied second, and said magenta toner is applied third.

5. The process as defined in claim 2 wherein the order of said magenta and yellow toner application is reversed.

6. The process as defined in claim 3 wherein the order of application of the yellow and cyan toners is reversed.

7. The process as defined in claim 4 wherein the order of application of the cyan and magenta toners is reversed.

8. The process as defined in claim 1 wherein said cyan toner comprises indanthrene blue identified in the Colour Index as CI69810, Special Blue X-2137; said magenta toner comprises disazo dye identified in the Colour Index as CI26050, CI Solvent Red 19; and said yellow toner comprises nitrophenylaminesulfonamide identified in the Colour Index as Foron Yellow SE-GLF, CI Disperse Yellow 33.

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