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[54] **SENSITIZED DEVELOPERS FOR ELECTROPHOTOGRAPHY AND ELECTRORADIOGRAPHY**
2 Claims, No Drawings

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ABSTRACT: The invention relates to a method of correcting the surface of a photoconductor during multicolor development processes wherein the sensitivity to color acceptance during exposure is varied by the developer of the previous steps, the invention residing in the color correction between development and exposure steps of either the whole surface or the image surface only by either including with a developer, or applying independently, a sensitizing dye in the next color exposure.

SENSITIZED DEVELOPERS FOR ELECTROPHOTOGRAPHY AND ELECTRORADIOGRAPHY

This invention relates to sensitized developers for photoconductive surfaces for use in electrophotography and electroradiography.

It is already well known to dye-sensitize photoconductive surfaces during the course of manufacture of the surfaces.

Dye-sensitization has the effect of causing better absorption of the light rays and activation of the photoconductor when exposed to an image.

To dye-sensitize a photoconductor film it is customary to incorporate in it a number of different colored dyes, the sensitivities of which are such that the photoconductor is exposed to the image, the photoconductor will be substantially uniformly effected by the various colors of the original which is being copied, so that the various colors of the colored original will be accurately represented in the final development.

For single-color work this dye sensitization is relatively effective except that the dye-sensitized paper has a colored appearance due to the greater sensitivity of the eye to certain colors, and therefore most dye-sensitized paper have a pinkish tinge to the human eye, a factor which for images where a white background is required is not desirable.

The dye-sensitized papers are also subject to the disadvantage that when multicolor development is to be effected, the first color down will desensitize the photoconductor base due to the overlaying image deposit acting as a mask to prevent the photoconductor beneath from being correctly activated by light of the required color.

Thus, in the known art the modification of electrophotograpic and electroradiographic layers to obtain increased sensitivity has shown that increased speed ensues if dyes or alternatively X-ray absorbers are added to the photoconductive material before coating. It is also practicable to achieve an increase in speed by dyeing the surface of the photoconductive layer after coating.

It has now been discovered that localized sensitization of the layer can be produced selectively by incorporation of a sensitizing dye for the electrophotographic layer, in the developer used to develop an electrostatic image.

Thus in one modification of an invention incorporating this discovery, it has been shown that the sensitizing dye may be first dissolved in a polar liquid and then incorporated with a resinous toner in a developer concentrate. The concentrate is then dispersed by grinding into the carrier liquid. An electrostatic image developed with such a dyed resinous toner dispersion if found to have a higher sensitivity to subsequent exposures to light than the nonimage areas.

Where photoconductivity is involved, and successive independent light exposures are required, it is essential that the successive developer deposits be not impaired by the underlying deposits, particularly as regards nonimage absorption of light. For example, one colored developer can act as an unwanted filter for a second exposure involving a second colored developer. According to one form of this invention, extra sensitization of the underlying photoconductor is achieved by incorporating the dye in the developer and hence in the area which is developed in the first step, after the first exposure. This means that the extra sensitization imparted by the developer causes the photoconductive sheet on second exposure to exhibit the same response to a given quantity of light irrespective of the density of the previous developed image. For example, if a cyan developer is printed down, the characteristics of the cyan deposit are such that 60 percent of the blue light may be reflected from the sheet; thus for the subsequent exposure through a blue filter (required to print the yellow developer) 40 percent of the blue light is absorbed by the cyan developer deposit, thus areas of the sheet which have no developer will receive 40 percent more light than the areas which have cyan developer for equal intensity of light impinging on them. If the sensitivity to blue light of the sheet beneath the cyan developer deposit can be increased, this factor can be overcome, that is, both the developed and the undeveloped areas discharge on exposure to the same level, and uniform second development results.

According to a further aspect of the invention, the sensitization of the photoconductive sheet to a given portion of the spectrum can also be arranged so that sensitization takes place in both the developed area and the undeveloped area. This is useful for the exposure and development of a continuous tone electrophotographic color pring from a color transparency using three color filters.

In prior art processes the normal technique for this form of color printing is to use a paper which is dyed with three dyes so as to give a panchromatic response for example:

a. yellow dye, sensitizing the paper for blue light

b. red dye, sensitizing the paper for blue light

c. blue dye, sensitizing the paper for red light

A typical procedure for the development of a three-color continuous tone print using panchromatically dyed paper is as follows:

Exposure of color transparency through color filter:	Color of Development
1. Red filter (for example Kodak Wratten No. 29)	Cyan
2. Green filter (for example Kodak Wratten No. 61)	Magenta
3. Blue filter (for example Kodak Wratten No. 47B)	Process Yellow

A similar color print can however not be produced according to this invention on a white unsensitized photoconductive sheet by making use of (1) the inherent blue sensitivity of the photoconductor, for example photoconductive zinc oxide, and (2) the use of dyed developers which sensitize the whole sheet, as follows:

Exposure of color transparency Through filter:	Color of Development
Blue filter (for example Kodak Wratten No. 47B)	Process Yellow developer, containing blue dye which sensitizes to red light
Red filter (for example Kodak Wratten No. 29)	Cyan Developer containing red dye which sensitizes to green light
Green filter (for example Kodak Wratten No. 61)	Magenta developer, containing no dye.

Sensitization of the first kind, that is localized imagewise sensitization, is achieved by confining the dye within the developer particles. Sensitization of the second kind, that is over the nonimage areas as well, is achieved by increasing the solubility of the dye in the carrier liquid, e.g. by adding solvents to the carrier liquid.

One advantage of this technique is that color latitude of an electrophotgraphic sheet can be extended, enabling colored images to be reproduced correctly at both the low- and the high-density ends of the scale, that is with very high densities unwanted filtration by the developer deposit obviously is disproportionate relative to the low densities.

Another advantage is that white (unsensitized) photoconductive layers can be used for color printing if required.

In a further modification of the invention, "white" dyes are added to enhance the apparent brightness of the developed images.

It will be seen that by use of this invention, it is possible to dye-sensitize with two colors only, as opposed to three, when carrying out three-color development for the reason that unsensitized photoconductor surfaces have a high sensitivity to

blue, and if therefore the first exposure is for a blue color and the subsequent development is carried out in the complementary color as is customary, that is yellow, highly sensitive image will result during exposure due to the ability of the surface to accept the blue color, but if now during the development of the first image with the yellow developer, a dye-sensitization agent is included in the developer which is selected to the next color which is to be exposed, then an overall film of sensitization for the next color can be achieved. Thus if the first developer contains a blue dye, sensitization for an image exposure through a red filter will result, and the next developer should then contain a red-sensitizing dye which sensitizes to green for the next exposure with a green filter and subsequent magenta developer.

The advantage of incorporating the sensitizing dyes in each previous developer is that the dye-sensitive material is not covered by the preceding development which would take place if the three colored dyes were included in the original surface, but deposition of the sensitizing dye is at a stage where it will remain effective over the required area. Dye sensitizing materials for zinc oxide are known, but the application by deposition with an image is the novel feature of this invention.

A further advantage which results from the deposition of dye-sensitizing material just prior to exposure of the photoconductive medium is that as most of the materials have a certain acid value, deterioration of the dye-sensitizing agent is not effected as is the case where the paper is prepared long before it is actually used.

To enable a full understanding of the invention to be had, three specific examples will now be referred to in detail, but it is to be clear that these are not to be taken as limiting the invention, since other color sequences fall readily within the scope of the invention.

EXAMPLE 1

1.1 An electrophotographic paper, film or plate is prepared by coating it with a layer of electrophotographic material of the following composition:

Pigment	
Zinc oxide, Durham Special Z.	1,400 grams
Binder	
Alkyd resin solution, short oil oxidizing alkyd resin solution manufactured by Monsanto Chemicals (Aust.) Ltd.	400 grams
Silicone resin solution for example DC804 of the Dow Corning Corp. U.S.A.	100 grams
Dyes	
Erioglaucine (alphazurine)	0.05 gram
Rose Bengal	0.05 gram
Erythrosin B	0.05 gram
Fluorescein	0.04 gram
Driers	
Cobalt Naphthenate	0.003 gram
Zinc Naphthenate	0.003 gram
Solvents	
Acetone	40 grams
White Spirits	1,000 grams
Perchlorethylene	1,000 grams

These materials are milled together to form a paint and applied to the paper, film or plate by dip-coating. The finish coating has a light buff color and has a response giving approximately equal sensitivity for red, green and yellow light.

1.20 As a first step in making a dye-sensitized developer a dye solution is made of the selected dye in methyl alcohol by weighing 1.0 gram of the dye and dissolving it in 100 milliliters of methyl alcohol. Typical dyes are listed in the following table:

The dyes listed in the following table are typical of those used to sensitize photoconductive white zinc oxide binder coatings.

Table of Dyes	Color Index
Rose Bengal (tetra-chloro-tetra iodo fluorescein)	CI 45440
Erythrosin B (tetra-iodo-fluorescein)	CI 45430
Fluorescein	CI 45350
Fluorescein (Sodium, water-soluble)	CI 45350
Eosin (water-soluble, yellow tetra-bromo-fluorescein)	CI 45380
Phloxine (tetra-chloro-tetra-bromo-fluorescein)	CI 45410
Malachite Green	CI 42000
Crystal Violet	CI 42555
Brilliant Green	CI 42040
Methylene Blue	CI 52015
Auramine	CI 41000
Acridine Orange	CI 46005
Rhodamine G	CI45160
Disulphine Blue	
Erioglaucine Blue (Alphazurine G)	CI 42045

The above dyes were obtained from British Drug Houses, England and George T. Gurr (Microscopical Stains and Reagents), London, England. Disulphine Blue was obtained from Imperial Chemical Industries.

1.21. A developer concentrate is prepared from the following materials:

Irgafin Sl phthalocyanine blue, coated X40 **dispersible copolymer, product of Geigy (Australia) Pty. Ohio,** 850 gram

Styrene-butadiene copolymer such as Solprene 40 of the Philips Petroleum Company, Akron, Ohio, U.S.A. 170 gram

Mineral Turpentine 500 gram

This concentrate is prepared by mixing the copolymer-coated pigment with 100 grams of mineral turpentine and then adding the Solprene X40 copolymer and finally the remaining 400 grams of mineral turpentine. The dye solution of the above section 1.20 is then added to the developer concentrate in the proportions of 0.1 milliliter of dye solution to 100 grams of concentrate, the dye in this case being for example Rhodamine G. (CI 45160).

1.22 The developer containing the dye is then dispersed in an iso-paraffinic carrier liquid such as the Isopar solvents of the Esso Company or Shellsol T of Shell Chemicals (Australia) Ltd., in the proportions of 1 gram of concentrate in 100 grams of carrier liquid to form a liquid developer.

1.23 The electrophotographic sheet of section 1.1 of this example is then charged electrostatically by means of the corona discharge from points or wires held at a high potential in relation to the sheet, for example to give a field of 5 kv. per inch. The sheet is then exposed to a colored image through a selected filter for example orange filter (Kodak Wratten No. 29) and then developed with the above blue developer which contains in addition the red dye.

1.24 The electrophotographic sheet of section 1.23 is then recharged electrostatically and reexposed to the colored image through a second filter for example green filter, (Kodak Wratten No. 61) and the sheet is then developed in a magenta developer.

The magenta developer is prepared as in section 1.21 by substituting a magenta pigment is place of the Irgafin Sl blue, for example, "Brillfast" Geranium 3543 supplied by Smith Reichold Ltd.

The response of the electrophotographic sheet under the blue-developed areas of section 1.23 is corrected by the presence of the red dye which sensitizes the photoconductor to green light to a degree depending on the density of the blue-developed image.

1.25 The electrophotographic sheet of section 1.24 is then recharged electrostatically and reexposed to the colored image through a third filter for example a purple filter, Kodak Wratten 47B, and developed in yellow pigment. The final result is an overprinted full-color representation.

EXAMPLE 2.

2.1 An electrophotographic paper, film or plate is prepared by coating it with a layer of electrophotographic material of the following composition:

Pigment	
Zinc Oxide, Durham Special Z.	1,200 grams
Binder	
Short oil modified alkyd resin Rhodene M8/50, product of Polymer Corporation	

(Aust.) Ltd.	400 grams
Dyes	
Eosin	0.135 gram
Phloxine	0.075 gram
Brilliant green	0.27 gram
Driers	
Zinc naphthenate	0.003 gram
Solvents	
Acetone	400 grams
Toluene	1,000 grams
Chlorothene	1,000 grams

These materials are milled together to form a paint and applied to the paper, film or plate by dip-coating. The finished coating has slight pink appearance, with approximately equal sensitivity for red, green and yellow light when used electrophotographically.

2.20 A dye-sensitized liquid developer is prepared for this example by dissolving the selected dye in alcohol and adding it to the developer material which follows in Section 2.21. The dye solution is made up in the proportions of 1.0 gram of the dye for example, Malachite green in 100 milliliters of methyl alcohol.

2.21 A developer concentrate is prepared from the following materials:

"Brillfast" Geranium 3543 pigment, red, supplied by Smith Reichold Ltd.	200 grams
Vinyl toluene/butadiene copolymer such as Pliolite VT of Goodyear Rubber Co., U.S.A. or a styrene/acrylate copolymer such as Pliolite ACL of Australian Synthetic Rubber Co., Altona, Victoria.	450 grams
Xylol	200 grams
Toluene	1,600 grams

These materials are milled to produce a homogeneous mixture by means of a high-speed mechanical mixer. The dye solution of the above section 2.20 is then added to the developer concentrate in the proportions of 0.2 milliliters of dye solution to 100 grams of concentrate, the dye for example being Malachite green, Color Index No. 42000.

2.22 The developer concentrate containing the dye is then dispersed in a cyclo-paraffinic carrier liquid such as cyclohexane in the proportions of 1 gram of concentrate in 100 grams of carrier liquid developer.

2.23 The electrophotographic sheet of section 2.1 of this example is then charged electrostatically by means of the corona discharge from points or wires, for example in a field of 10 kv. per inch. The sheet is then exposed to a colored image through a selected filter for example an orange filter, Kodak Wratten No. 29 and then developed with the developer of section 2.22 which contains in addition the green dye which sensitizes the sheet underlying the image to red light.

2.24 The electrophotographic sheet of section 2.23 is then recharged electrostatically and then exposed to a colored image through a selected orange (red) filter for example Kodak Wratten No. 29. The resultant electrostatic image is then developed in a cyan developer of the type described in section 2.21 in which a phthalocyanine blue pigment such as Irgafin Sl is substituted for the magenta pigment and which in addition a yellow dye which sensitizes to purple light, for example Fluorescein, CI No. CI 45350.

2.25 The electrophotographic sheet of section 2.24 is then recharged electrostatically and then exposed to the colored image through a selected purple filter for example Kodak Wratten No. 47B. The resultant electrostatic image is then developed with a yellow developer, made by substituting a yellow pigment in the formulation of section 2.21, for example Microlith Yellow 2G, a diazo pigment supplied by C.I.B.A., Switzerland.

EXAMPLE 3.

3.1 An electrophotographic paper, film or plate is prepared by coating the paper or the like with a layer of electrophotographic material of the following composition:

Pigment	
Durham Special Z zinc oxide (supplied by Harrisons Ramsay Ltd., Sydney, Aust.)	1,300 grams
Binder	
Alkyd modified acrylic resin, Lustrasol AU-180/50, supplied by Reichold Chemicals Inc. (Aust.) Pty. Ltd.	400 grams
Dyes	
Eosin	0.04 gram
Phloxin	0.05 gram
Erioglaucine	0.05 gram
Driers	
Cobalt naphthenate	0.05 gram
Solvents	
Acetone	40 grams
Toluene	500 grams
Chlorothene	800 grams

The finished coating has an off-white appearance and approximately equal sensitivity to red, green and yellow light.

3.20 A dye-sensitizing solution is made up as in section 1.20.

3.21 A developer concentrate is prepared from the following materials:

Irgafin Sl, phthalocyanine blue, coated with a dispensable copolymer, product of Geigy (Australia) Pty. Ltd.	50 grams
Long oil alkyd resin, for example Rhodene L42/70 of Polymer corporation Ltd. Australia, a safflower oil modified, pentaerythritol esterified, alkyd resin of 64 per cent oil length, solution in white spirits of 70 % solids.	200 grams

This concentrate is prepared by mixing the copolymer-coated pigment with 50 grams of mineral turpentine and then adding the alkyd resin and finally 200 grams of white spirit. The dye solution of the above section 3.20 is then added to the developer concentrate in the proportions of 0.2 milliliters of the dye solution to 100 grams of concentrate, the dye in this case being for example Eosin, CI No. 45380.

3.22 The developer containing the dye is then dispersed in an isoparaffinic carrier liquid such as the Isopar Solvent G of the Esso Company or Shellsol T of the Shell Chemicals (Australia) Co., in the proportions of 1 gram of concentrate in 100 grams of carrier liquid to form a developer.

3.23 The electrophotographic sheet of section 3.1 of this example is then charged electrostatically and exposed to a colored image projected through a selected filter for example an orange (red) filter, for example Kodak Wratten No. 29. The resultant electrostatic image is then developed in a cyan developer of the type described in section 3.21, containing the Eosin CI No. 45380.

3.24 The electrophotographic sheet of section 3.23 of this example is the recharged electrostatically and exposed to the colored image projected through a second filter for example a green filter such as Kodak Wratten No. 61. The resultant electrostatic image is then developed in a magenta developer of the type described in Section 3.21 in which Magenta pigments Isol Ruby Fast Red (60 percent) (Robert Bryce Pty. Ltd.), and Brillfast Fast Red (40 percent) (Reichold Chemical Corp. are substituted for the Irgafin Sl, and which in addition contains a yellow dye to sensitize to purple light for example Fluorescein CI No. 45350.

3.25 The electrophotographic sheet of section 3.24 is then recharged electrostatically and then exposed to the colored image through a selected purple filter for example Kodak Wratten No. 47B. The resultant electrostatic image is then developed with a yellow developer, made by substituting a yellow pigment in the formulation of section 3.21 for example Fastona Yellow 3G 3965 of Smith Reichold Ltd., an aniline-anilide yellow pigment.

The final result is an over-printed full-color representation.

The following examples relate to the modification of the invention in which (*a*) the initial photoconductive sheet has not been sensitized by the addition of dyes and (*b*) the sheet is sensitized over its whole area during second ans subsequent exposures.

EXAMPLE 4.

4.1 An electrophotographic paper, plate or film is prepared by coating its surface with a layer of material of similar composition to that of example 1, section 1.1, from which the dyes however are omitted. The resultant coating is white in appearance and is characterized by higher intrinsic sensitivity to blue light than red or green.

4.20 As a first step in making a dye-sensitized developer, a dye solution is made of the selected dye in this case Erioglaucine blue, for example, in ethyl alcohol by weighing 1.0 grams of the dye and dissolving it in 100 milliliters of ethyl alcohol. The dye dye solution is then dissolved in a long oil alkyd resin, such as P470, a soya modified penta alkyd resin of 65 % oil length, product of Polymer Corporation (Australia) Ltd., in the proportions 1 part by volume of alcohol dye solution to 10 parts of resin.

4.21 A developer concentrate is prepared from similar materials to those of example 1, section 1.21, modified in that a yellow pigment such as Microlith Yellow 2GT, of C.I.B.A., is substituted for the Irgafin Sl blue, and to this developer concentrate there is added 50 grams of dyed P470 resin prepared as in Section 4.20 and the concentrate is then milled to produce a homogeneous mixture.

4.22 The final concentrate of section 4.21 is dispersed in an iso-paraffinic carrier liquid such as Isopar G of the Esso Company in the proportions of 1 gram of concentrate in 100 grams of carrier liquid to form a liquid developer.

4.23 The electrophotographic sheet of section 4.1 of this example is charged electrostatically and then exposed to a colored image through a blue filter for example Kodak Wratten No. 47B, and then developed with the above yellow developer which in addition contains blue dye. The blue dye sensitizes the imaged areas and also the nonimage areas to red light, for example the blue dye Erioglaucine blue, dispersed in the resin.

4.24 The electrophotographic sheet of section 4.23 is then recharged electrostatically and reexposed to the colored image through a second filter for example an orange filter (Kodak Wratten No. 29), and then developed with a blue (cyan) developer which contains in addition a red dye. This developer is made in a similar way to section 1.21 of example 1, using Irgafin Sl blue pigment, and Rhodamine G DYE.

4.25 The electrophotographic sheet of section 4.24 is then recharged electrostatically and reexposed to the colored image through a third filter, for example green filter Kodak Wratten No. 61. The latent electrostatic image so produced is developed with a magenta developer prepared as in section 1.21 by substituting a magenta pigment such as "Brillfast" Geranium 3543 red for the Irgafin Sl blue. The final result is an overprinted full-color continuous tone representation.

EXAMPLE 5.

In this example the electrophotographic sheet is coated with the photoconductive material of section 2.1 differing in that the dyes are omitted. The developers of this example are the developers of section 2.21 for example to which are added dyes in alcohol and alkyd resin solution as described in Section 4.20.

EXAMPLE 6.

The materials of Example 4 are modified by substituting for the alkyd resin 470P one or more of the following resins to disperse the dye:

Trade name and type	Oil type	Oil length, percent	Acid value	Diluent	Supplier
Rhodene L42/70 Penta esterified	Safflower	64	6–10	White spirit	Polymer Corporation (Aust.).
Rhodene P2/70 Penta esterified	Linseed	70	6–10	do	Do.
Beckosol P472 Penta alkyd	Safflower	67	3–7	do	Reichold Chemicals (Aust.).
Beckosol 1318 Penta alkyd	Linseed	70	8–12	do	Do.

EXAMPLE 7

The materials of Example 4 are modified by substituting for the alkyd resin 470P one or more of the following vegetable oils to dissolve and disperse the dye:

Oil	Acid No.	Supplier
Safflower oil, alkali refined	0.2–0.5	Meggitt's Ltd. Aust.
Soya bean oil, alkali refined	0.15–0.5	Meggitt's Ltd. Aust.
Dehydrated castor oil	max. 5.0	Meggitt's Ltd. Aust.
Oiticica oil		A.C. Hatrick Ltd. Aust.
Tung oil		Meggitts's Ltd. Aust.
Cotton seed oil		Meggitt's Ltd. Aust.
Sunflower seed oil		Meggitt's Ltd. Aust.
Oiticica oil		Meggitt's Ltd. Aust.

What we claim is:

1. The method of dye sensitization of electrophotographic, sequentially developed, superimposed and differently colored images, which comprises dye-sensitizing during each sequential step to correct the image surface at each stage for the next color exposure which requires correction, said dye-sensitization being effected by adding to or applying together with a liquid developer, in an imagewise manner, a nonphotoconductive dye-sensitizing medium for the color of the next exposure to compensate for the pressure of the deposited developer shielding of the photoconductive surface, whereby at least one of the developers, other than that last applied, is arranged to apply a sensitizing dye imagewise to the areas where correction of photoconductor sensitivity of the photoconductor is necessary to correct the photoconductor to compensate for the presence of the deposited developer.

2. The method of claim 1 wherein the electrophotographic surface is sensitized for red, green and blue light, and comprising the following steps; effecting a first exposure through a filter to expose one of said colors, developing the thus formed latent electrostatic image by means of liquid developer of complementary color containing a correcting dye for the second exposure, effecting the said second image exposure through a filter of the required color, developing same with a complementary liquid developer containing a correcting dye for the next exposure, effecting a further exposure for the remaining color, and developing same with a liquid developer of complementary color.

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