

1

3,682,630

**ELECTROPHOTOGRAPHIC PRINTING ELEMENT
CONTAINING CYANINE SENSITIZERS AND A
MULTICOMPONENT POLYMERIC BINDER**

Woo C. Park, Chicago, Ill., assignor to
A. B. Dick Co., Niles, Ill.

No Drawing. Filed June 11, 1970, Ser. No. 45,577

Int. Cl. G03g 5/08, 13/22

U.S. Cl. 96—1.6

13 Claims

ABSTRACT OF THE DISCLOSURE

An electrophotographic printing element formed of a paper base sheet having a photoconductive coating containing a cyanine compound whereby the speed can be increased, the coating weight reduced, and a whiter copy sheet made available for better image contrast.

This invention relates to electrophotographic elements in the form of copy sheets having photoconductive coatings for use in electrostatic image development and it relates more particularly to an improvement in photoconductive compositions used in the preparation of light sensitive photoconductive coatings.

A typical electrostatic process includes the preparation of an electrophotographic element such as a paper base sheet having a photoconductive coating formed of a photoconductive insulating material, such as zinc oxide, dispersed in an insulating binder, such as a silicone or modified alkyl resin. The recording element is subjected to corona discharge at high voltage to produce an electrostatic charge over the photoconductive surface. By focusing a light image onto the charged surface, the portions irradiated by the light rays are rendered conductive to discharge the electrostatic charge to leave the remainder of the surface in a charged condition which defines a latent electrostatic image. The image is rendered visible by application of a developing powder or liquid whereby the colored particles adhere electrostatically to the charged areas of the sheet and the image is subsequently fixed directly to the photoconductive coating, as by means of heat, adhesive, vapor or the like. Instead, use can be made of a reverse toner whereby the colored particles are deposited on the unimaged portions of the copy sheet. A detailed description of a typical electrostatic printing process is set forth in the Greig Patent No. 2,874,063. The patent describes a process in which a copy sheet having a photoconductive coating containing a relatively pure zinc oxide is charged by corona discharge to a potential of approximately 600-800 volts. A latent image is formed by photographic exposure and the image is developed with a developer composition such as iron particles mixed with a powder of carbon pigmented resin.

An electrostatic recording element of the type described is usually prepared by first mixing a finely divided photoconductor, such as zinc oxide, and the electrically insulating film forming vehicle, such as a silicone resin, with a volatile solvent. The mixture is coated onto the base sheet, dried and then cut to size.

The photoconductive layers heretofore produced are slow in response to light whereby considerable time is required during the exposure period to form the latent electrostatic image and other limitations are imposed from the standpoint of the time and intensity of the exposure.

To obviate these problems, the art has sought to sensitize the photoconductive materials, such as the zinc oxide used in the photoconductive coating, as by the addition of certain sensitizing dyestuffs which are capable of absorbing radiant energy in bands of wave lengths to which the

2

photoconductive material is substantially insensitive and which are capable of transferring the absorbed energy to the zinc oxide or other photoconductive material. Amongst the sensitizing dyes that have been used with zinc oxide are fluorescent dyes, eosin dyes, erythrosin dyes, rose bengal, malachite green, crystal violet, basic fushin, methyl green, brilliant green, methylene blue, acridine orange, aldazarin red and other dye systems more fully described in the following U.S. patents, namely: 3,132,942; 3,121,008; 3,110,591; 3,052,540; 3,051,569; 2,959,481; 3,047,384; 3,125,447; 3,128,179; 3,250,613; 3,250,615; 3,469,979; 3,271,144; 3,274,000; 3,346,161 and, 3,403,023, amongst others.

While such dye sensitization improves spectral response and, to some extent, the speed of the photoconductor for charge acceptance and retention, such technique has not enjoyed widespread success since the advantages of strongly dyeing the zinc oxide layer offsets the sensitivity that is supplied to the photoconductive zinc oxide. Such coloration of the photoconductive layer is undesirable from the standpoint of aesthetic effect, contrast between the image and background and image definition.

Such dye sensitized systems are also deficient from the standpoint of the high speed required for the more recently developed copying machines employing electrostatic techniques. While increased speed might be achieved by increase in dye concentration, the corresponding increase in color would be objectionable and even then adequate speed is difficult to achieve.

Another disadvantage which has been experienced with photoconductive coatings of the type heretofore produced, with or without dye sensitization, is the limitation of the coating to the use of resinous binder systems formulated of expensive organo-silicon resin or slower alkyd or modified alkyd resins thereby to nullify some of the effects of dye sensitization. Further, such zinc oxide photoconductive coatings have been found to be objectionable, not only because of the color introduced by the sensitizing dyestuffs but because coatings of high coating weights are required thereby to increase the weight of the copy sheet and produce a copy sheet having an unnatural feel.

It is an object of this invention to produce electrostatic copy paper having greater spectral response and higher speeds without corresponding increase in dye concentration or discoloration of the photoconductive coating and it is a related object to produce an electrostatic copy sheet of the type described which is whiter in color, which has less coating and corresponding lower coating weights, which is lesser in cost, which has better hand and feel and which has markedly increased speed for the production of copy of good quality.

As used herein, the term "speed" is used to define light sensitivity of the electrophotographic coating and it is measured by the amount of light in foot candle seconds required to decay the charge on the paper to a very low or zero residual potential. Thus the lower the numerical value, the faster the light sensitivity or speed of the coating. The term "dark decay," measured in volts per second, relates to the loss of charge of the electrophotographic coating in the dark. Another property used to measure electrophotographic coatings is charge acceptance which is measured in volts.

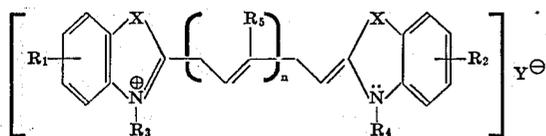
Electrophotographic coating employed in present practice are formulated of photoconductive materials, such as zinc oxide of the type marketed by the New Jersey Zinc Company under the trade name "Photox 80 zinc oxide," or of the type marketed by the American Zinc Company under the trade name "Azo-ZZZ-661 zinc oxide," with an insulating resinous binder such as styrene-ethyl acrylate, silicone resins, modified urethane-oil silicone resins, modified polyvinyl acetate, and the like, or other film forming

3

insulating resins and pigments as described in U.S. Pats. 3,052,539; 3,121,006; 3,121,007, and 3,132,241.

Dyestuffs which have been used to increase light sensitivity of the described electrophotographic coatings include Bromo Phenol Blue, Dibromofluorescein, Erythrosine B, Rose Bengal, Sulpho Rhodamine, Rhodamine B Extra, Eosin OJ concentrate, Auromine 0 concentrate, Quinoline Yellow, Bromo Cresol Purple, Phloxine B, Acradine Orange, Fuchsin, Methylene Blue, Kiton Blue, Tartrazine concentrate, or others of the dyestuffs described in the aforementioned list of patents.

It has been found that photoconductive coatings, with or without dye sensitization, can be markedly increased in speed without addition of color by the formulation of the coating to contain one or more cyanine compounds represented by the following structural formula:



in which R_1 , R_2 and R_5 are selected of hydrogen or an alkyl group having from 1 to 2 carbon atoms, such as methyl and ethyl; R_3 and R_4 are selected of an alkyl or alkylene group having from 1 to 2 carbon atoms, such as methyl, ethyl, vinyl and the like; X is either sulfur or oxygen; Y is a halogen such as iodine, bromine, or chlorine; and n is either 0, 1, 2 or 3. Cyanine compounds of the type described and which may be used in the practice of the invention are represented by 1,1'-diethyl-2,2'-dicarbocyanine iodide; pinacyanol iodide; 1,1'-diallyl-6,6'-dimethyl-2,2'-carbocyanine iodide; 1,1'-diethyl-2,2'-quinocyanine iodide; 3-ethyl-2-[5-(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide; 3,3'-diallylthiacarbocyanine iodide; 3,3'-diethyl-9-methylthiacarbocyanine iodide; 3,3'-diethyl-9-methylthiacarbocyanine iodide.

The desirable effect can be achieved when the cyanine compound is present in the photoconductive coating composition in an amount of at least 0.0001% by weight of the coating composition and little, if any, additional benefit is secured when present in the coating composition in an amount greater than 0.2% by weight. In the preferred practice, the amount of cyanine compound based upon the weight percent of the coating composition is within the range of 0.005% to 0.05% by weight. When calculated on the basis of the photoconductive component such as zinc oxide, the amount of cyanine compound or mixtures thereof may be employed within the range of 0.003% to 0.3% by weight and preferably within the range of 0.01% to 0.1% by weight.

When a sensitizing dye component is employed in the composition with the cyanine compound or compounds in the photoconductive coating, the amount thereof will correspond to that conventionally employed, as described in the aforementioned patents which are addressed to sensitization with dyestuffs.

The cyanine compounds are unique in that the marked increase in speed is noticeable primarily in photoconductive coatings formulated with a binder component selected of a polyvinyl acetate, a mixture of polyvinyl acetate, polystyrene and polyethyl acrylate, or a mixture of polystyrene and polyethyl acrylate, in which the polyethyl acrylate component can be substituted with other polyalkyl acrylates or in which the alkyl groups have from 1 to 3 carbon atoms. Representative are the three component binders of polyvinyl acetate-polystyrene-polyethyl acrylate marketed by the De Soto Chemical Company under the designations E-202, E-033, E-041, E-831 and 948-44.

Having described the basic concepts of the invention, 75

4

the following examples will be given by way of illustration, but not by way of limitation, of the practice of the invention:

PHOTOCONDUCTIVE COATING COMPOSITIONS

Example 1

Zinc oxide	-----grams	100
Toluene	-----cc	100
De Soto resin E-041	-----grams	32
Dye blend	-----cc	1
3-ethyl-2-[5-(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide (2% solution in methanol)	-----cc	1

Example 2

Zinc oxide	-----grams	100
Toluene	-----cc	100
De Soto resin E-041	-----grams	32
3-ethyl-2-[5-(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide (2% solution in methanol)	-----cc	1

Examples 3 to 9

The compositions are the same as in Example 1 except that in Example 3 the compound 1,1'-diethyl-2,2'-dicarbocyanine iodide is substituted for the compound 3-ethyl-2-[5-(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide. In Example 4 the compound pinacyanol iodide is substituted for the compound 3-ethyl-2-[5-(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide. In Example 5 the compound 1,1'-diallyl-6,6'-dimethyl-2,2'-carbocyanine iodide is substituted for the compound 3-ethyl-2-[5-(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide. In Example 6 the compound 1,1'-diethyl-2,2'-quinocyanine iodide is substituted for the compound 3-ethyl-2-[5-(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide. In Example 7 the compound 3,3'-diallylthiacarbocyanine iodide is substituted for the compound 3-ethyl-2-[5-(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide. In Example 8 the compound 3,3'-diethyl-9-methylthiacarbocyanine iodide is substituted for the compound 3-ethyl-2-[5-(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide. In Example 9 the compound 3,3'-diethyl-9-methylthiacarbocyanine iodide is substituted for the compound 3-ethyl-2-[5-(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide. Substitutions of the cyanine compounds in the above examples are made in equivalent amounts.

The dye blend in Examples 1-9 is a solution of 0.2 g. of fluorescein sodium, 0.18 g. of bromophenol blue sodium, 0.1 g. of euchrysin and 0.02 g. of eosine dissolved in 50 cc. methanol.

Example 10

The composition is the same as in Example 1 except that polyvinyl acetate is substituted for the De Soto resin in equivalent amounts.

Example 11

The composition is the same as in Example 1 except that a polystyrene-polyethyl acrylate is substituted for the De Soto resin in equivalent amounts.

The zinc oxide, toluene and resinous binder are mixed for three minutes. Thereafter addition is made of the dye blend, when used, followed by the addition of the cyanine solution with mixture in an Osterizer for another three minutes.

The prepared coating composition is applied as a coating onto conductive paper base stock (Weyerhaeuser "Plainwell" 35 pound paper) in a coating weight of 20 pounds per 3000 square feet of surface area. The coated paper is air dried or drying can be accelerated by air drying at an elevated temperature from room temperature to 350° F.

5

The coated paper electrophotographic printing element can be charged and exposed in the conventional manner and developed to provide a visible image with conventional liquid or powder developers used in the electrostatic printing. The electrometer data run on sheets prepared with the composition of Example 1 gives a speed 3.7 times greater than the speed of paper coated with the same composition but without the cyanine compound and without loss in charge acceptance.

The invention permits the use of resinous binder systems in the photoconductive coating which is capable of accepting a high charge, and the ability to sensitize these resins to so-called fast systems. Because of the increase in speed and high charge acceptance, use can be made of lower coating weight of 8 to 25 pounds per 3000 square feet of surface area without undesirable effect on copy quality. Thus the amount of coating applied to the sheet can be reduced by at least 40% compared to conventional coating weights applied in current construction. This not only reduces the weight of the Electrofax type paper but it also operates markedly to reduce the cost of the photoconductive element while also improving the feel and appearance thereof. The ability to reduce or eliminate the colored dye sensitizers also permits the production of whiter sheets with better contrast between the developed image and background.

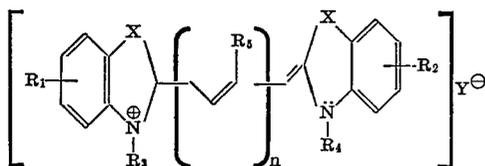
Significant also is the influence that the cyanine compound has on speed whereby it becomes possible to produce a series of different electrostatic copy papers in which the speeds can be varied simply by variation in concentration of the cyanine compound or compounds in the coating.

It will be apparent from the foregoing that I have provided a photoconductive coating composition for use in the preparation of photoconductive printing elements which is whiter in color, lower in weight, less expensive to produce and which is capable of high speeds and good spectral response by comparison with sheets of the type heretofore employed.

It will be understood that changes may be made in the details of formulation and operation without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. An electrophotographic printing element comprising a conductive base sheet and a coating on the base sheet containing a photoconductive zinc oxide, an insulating resinous binder of a mixture of polyvinyl acetate, polystyrene and a polyalkyl acrylate in which the alkyl group contains 1-3 carbon atoms, and a cyanine compound having the structural formula:



in which R_1 , R_2 and R_5 are groups selected from the group consisting of hydrogen and an alkyl group containing from 1 to 2 carbon atoms, R_3 and R_4 are groups selected from the group consisting of an alkyl group and an alkylene group containing from 1 to 2 carbon atoms, Y is a halogen group, X is a group selected from the group consisting of oxygen, sulfur and an ethylenic group, and n is an integer of 0, 1, 2 or 3.

2. An electrophotographic printing element as claimed in claim 1 in which the cyanine compound is selected from the group consisting of 1,1'-diethyl-2,2'-dicarbocyanine iodide; pinacyanol iodide; 1,1'-diallyl-6,6'-dimethyl-2,2'-carbocyanine iodide; 1,1'-diethyl-2,2'-quinocyanine iodide;

6

3-ethyl-2-[(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide; 3,3'-diallylthiacarbocyanine iodide; 3,3'-diethyl-9-methylthiacarbocyanine iodide; and 3,3'-diethyloxcarbocyanine iodide.

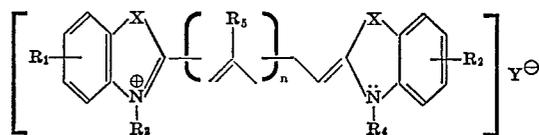
3. An electrophotographic printing element as claimed in claim 1 in which the cyanine compound is present in the coating in an amount within the range of 0.003% to 0.3% by weight of the photoconductive compound.

4. An electrophotographic printing element as claimed in claim 1 in which the cyanine compound is present in the coating in an amount within the range of 0.01% to 0.1% by weight of the photoconductive compound.

5. An electrophotographic printing element as claimed in claim 1 which includes a dye sensitizer to increase the light sensitivity of the coating.

6. An electrophotographic printing element as claimed in claim 1 in which the insulating resinous binder is a mixture of polyvinyl acetate, polystyrene and polyethyl acrylate.

7. In the method for the preparation of copies by an electrophotographic copy process wherein an electrophotographic recording element is given a blanket electrostatic charge and then the charged recording element is exposed to light modulated by an image to produce a latent electrostatic image, the improvement wherein the electrophotographic recording element comprises a conductive base sheet and a coating on the base sheet containing photoconductive zinc oxide, an insulating resinous binder of a mixture of polyvinyl acetate, polystyrene and a polyalkyl acrylate in which the alkyl contains 1-3 carbon atoms and mixtures of polystyrene and a cyanine compound having the structural formula:



in which R_1 , R_2 and R_5 are groups selected from the group consisting of hydrogen and an alkyl group containing from 1 to 2 carbon atoms, R_3 and R_4 are groups selected from the group consisting of an alkyl group and an alkylene group containing from 1 to 2 carbon atoms, Y is a halogen group, X is a group selected from the group consisting of oxygen, sulfur and an ethylenic group, and n is an integer of 0, 1, 2 or 3.

8. The method as claimed in claim 7 in which the cyanine compound is selected from the group consisting of 1,1'-diethyl-2,2'-dicarbocyanine iodide;

pinacyanol iodide; 1,1'-diallyl-6,6'-dimethyl-2,2'-carbocyanine iodide; 1,1'-diethyl-2,2'-quinocyanine iodide;

3-ethyl-2-[(3-ethyl-2-benzothiazolinyldene)-1,3-pentadienyl]-benzothiazolium iodide; 3,3'-diallylthiacarbocyanine iodide; 3,3'-diethyl-9-methylthiacarbocyanine iodide; and 3,3'-diethyloxcarbocyanine iodide.

9. The method as claimed in claim 7 in which the cyanine compound is present in the coating composition in an amount within the range of 0.001% to 0.2% by weight.

10. The method as claimed in claim 7 in which the cyanine compound is present in the coating composition in an amount wherein the range of 0.005% to 0.05% by weight.

11. The method as claimed in claim 7 in which the coating composition includes a dye sensitizer to increase the light sensitivity of the coating.

7

8

12. The method as claimed in claim 7 in which the coating is applied onto the base sheet in a coating weight within the range of 8 to 25 pounds per 3000 square feet of surface area.

3,132,942	5/1964	Stewart	-----	96—1
3,128,179	4/1964	Kendall et al.	-----	96—1
3,052,540	9/1962	Greig	-----	96—1

13. The method as claimed in claim 7 in which the base sheet is a conductive paper base sheet.

OTHER REFERENCES

Hamba and Hishiki, J. of P. Chem., vol. 69, #3, March 1965, pp. 774-779, "Color Sensitization of ZnO With Cyanine Dyes."

References Cited

UNITED STATES PATENTS

3,245,786	4/1966	Cassiers et al.	-----	96—1
3,165,405	1/1965	Hoesterey	-----	96—1
3,003,870	10/1961	Jarvis et al.	-----	96—1

10 JOHN C. COOPER, Primary Examiner

U.S. Cl. X.R.

96—1 PC, 1.7, 1.5; 260—901, 240.6, 240.65

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,682,630 Dated August 8, 1972

Inventor(s) Woo C. Park

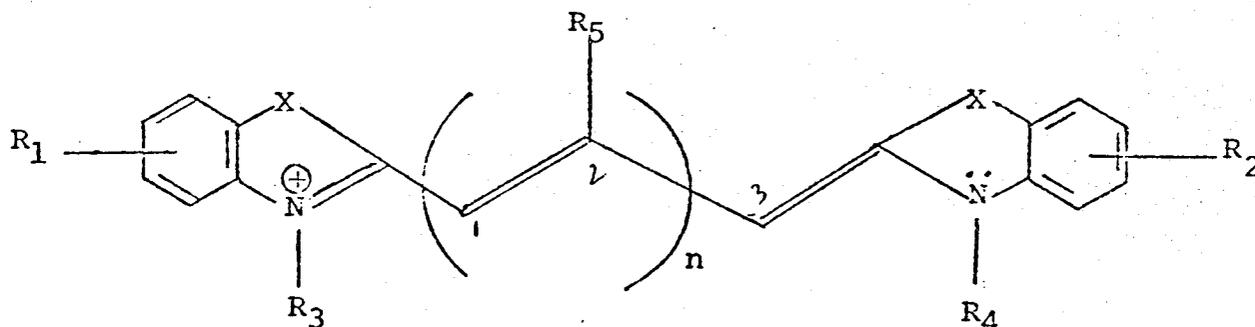
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

column 3, line 20;

column 5, line 55;

column 6, line 40;

substitute the following structural formula for the formula in the patent:



Signed and sealed this 6th day of March 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents