1

3,738,832 COLOR ELECTROPHOTOGRAPHIC PROCESS EMPLOYING LIQUID DEVELOPER CON-TAINING GELATIN

Seiji Matsumoto, Yasuo Tamai, and Takao Komaki, Asaka, Japan, assignors to Xerox Corporation, Stamford, Conn.

No Drawing. Filed July 9, 1970, Ser. No. 53,631 Int. Cl. G03g 13/10, 9/04

U.S. Cl. 96—1.2 8 Claims 10

ABSTRACT OF THE DISCLOSURE

There is disclosed a color electrophotographic imaging process utilizing a liquid developer composition containing a gelatin additive so as to enhance the properties of the resulting color image in a direct or combination color imaging process. It is further disclosed that upon cleaning each image prior to the subsequent recycling utilizing additional color compositions with a low boiling point solvent that the qualities of the resulting image may be further 20 enhanced.

BACKGROUND OF THE INVENTION

The subject matter of this invention is directed toward 25 an imaging system and more specifically to a colored electro-photographic imaging process.

Several methods are known whereby a colored image may be produced from the application of electrophotography. One such method consists in the formation of three colored images separately on the respective photoconductive insulating plate and the transfer thereof, one by one, onto a suitable transfer material in registration. The second method is known whereby three colored images are formed through superimposition on the photoconductive insulating layer of a photoconductive plate. The former process is referred to as a transfer process and the latter as a direct or combination process.

According to the transfer process the electrophotosensitive material is corona charged in the dark and selectively exposed to a color negative original, in the first instance through a red filter, then through a green filter and lastly, through a blue filter. After exposing to a red filter, the resulting electrostatic latent image is reverse developed by way of cyan toners with the resulting toner image being transferred to the surface of a sheet of white paper. Next, a second electrophotosensitive plate is similarly charged in the dark and exposed with the same color negative film through the green filter, and reverse developed by means of magenta toners. This magenta image is then transferred in registration to the paper substrate onto which the cyan image was transferred. Lastly, a yellow image is obtained in a similar manner by exposure of the negative to a third photosensitive plate to a blue filter and reverse developed by means of a yellow toner and then transferred in registration as before. A colored positive image is thus obtained. Although the above-described process has been found to be suitable for use, certain disadvantages exist which make the particular approach somewhat undesirable. For example, the above-described process requires the transfer of each individual image in registration to produce the final color print. To accomplish this and still maintain the proper color balance is very difficult.

In the direct process of producing a color image, three colored toner images are produced on the same photosen-

2

sitive member through the repetition of charging, exposing and developing one on top of the other by superimposition. For example, the photosensitive material may be prepared by coating a conductive substrate with a composition comprising a panchromatic photoconductor. The resulting photosensitive plate is charged uniformly in the dark and exposed to the original to be reproduced in the first instance through a red filter, following which the resulting electrostatic latent image is developed by means of cyan toners with the resulting toner image being fixed to the photosensitive layer by an appropriate technique. After dark adaptation, the above-mentioned photosensitive layer is again charged, exposed to a green filter and developed with a magenta toner in coincidence with the before-mentioned cyan image and fixed to the surface of the photosensitive layer. The photosensitive plate is again dark adapted and through a repetition of the above-steps a yellow toner image is obtained in registration with the first two cyan and magenta images. By this technique a colored image is produced through super-imposition of colors. Although this approach in the formation of the color image has been found suitable, certain disadvantages persist which make the approach undesirable. For example, it is necessary that the previously formed toner image not exert an adverse effect upon the subsequent charging exposure and development steps. Due to the presence of the toner on the photosensitive member as a result of the previous image development step, the second and subsequent procedures are invariably subjected to the effects of the toners previously used. For example, when the sensitive layer is charged electrically, the toner deposited thereon is charged. During the development phase the charged toner absorbs the toner being used during the subsequent development steps with the consequences that the colors will become mingled. Further, the toner present on the photosensitive layer absorbs light during the subsequent exposure step of the process so as to impede attenuation of electric charge where desired and as a result degrades sensitivity so that the toner of the subsequent steps will be caused to adhere in an increased amount as compared to a corresponding amount of light, thereby also producing colors not fully representative of the original.

Therefore, it is an object of this invention to provide an imaging system capable of overcoming the abovenoted disadvantages.

A further object of this invention is to provide a novel electrophotographic color imaging system.

Still a further object of this invention is to provide a direct color imaging process which eliminates the problems of color mingling which in the past have plagued such an imaging process.

Yet, still a further object of this invention is to provide an imaging process whereby the charge retention properties of toner present on the photosensitive member may be inhibited so as to enhance the properties of the photosensitive member.

Another object of this invention is to provide a novel combination color imaging process.

SUMMARY OF THE INVENTION

The foregoing objects and other are accomplished in accordance with the present invention generally speaking by providing an imaging system wherein colored images are electrophotographically formed on the surface of a support member according to the direct or combination

3

process. An electrostatic latent image is formed on the surface of a photosensitive member and the resulting latent image is developed with a liquid developer, comprising a dielectric or electrically insulating carrier liquid having dispersed therein a pigmented toner component. The toner component deposits on the photosensieive layer in conformity with the electrostatic latent image to produce a visible image. The liquid developer comprises in addition to the carrier and toner components a concentration of finely divided par- 10 ticles of gelatin. Following development of the latent image the photosensitive layer is cleaned with a low boiling point solvent. The process steps are then repeated at least one time with a second colored image being developed in registration with the initially developed image. 15 The process can be repeated until the desired color image of two or more colors is produced. Following the final development step the image may be fixed in situ to the surface of the photoconductive member or selectively transferred to the surface of a specified support substrate. 20

It has been determined in the course of the present invention that upon the use of a liquid developer composition containing a gelatin additive when developing an electrostatic latent image, it is possible in a direct or combination color imaging system to enhance the resulting color image. Further, it has been determined that upon cleaning between each imaging step of the resulting imaged member with a low boiling point solvent that the resulting quality of the image produced is further enhanced.

For the purpose of the present invention, any suitable type of photosensitive layer which will support an electrostatic latent image of negative polarity may be utilized. For example, the photosensitive layer may comprise a dispersion of photoconductive pigment such as ZnO, CdS, CdS.nCdCO₃, ZnS and TiO₂ blended with an electrically insulating binder resin such as a silicone resin, an alkyd resin or polyvinyl chloride-polyvinyl acetate copolymer. Generally, the photoconductive pigment is blended at a weight ratio of 3:1 to 8:1 with the insulating resin.

Any suitable base material may be used as the support for the photoconductive layer. Generally it is preferred that the support material have an electrical resistance less than that of the photoconductive layer so that it will act as a ground when the electrically charged coating is exposed to light. Typical conductive materials include aluminum, brass, copper, zinc, conductive paper and any suitable plastic substrate having the necessary conductivity properties, such as by applying a metallic layer to the surface of a polyethylene terephthalate 50 (Mylar) sheet. Any suitable technique may be used to establish the electrostatic charge on the surface of the photosenstive member. Typical techniques utilized include the use of a corrotron or scorotron to generate corona discharge and deposit electrostatic charge on the surface of the particular photosensitive member. This is achieved by applying a high electrical potential to a fine conducting wire to generate a corona discharge.

The liquid developer of the present invention comprises a suspension of finely divided particles in a dielectric liquid. The carrier liquid is generally a non-polar liquid 60 of high electrical resistance. Liquids having a high volume resistivity or electrical resistance, preferably at least about 109 ohms-cm. or greater and a low dielectric constant, preferably less than about 3, may be used in the course of the present invention. Typical liquids include aromatic hydrocarbons, such as benzene, toluene, xylene, aliphatic hydrocarbons such as hexane, and heptane, halogenated hydrocarbons such as trichloroethylene and carbon tetrachloride, and various silicone oils and mixtures thereof. Other suitable saturated hydrocarbons include decane, dodecane, and tetradecane, molten paraffin, molten beeswax, and other molten thermoplastic materials, kerosene fractions, commercially available from

4

Odorless Solvent, long chain unsaturated aliphatic hydrocarbons such as Isopar G commercially available from the Humble Oil Company of New Jersey and mixtures thereof.

Any suitable pigment particle or toner may be suspended in the insulating liquid and is utilized to make visible the electrostatic latent image. For example, Phthalocyanine blue (C.I. 74160), Diane blue (C.I. 21180) and Milori blue (an inorganic pigment equivalent to ultramarine) may be used as the cyan toner; Brilliant Carmine 6B (C.I. 15850), Quinacridone Magenta (C.I. Pigment Red 122) and Thioindigo Magenta (C.I. 73310) as the magenta toner; and Benzindine Yellow (C.I. 21090, and C.I. 21100) and Hansa Yellow (C.I. 11680) as the yellow toner. It is preferred that the quantity of toner present in the carrier liquid be in the range of from about 0.01 to 10% by weight of the developer. The developer composition of the present invention is characterized by containing from about 5 to 50% by weight of the toner of a finely granulated, gelatin component. The finely granular gelatin can be prepared by mechanically pulverizing flakes of gelatin or gelatin gel or by dispersing an aqueous solution of gelatin in a nonsolvent for the gelatin.

In the present invention a latent electrostatic image of a negative polarity is formed on the surface of a suitable photosensitive member. The charge supporting member is brought into contact with a liquid developer which assumes a positive electric charge and contains in a dispersed state finely granular coloring material or toner and finely granular gelatin as mentioned above. Following development of the latent image the carrier liquid generally evaporates so as to leave the deposited toner particles and gelatin particles on the surface of the photosensitive member corresponding to said charge pattern. Upon drying of the image the particles affix themselves to the surface of the substrate or photosensitive member. Next, the developed surface is cleaned with a low boiling point solvent after the development step but prior to the subsequent charging step. This step of cleaning has the effect of washing away excess developing agent adhering to the surface of the sensitive or photosensitive layer. The specific step of cleaning after that of developing may be carried out only once with the low boiling point solvent but it is preferred to repeat the process several times. When the cleaning is carried out several times, it is sufficient to use the low boiling point solvent component only in the last cleaning run. As the low boiling point solvent suitable for the purpose of this cleaning, it is desirable to use aliphatic and alycyclic hydrocarbons having a low polarity or halogenated hydrocarbons such as chlorofluorinated hydrocarbons. The aliphatic and alycyclic hydrocarbons are desired to have molecular weights not exceeding about 100. Typical hydrocarbons include methane, ethane, propane, butane, pentane, cyclooctane, cycloheptane, cyclopentane, cyclopropane, cyclopentadiene and cyclo-butane. The chlorofluorinated hydrocarbons are desired to have molecular weights in the range of from about 150 to 250. Typical chlorofluorinated hydrocarbon solvents include trichlorofluoroethane (Freon T.F.), trichlorofluoromethane (Freon 11) and dichlorodifluoromethane (Freon 11).

The electrostatic latent image of the present invention may be formed on the surface of the photoconductive member by any suitable technique such as by applying an electrostatic charge to the surface of the photosensitive member through a stencil or by the more conventional electrophotographic steps which entail uniformly charging the surface of the photoconductive member and selectively discharging the charged plate so as to form an electrostatic charge pattern.

PREFERRED EMBODIMENTS

rials, kerosene fractions, commercially available from

To further define the specifics of the present invention
the Standard Oil Co. of Ohio under the trade name Sohio 75 the following examples are intended to illustrate and not

5

limit the particulars of the present invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE

Finely pulverized photoconductive zinc oxide is sensitized spectroscopically through absorption thereto of patent blue (for red sensitization), rose bengal (for green sensitization) and fluorescein (for blue sensitization). The sensitized zinc oxide is blended with an alkyd resin incorporating therein cobalt naphthenate as a hardening agent. The resulting composition is coated on a substrate of polyethylate terephthalate having vacuum deposited on its surface an aluminum layer of about 100 microns. This structure is used as the photosensitive member.

The photosensitive surface of the resulting member is charged electrostatically to a negative potential by means of a corona discharge unit, and exposed to a red light projected through an image to produce an electrostatic latent image thereon. The resulting image is developed with a cyan liquid developer having the following composition to produce a toner image of cyan particles:

Phthalocyanine blueg_	0.2
Varnish obtained by heating rosin-modified phenyl-	
formaldehyde resin and linseed oilg_	0.5
Polymeric linseed oilg_	0.3
Finely granular gelatin (having an average particle	
diameter 0.2μ) ¹ g_	0.05
Cyclohexaneml	800
Keroseneml_	200

 $^{\mathbf{1}}$ The finely granular gelatin was obtained by dispersing the aqueous solution of gelatin in acetone.

The layer containing the toner image is first cleaned with refined iso-paraffin and then with chlorofluorinated hydrocarbon (Diflon S3 made by Daikin Industry Co., Ltd.) 35 and then dried. At this time, the drying may be accelerated by supplying a current of hot air or air at room temperature

The sensitive layer is negatively charged with corona discharge, exposed to green light projected through the image to have an electrostatic image formed thereon, developed with a magenta developing agent having the following composition to obtain a toner image of magenta over the toner image of cyan:

Brilliant carmine 6Bg_	0.32
Varnish obtained by heating rosin-modified phenol-	
formaldehyde resin with linseed oilg_	0.5
Polymeric lineseed oilg_	
Finely granular gelatin (having an average particle	
diameter 0.2μ)g_	80.0
Cyclohexaneml_	800
Keroseneml	200

The toner of magenta deposited over areas in which the toner of cyan had been deposited at higher density, had a density equal to or slightly lower than in areas in which there had been deposited no toner of cyan. Similarly to the development with cyan, this sensitive layer is cleaned with refined isoparaffin and chlorofluorinated hydrocarbon and then dried.

The sensitive layer is again charged negatively, exposed to blue light projected through the image, and developed with a developing agent of yellow having the following compositon to obtain an image of three colors:

Benzidine yellow Cg_	3.0	
Varnish obtained by heating rosin-modified phenol-		
formaldehyde resin and linseed oilg_	0.6	
Cyclohexaneml_	800	
Keroseneml	200	7

(Since this developing agent was used in the last stage of the three-color combination, it did not require incorporation of finely granular gelatin.) In the case of the present example of this invention, notwithstanding 75

6

the absorption of blue light by cyan and magenta toners, the toner of yellow deposited over areas in which the toner of cyan and/or magenta had been deposited at higher density had a density equal to or slightly lower than in areas in which there had been deposited neither of the toners.

Although the present examples are 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 and modifications may be used if desirable. In addition, other materials may be incorporated in the photosensitive materials, developer composition and other elements of the invention which will enhance, synergize or otherwise desirably effect the properties of these materials for their present use.

Anyone skilled in the art will have other modifications occur to them 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. An electrophotographic imaging process comprising forming an electrostatic latent image on the surface of an electrophotographic member, developing said latent image with a liquid developer comprising an electrically insulating carrier liquid having dispersed therein a pigmented toner and finely divided particles of gelatin said gelatin being present in an amount of 5–50% by weight of the toner, washing the imaged surface of said photosensitive member with a low boiling point solvent and repeating said process steps at least one additional time utilizing a second liquid developer composition comprising a pigmented toner such that a second colored image is developed in registration with the initially developed image.

2. The process as disclosed in claim 1 further including the step of fixing said color image to the sur-

face of said photosensitive member.

3. The process as disclosed in claim 1 wherein said color image is selectively transferred to the surface of a support substrate.

4. The process as disclosed in claim 1 wherein said low boiling point solvent is selected from at least one member of the group consisting of aliphatic, alycyclic and chlorofluorinated hydrocarbons.

5. The process as disclosed in claim 4 wherein said low boiling point solvent comprises a chlorofluorinated hydrocarbon having a molecular weight ranging from about 50 150 to 250.

6. The process as disclosed in claim 4 wherein said aliphatic and alycyclic hydrocarbons have molecular weights not exceeding about 100.

7. The process as disclosed in claim 1 wherein said washing step is repeated at least more than one time between each imaging cycle with the low boiling point solvent being utilized only in the last of the washing steps preceding the subsequent imaging cycle.

8. A color electrophotographic imaging process which comprises forming an electrostatic latent image on the surface of an electrophotographic member, developing said latent image with a liquid developer comprising a pigmented toner component and a finely divided granular gelatin additive said gelatin being present in an amount of 5-50% by weight of the toner, said toner component comprising a cyan pigment, washing said imaged member at least one time with a solution comprising a low boiling point solvent, repeating said imaging and development steps utilizing as a toner component with the 70 second imaging cycle a magenta composition washing said imaged member as in the first cycle and repeating once again the imaging and development step utilizing as the toner component with the third imaging cycle a yellow pigment to produce said color image.

7 References Cited UNITED STATES PATENTS

3,523,906 3,276,896 3,444,083 3,432,329

3,383,209 3,692,523

8

Re	ferences Cited	OTHER REFERENCES
UNITED	STATES PATENTS	Derwent Belgium Patents Report No. 22/69, Belgium
8/1970	Vrancken 252—62.1 X	Pat. 724,581, published in Derwent on May 2, 1969.
	Fisher 96—1 LX X	GEORGE F. LESMES, Primary Examiner
5/1969	Oliphant 252—62.1	
3/1969	Van Den Heuvel et al.	J. R. MILLER, Assistant Examiner
	252—62.1 X	U.S. Cl. X.R.
5/1968	Cassiers et al 252—62.1 X	
9/1972	Tamai et al 96—1.4 10	96—1 LY, 1.4; 117—37 LE; 252—62.1