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3,512,966

**PROCESS OF ELECTROPHOTOGRAPHIC
RECORDING EMPLOYING PERSISTENT
ORGANIC PHOTOCONDUCTIVE COM-
POSITIONS**

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ABSTRACT OF THE DISCLOSURE

Photoconductive members containing an organic photoconductor, dyestuff sensitizer, and an activator selected from the group consisting of organic carboxylic acids, nitrophenols, nitroanilines, and carboxylic acid anhydrides, require only extremely short exposure times, have relatively long persistent conductivity and the persistent conductivity can rapidly be erased by heat.

These photoconductive members are highly useful in electrophotographic processes requiring persistent photoconductivity.

This invention relates to organic photoconductors and, more particularly, to organic photoconductive compositions for use in processes in which the conductivity of the photoconductor must persist after exposure of the photoconductor to light.

An example of such a "persistent photoconductivity" process comprises exposing an inorganic photoconductive phosphor, such as zinc cadmium sulfide to a light pattern, whereby a latent conductivity image is formed in the exposed areas of the phosphor. The phosphor then is electrostatically charged in the dark and an electrostatic pattern is formed on the non-conductive areas of the phosphor. The electrostatic charge pattern is developed with toner by one of the conventional methods.

Most of these inorganic photoconductors exhibit only short persistence and the other known materials either have the same disadvantage or other disadvantages, such as slow exposure speed and non-erasable persistence. For example, the prior art persistent organic photoconductor of Example I has slow exposure speed and, the persistent material of U.S. Pat. 3,113,022 is not only slow, but the persistence cannot be erased.

It has now been found that organic photoconductive compositions, which contain both a dyestuff and an activator selected from the group consisting of organic carboxylic acids, nitrophenols, nitroanilines, and carboxylic acid anhydrides, require only extremely short exposure times, have relatively long persistent conductivity and the persistent conductivity can rapidly be erased by heat. The organic photoconductive compositions of the present invention can be used in the above-described process of exposure, charging, and developing, or the compositions can be used in the persistent photoconductive process described in the copending application Ser. No. 474,583, filed July 26, 1965. Further, these materials can be used in conjunction with a toner transfer process, in which the toner of the developed image on the photoconductive composition is transferred to paper, and in conjunction with a charge transfer process in which the electrostatic charge pattern is transferred to a dielectric paper.

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Examples of organic photoconductors which can be used in the present invention include what can be termed "small molecule" photoconductors dispersed in a binder, and polymeric photoconductors which can be self supporting.

The "small molecule" photoconductors include the following: oxadiazoles: 2,5 - bis[4'-diethylaminophenyl]-1,3,4 - oxadiazole, 2,5 - bis - [4' - (n - propylamino) - 2'-chlorophenyl - (1')]-1,3,4 - oxadiazole or 2,5 - bis - [4'-N - ethyl - N - n - propylaminophenyl - (1')]-1,3,4 - oxadiazole; triazoles, e.g. 1 - methyl - 2,5 - bis - [4' - diethylaminophenyl] - 1,3,4 - triazole; imidazoles, e.g. 2 - (4' - dimethylaminophenyl) - 6 - methoxy - benzimidazole; oxazoles, e.g. 2 - (4' - chlorophenyl) - phenanthrene - (9'-10':4,5) - oxazole; thiazoles, e.g. 2 - (4' - diethylaminophenyl) - benzthiazole; thiophenes, e.g. 2,3,5 - triphenylthiophene; triazines, e.g. 3 - (4' - aminophenyl) - 5,6 - di-pyridyl - (2') - 1,2,4 - triazine or 3 - (4' - dimethylaminophenyl) - 5,6 - di(4'' - phenoxyphenyl) - 1,2,4 - triazine; hydrazones, e.g. 4 - dimethylaminobenzaldehyde isonicotinic acid hydrazone; styryl compounds: 2 - (4' - dimethylaminostyryl) - 6 - methyl - 4 - pyridone, 2 - (4' - dimethylaminostyryl) - 5 - (or 6) - amino - benzimidazole or bis(4 - dimethylaminostyryl) ketone; azomethines, e.g. 4 - dimethylaminobenzylidene - β - naphthylamine; acylhydrazones: 4 - dimethylaminobenzylidenebenzhydrazide, 4 - dimethylaminobenzylidene - 4 - hydroxybenzoic hydrazide, 4 - dimethylaminobenzylidene - 2 - aminobenzoic hydrazide, 4 - dimethylaminobenzylidene - 4 - methoxybenzoic hydrazide, 4 - dimethylaminobenzylidene - iso - nicotinic hydrazide, 4 - dimethylaminobenzylidene - 2 - methylbenzoic hydrazide; pyrazolines: 1,3,5 - triphenylpyrazoline, 1,3 - diphenyl - 5 - [4' - methoxyphenyl]-pyrazoline, 1,3 - diphenyl - 5 - [4' - dimethylaminophenyl]pyrazoline; 1,5 - diphenyl - 3 - styrylpyrazoline; 1-phenyl - 3 - [4' - dimethylaminostyryl] - 5 - [4' - dimethylaminophenyl] - pyrazoline; imidazolones; 4 - [4'-dimethylaminophenyl] - 5 - phenylimidazolone, 4 - furfuryl - 5-phenylimidazolone; imidazolethiones: 4 - [4' - dimethylaminophenyl] - 5 - phenylimidazolethione, 1,3,4,5 - tetraphenylimidazolethione; 1,3,5 - triphenyl - 4 - [4' - dimethylaminophenyl]imidazolethione; 1,3,4 - triphenyl - 5 - furfurylimidazolethione; benzimidazoles; 2 - [4' - dimethylaminophenyl] - benzimidazole, 1 - methyl - 2 - [4' - dimethylaminophenyl] - benzimidazole, 1 - phenyl - 2 - [4' - dimethylaminophenyl] - benzimidazole; benzoxazoles, e.g. 2 - [4' - dimethylaminophenyl] - benzoxazole; and benzo-thiazoles, e.g. 2 - [4' - dimethylaminophenyl] - benzo-thiazole.

Suitable binders for use with the small molecule photoconductors comprise polymers having fairly high dielectric strength and which are good electrically insulating film-forming vehicles. Materials of this type comprise styrene-butadiene copolymers; silicone resins; styrene-alkyd resins; soya-alkyd resins; polyvinyl chloride; polyvinylidene chloride; vinylidene chloride-acrylonitrile copolymers; polyvinyl acetate; vinyl acetate-vinyl chloride copolymers; polyvinyl acetals, such as polyvinyl formal; polyacrylic and methacrylic esters, such as polymethyl methacrylate, poly - n - butyl methacrylate, polyisobutyl methacrylate, etc.; polystyrene; nitrated polystyrene; polymethylstyrene; isobutylene polymers; polyesters, such as polyethylene - alkaryloxyalkylene terephthalate; phenol-formaldehyde resins; ketone resins; polyamide; polycarbonates; etc. Methods of making resins of this type have been described in the prior art, for example, styrene-alkyd

resins can be prepared according to the method described in U.S. Pat. 2,361,019 and 2,258,423.

Suitable polymeric photoconductors are, for example, poly - N - acrylylphenothiazine, poly - N-(β -acryloxyethyl)-phenothiazine, poly - N - (2-acryloxy propyl)-phenothiazine, polyallylcarbazole, poly-N-2-acryloxy-2-methyl-N-ethyl carbazole, poly - N(2 - p-vinylbenzoyl-ethyl)-carbazole, poly-N-propenylcarbazole, poly-N-vinylcarbazole, poly - N - 2-methacryloxypropyl carbazole, poly-N-acrylyl-carbazole, poly-4 - vinyl - p-(-Ncarbazy)-toluene, poly (vinylanisal acetophenone), and polyindenes.

Other suitable polymeric photoconductors are those disclosed in copending applications, Ser. No. 332,835, filed Dec. 23, 1963; Ser. No. 404,902, filed Oct. 19, 1964, now U.S. Pat. No. 3,294,763, and Ser. No. 304,696, filed Aug. 26, 1963, now U.S. Pat. No. 3,268,550.

If desired, the monomers of the polymeric photoconductors can be copolymerized with each other or with other monomers, such as vinyl acetate, methylacrylate, vinylcinnamate, polystyrene, 2-vinylpyridine.

Sensitivity of the above organic photoconductors can be extended from the ultraviolet into the visible range of the electromagnetic spectrum by the addition of a dyestuff sensitizer and preferably a cationic dyestuff sensitizer. In addition, according to the present invention, the persistent photoconductivity properties of these organic photoconductors can be improved by the addition of an activator selected from the group consisting of organic carboxylic acids, nitrophenols, nitroanilines, and carboxylic acid anhydrides. In general, the quantity of the dyestuff sensitizer added to the photoconductor ranges from about 0.01 to about 5%, with the preferred range being from 0.5 to about 3%. The quantity of activator added to the organic photoconductor varies according to the compound used and ranges from about 0.1 to about 10%. The preferred amount for most of the compounds is about 4%. Mixtures of several activators and several dyestuffs may be used in place of a single activator in a single dyestuff.

Examples of the dyestuff sensitizers are triarylmethane dyestuffs such as Malachite Green, Brilliant Green, Victoria Blue B, Methyl Violet, Crystal Violet, Acid Violet 6B; xanthene dyestuffs, namely rhodamines, such as Rhodamine B, Rhodamine 6G, Rhodamine G Extra, and Fast Acid Eosin G, as also phthaleins such as Eosin S, Eosin A, Erythrosin, Phloxin, Rose Bengal, and Fluorescein; thiazine dyestuffs such as Methylene Blue; acridine dyestuffs such as Acridine Yellow, Acridine Orange and Trypaflavine; and cyanine dyestuffs such as Pinacyanol, Cryptocyanine and Cyanine.

Activators of the present invention are: organic carboxylic acids, such as benzoic acid, phthalic acid and tetrachlorophthalic acid, dibromomaleic acid, 2-bromobenzoic acid, 2-nitrobenzoic acid, 3-nitrobenzoic acid, 4-nitrobenzoic acid, 3-nitro-4-ethoxybenzoic acid, 2-chloro-4-nitrobenzoic acid, 3 - nitro-4-methoxybenzoic acid, 4-nitro-1-methylbenzoic acid, 2-chloro-5-nitrobenzoic acid, 3-chloro-6-nitrobenzoic acid, 4-chloro-3-nitrobenzoic acid, 5-chloro-3-nitro-2-hydroxybenzoic acid, 4 - chloro-2-hydroxybenzoic acid, 2,4-dinitrobenzoic acid, 2-bromo-5-nitrobenzoic acid, 2-cyanocinnamic acid, 2,4-dichlorobenzoic acid, 3,5-dinitrobenzoic acid, 3,5-dinitrosalicylic acid, malic acid; nitrophenols, such as 4-nitrophenol, and picric acid; carboxylic acid anhydrides such as maleic anhydride, phthalic anhydride, tetrachlorophthalic anhydride, and dibromomaleic anhydride; and nitroanilines, such as 2,2', 4,4', 6,6' - hexanitrodiphenylamine, picramide, 2,4-dinitroaniline, 3-chloro-6-nitroaniline, picramic acid, p-nitroaniline, 2,6-dichloro-4-nitroaniline, 2-methyl-4-nitroaniline, 4 - chloro-2-nitroaniline, 4 - amino-4-nitrobenzoic acid, p-(2,4-dinitroaniline)phenol, 2, 4 - dinitrophenylamine, 2-nitrodiphenylamine.

For use in the previously mentioned persistent photoconductivity processes, the organic photoconductive com-

position is carried on a support having a surface resistivity of about 1 to 10 megohms per square. Examples of such supporting materials are conductive paper and metals, such as copper, aluminum, zinc, tin, iron and lead. If the process includes contact reflex exposure instead of optical exposure, the support should be substantially transparent. A layer of polyethylene terephthalate coated with a thin layer of aluminum or copper and NESA glass are examples of transparent supports.

Solvents for preparing coatings of the organic photoconductive compositions include benzene, toluene, acetone, 2-butanone, chlorinated hydrocarbons, e.g., methylene chloride, ethylene chloride, etc., ethers, e.g., tetrahydrofuran, or mixtures of these solvents, etc. The prepared coatings can be applied on the support in any well known manner, such as doctor-blade coating, spin-coating, dip-coating, and the like.

Because these organic photoconductive compositions exhibit persistent conductivity after exposure, this persistent conductivity must be erased before the photoconductive composition can be re-exposed. Otherwise, the second exposure will be superimposed on the first exposure. This erasure is accomplished, according to the present invention, by heating the photoconductive composition for not longer than about 5 seconds. The preferred erasure temperature range is about 100° C. to about 150° C. with the preferred temperature being 125° C. There are a number of suitable heating means for erasing the persistent conductivity in the photoconductor. For example, a heating element, such as a plate, can be used or the photoconductor can be passed through heated rollers at a linear velocity of 20 feet per minute, both the plate and the rollers being within the above temperature range. Other heating means includes an A.C. electric field to cause induction heating.

The general nature of the invention having been set forth, the following examples are now presented as illustrations, but not limitations, of the methods of making the compositions of the invention and the method and means of using the compositions of the invention. The use of the term "negative toner" in the following examples means toner which is attracted to a positive electrostatic charge or which is negatively charged. "Positive toner" means toner which is positively charged or attracted to a negative electrostatic charge.

EXAMPLE I

The following is a comparison between essentially the same persistent conductive composition of Example I of British Pat. 977,200 and the same composition to which is added one of the activators of the present invention.

Two photoconductive compositions were prepared. One composition contained 1 gm. of polyvinyl chloride (dissolved in tetrahydrofuran), 1 gm. of 2,5-bis(4'-dimethylaminophenyl-1')-1,3,4-oxadiazole (dissolved in 1,1',2,2'-tetrachloromethane) and .01 gm of a dyestuff, Rhodamine B. The other photoconductive composition was the same except it included .06 gm. of 2,2',4,4',6,6'-hexanitrodiphenylamine, one of the activators of the present invention. (In the British example, the oxadiazole contained diethyl - substituents rather than dimethyl - substituents.) Both of the photoconductive compositions were coated on aluminum slides with a doctor blade set at a 5 mil wet gap.

These photoconductor slides were compared both in the xerographic mode (i.e. charging, exposing, and developing) and the persistent mode (i.e. exposing, charging, and developing). In the xerographic mode, both photoconductors were exposed to a 40 watt incandescent bulb at 40 cm. through a positive master. In the persistent mode, the same master and distance were used, but the exposure of the photoconductors was with a 375 watt GE photoflood EBR. The persistent images remaining in the photoconductors from one exposure were erased by heating at about 125° C. for about 5 seconds prior to the next

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exposure. For the comparison, the cascade developed images on the photoconductor were transferred to paper. The results of this comparison for various exposure times are shown in the following tables:

XEROGRAPHIC MODE

Exposure time (in seconds)	Quality of copy	
	Dyestuff only	Dyestuff+activator
0.25-----	Poor-----	Fair.
0.5-----	Fair-----	Fair.+
1.0-----	Good-----	Good.+
2.0-----	Very good-----	Very good.+

PERSISTENT MODE

Exposure time (in seconds)	Quality of copy	
	Dyestuff only	Dyestuff+activator
0.1-----	No image-----	Good.
0.25-----	do-----	Do.
0.5-----	Fair-----	Very good.

The above tables show that, in the xerographic mode, the photoconductive composition of the present invention gave only slightly better image quality than the photoconductive composition containing dyestuff only, whereas, in the persistent mode, the photoconductive composition of the present invention was at least 5 to 10 times better than the photoconductive composition containing the dyestuff only.

EXAMPLE II

A photoconductor of the present invention was prepared in the following manner: 40 mg. of 3,5-dinitrobenzoic acid was dissolved in 14.3 grams of a 5.3% polyvinyl carbazole solution of 1,2-dichloroethane. To this was added 10 mg. of Malachite Green oxalate dye which was dissolved in 1.0 ml. of 50% each of methylethyl ketone and methyl alcohol. To insure proper mixing, the prepared solution was agitated for about one hour. Then, the solution was coated on an aluminum plate using a doctor blade set at 7 ml. wet gap. The resulting dried photoconductive coating was approximately 9 microns thick. The prepared photoconductor was exposed to a 40 watt incandescent lamp at a distance of 14 inches through a positive master for one second. An insulating material of polyvinyl acetate which was part of a continuous roll was brought into contact with the exposed photoconductor and the two of them passed between a pair of conductive rollers having a 700 volt D.C. potential. The polarity of the roller in contact with the photoconductor was negative. Immediately after passing through the roller and with the voltage still applied, the insulating material was separated from the photoconductor and a negative electrostatic pattern was formed on the insulating material corresponding to the exposed areas of the photoconductor. The exposed photoconductor was repeatedly brought into contact with other portions of the continuous roll of insulating material and passed through the rollers with the voltage applied (as stated above) until 48 positive electrostatic charge patterns were prepared. These charge patterns then were developed with negative toner using a biased magnetic brush to yield 48 positive copies of the positive image.

EXAMPLE III

The photoconductor of Example II was prepared. This photoconductor was exposed to a 40 watt incandescent lamp at a distance of 14 inches through a positive master for 0.25 second. Then, the exposed photoconductor was passed under a corona discharge unit having a potential of +6000 volts and a positive electrostatic charge pattern formed on the surface of the exposed photoconductor. The exposed and charged photoconductor was cascade developed with a negative toner, the toner being attracted to the unexposed areas to yield a positive copy.

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EXAMPLE IV

Polyvinyl carbazole, 0.7 g., was dissolved in 10 ml. of 1,2-dichloroethane. To this was added 7 mg. picric acid and 7 mg. Victoria Blue B dye which was dissolved in 0.5 ml. of 50% each methyl ethyl ketone and methyl alcohol. The solution was coated on an aluminum plate using a doctor blade set at a 7 mil gap. The dried photoconductor was exposed for 2 seconds to 100 watt incandescent lamp at a distance of 12 inches through a negative master. An insulating sheet of polyvinyl acetate was brought into contact with the exposed coating and the two of them passed between a pair of conductive rollers having an applied potential of 600 volts, the polarity of the roller in contact with the photoconductor being positive. Immediately after passing through the rollers and with the voltage still applied, the insulating sheet and photoconductor were separated and a positive electrostatic pattern corresponding to the exposed areas of the photoconductor is formed on the insulating sheet. The electrostatic image on the insulating sheet then was developed by magnetic brush carrying a positive toner to form unfixed positive copy. A sheet of common stock paper was brought into contact with the unfixed toner image and by applying pressure, the toner image was transferred to the paper and fixed by heating.

EXAMPLE V

A solution was prepared by dissolving 20 mg. of tetrachlorophthalic anhydride and 5 mg. of Malachite Green oxalate in 7 g. of a 5.3% polyvinyl carbazole solution of dichloroethane. The solution was coated on an aluminum plate using a doctor blade set at a 7 mil wet gap. The prepared photoconductor then was exposed to a 100 watt incandescent lamp for 5 seconds at a distance of 14 inches through a positive image. The exposed photoconductor was brought into contact with an insulating sheet of polyvinyl acetate and the two of them passed between conductive rollers having an applied voltage of 900 volts, the polarity of the roller in contact with the photoconductor being negative. Immediately after passing through the conductive rollers and with the voltage still applied, the photoconductor and insulating sheet were separated and a negative electrostatic charge pattern was formed on the insulating sheet corresponding to the exposed areas of the photoconductor. The electrostatic charge pattern was cascade developed with a negative toner composition to form a positive copy.

EXAMPLE VI

The photoconductor of Example V was exposed to a 40 watt incandescent lamp for two seconds at a distance of 12 inches through a positive master. Following this, the photoconductor was electrostatically charged with a corona discharge unit having a potential of -6000 volts. The negative electrostatic charge pattern which formed on the photoconductor was cascade developed with positive toner and the unfixed toner image was transferred to paper.

EXAMPLE VII

Instead of using a polymeric photoconductor, a small molecule photoconductor was prepared as follows: 0.5 g. of 1-phenyl-3-(4'-dimethylaminostyryl) - 5 - (4''-dimethylaminophenyl)pyrazoline was dissolved in a 10% solution of polystyrene in benzene. To this solution was added 10 mg. of 3,5-dinitrobenzoic acid and 5 mg. of Malachite Green, which was dissolved in 0.5 ml. of 50% each methylethyl ketone and methyl alcohol. This solution was coated on an aluminum strip using a doctor blade set at a 5 mil wet gap. The prepared photoconductor was exposed for 5 seconds to a 25 watt incandescent lamp at a distance of 14 inches through a negative image. An insulating sheet of polystyrene was brought into contact with the photoconductor and the two of them passed through conductive rollers with an applied potential of

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700 volts, the polarity of the rollers in contact with the photoconductor being positive. Immediately after passing through the rollers and with the voltage still applied, the insulating sheet was separated from the photoconductor and a positive electrostatic charge pattern corresponding to the exposed area of the coating was formed on the insulating sheet. The electrostatic charge pattern was developed by a magnetic brush carrying a negative toner to form a positive copy.

EXAMPLE VIII

The photoconductor of Example VII was prepared. This photoconductor was exposed through a positive master for 0.25 second to a 250 watt photoflood light source at a distance of 14 inches. The photoconductor then was electrostatically charged with a corona discharge unit having a potential of +6000 volts and a positive electrostatic charge pattern formed on the photoconductor. The charge pattern was cascade developed with negative toner to yield a positive copy of the master.

EXAMPLE IX

Another small molecule photoconductor was prepared by dissolving 0.5 g. of 1-phenyl-3-(4'-dimethylaminostyryl)-5-(4'-dimethylaminophenyl)pyrazoline in 2.5 g. of polystyrene (20% soln.) in benzene. To this solution was added 0.03 g. 4,4',6,6'-tetranitrodiphenic acid and 0.005 g. Malachite Green oxalate in 5 ml. of dichloroethane. The solution was coated on an aluminum plate with a 8 mil gap. The prepared photoconductor on the plate was exposed for 5 seconds to a 40 watt incandescent lamp at a distance of 12 inches through a positive master. After bringing an insulating sheet which was part of a continuous roll of polyvinyl acetate coated paper in contact with the photoconductor, the photoconductor and the sheet were passed between conductive rollers with an applied potential of 900 volts, the rollers in contact with the photoconductor being negative. Immediately after passing through the rollers and with the voltage still applied, the sheet separated from the coated slide and a negative electrostatic pattern corresponding to the exposed areas of the coating was formed on the insulated sheet. Ten electrostatic patterns were formed by bringing the exposed photoconductor sequentially into contact with other portions of the continuous roll and passing them through the conductive rollers, as described above. After ten electrostatic patterns were formed, these patterns were developed by cascade development using a negative toner to form ten positive copies.

EXAMPLE X

The photoconductor of Example IX was prepared. This photoconductor was exposed through a positive master to a 40 watt incandescent lamp at a distance of 12 inches for 0.5 second. Using a corona discharge unit having a potential of +6000 volts, a positive electrostatic charge was applied to the exposed photoconductor. The electrostatic charge pattern which formed was cascade developed with negative toner and the toned image was transferred to paper and fixed by heating.

EXAMPLE XI

A photoconductor was prepared by dissolving 0.13 g. of 1,3-diphenyl-5-(4'-dimethylaminophenyl)pyrazoline in 2.5 g. of 20% polystyrene in benzene. To this solution was added 0.005 g. of picric acid and 0.005 g. Malachite Green oxalate in 5 ml. of 1,2-dichloroethane. The solution was coated on an aluminum plate with a 5 mil gap. The prepared photoconductor on the plate was exposed for 10 seconds to a 100 watt incandescent lamp at a distance of 12 inches through a negative master. After bringing an insulating sheet of polyvinyl acetate in contact with the exposed photoconductor, the photoconductor and the sheet were passed between conductive rollers with an applied potential of 900 volts, the rollers in contact with the photoconductor being positive. Immediately after passing

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through the rollers and with the voltage still applied, the sheet separated from the photoconductor and a positive electrostatic pattern corresponding to the exposed areas of the coating was formed on the insulated sheet. The electrostatic charge pattern was developed by magnetic brush development using a negative toner to form a positive copy.

EXAMPLE XII

The photoconductor of Example XI was prepared. This photoconductor was exposed through a positive master to a 40 watt incandescent lamp at a distance of 12 inches for two seconds. Using a corona discharge unit having a potential of +6000 volts, an electrostatic charge was applied to the exposed photoconductor. The positive electrostatic charge pattern which formed was cascade developed with negative toner to yield a positive copy of the master.

EXAMPLE XIII

A solution of 0.8 g. of 1, 3, 4, 5-tetraphenyl-imidazole-2-thione, 0.5 g. of methylal of polyvinyl alcohol in 2 g. of methylethyl ketone was prepared. To this solution was added 0.03 g. 4,4',6,6'-tetranitrodiphenic acid and 0.008 g. Ethyl Violet in 0.5 ml. of 50% each methylethyl ketone and methanol. The solution was coated on an aluminum plate with a 3 mil gap. This photoconductor was exposed for 1 second to a 375 watt incandescent lamp at a distance of 12 inches through a negative master. After bringing an insulating sheet in contact with the photoconductor, the photoconductor and the sheet were passed between conductive rollers with an applied potential of 600 volts, the rollers in contact with the photoconductor being positive. Immediately after passing through the rollers and with the voltage still applied, the sheet was separated from the photoconductor and a positive electrostatic pattern corresponding to exposed areas of the coating was formed on the insulated sheet. The electrostatic charge pattern was developed by magnetic brush development using a negative toner to form a positive copy.

EXAMPLE XIV

A photoconductive formulation was prepared by adding 14.3 g. of a 5.3% polyvinyl carbazole solution of 1,2-dichloroethane to 1 ml. of a solution of 7.5 mg. of Malachite Green oxalate in a 50% methylethyl ketone and methyl alcohol, having dissolved therein 30 mg. of 3,5-dinitrobenzoic acid. The photoconductive formulation was agitated for one hour. Then, the photoconductor was coated on a semi-transparent aluminized polyethylene terephthalate using a doctor blade at 8 mil wet gap. The resulting dried photoconductive coating was roughly 10 microns thick. This photoconductor was placed face down in intimate contact on a positive master and exposed to filtered light (4,000 to 5,800 Å.) from a 500 watt incandescent lamp at a distance of 14 inches. An insulating material of polyvinyl acetate, which was part of a continuous roll, was brought into contact with the contact reflex exposed photoconductor and the two of them passed between a pair of conductive rollers having a 900 volt potential. The polarity of the roller in contact with the photoconductor was negative. Immediately after passing through the roller and with the voltage still applied, the insulating material was separated from the photoconductor and a negative electrostatic pattern was formed on the insulating material corresponding to the exposed areas of the photoconductor. This charge pattern then was developed with a negative toner using a biased magnetic brush to yield a positive copy of the master. Ten copies from the same exposure were made by the above procedure.

EXAMPLE XV

A photoconductor having the same formulation as Example II, was exposed for 8 seconds to a negative master

by an incandescent light source of 40 watts at a distance of 14 inches. The exposed photoconductor was attached to the upper roller of a pair of conductive rollers having a 700 volt potential across them, the upper roller being at a positive potential. A roll of insulating material of polyvinyl acetate was positioned to feed between the two rollers. By rotating the upper roller 100 times, 100 electrostatic patterns were formed on the insulating material. These positive charge patterns were developed with a magnetic brush using negative toner to form 100 positive copies of the negative master.

EXAMPLE XVI

To obtain copies of two different masters, the photoconductor of the formulation of Example II, was exposed to the positive master of Example II and the procedure of that example was followed to make a copy of the master. The exposed photoconductor having a persistent conductivity image therein, then was passed through heated rollers at 120° C. at a linear velocity of 20 feet per minute. The heating erased the persistent conductivity image in the photoconductor. This photoconductor then is exposed to the negative master of Example IV and the procedure of that example followed to form a copy of that master.

EXAMPLE XVII

A photoconductive composition was prepared consisting of 0.5 gm. of 1,3-diphenyl-5-(p-dimethylamino)-phenylpyrazoline, 2 gms. of 10% polystyrene, 5 ml. of dichloroethane, 0.03 gm. of 2,2',4,4',6,6'-hexanitrodiphenylamine and 0.005 gm. of Malachite Green oxalate. This photoconductive composition was coated on an aluminum slide using a doctor blade set at a 7 mil wet gap. The prepared photoconductor was exposed for one second to a 40 watt tungsten bulb at 14 inches through a positive master. The exposed photoconductor was brought into contact with an insulating sheet of polyvinyl acetate and the two of them passed between conductive rollers having applied voltage of 600 volts, the polarity of the roller in contact with the photoconductor being negative. Immediately after passing through the conductive rollers and with the voltage still applied, the photoconductor and insulating sheet were separated and a negative electrostatic charge pattern was formed on the insulating sheet corresponding to the exposed areas of the photoconductor. The electrostatic charge pattern was magnetic brush developed with a negative charged toner to form a positive copy of the master.

EXAMPLE XVIII

A photoconductive composition was prepared by using 0.5 gm. of 1,3,5-triphenyl pyrazoline, 5 gms. of 10% polystyrene, 0.03 gm. of 2,2',4,4',6,6'-hexanitrodiphenylamine, 0.005 gm. Malachite Green oxalate, and 5 ml. of dichloroethane. The photoconductive composition was coated on an aluminum slide with a doctor blade set at a 7 mil wet gap. Using the same procedure of Example XVII except the prepared photoconductor was exposed for 4 seconds, a negative electrostatic charge pattern was formed on the insulating sheet. This charge pattern was developed with negatively charged toner using cascade development to yield a positive copy of the master.

EXAMPLE XIX

A photoconductive composition was prepared which included 14.3 gms. of 7% polyvinyl carbazole, .04 gm. of 2,2',4,4',6,6'-hexanitrodiphenylamine and 0.01 gm. of Malachite Green oxalate. The photoconductive composition was coated on an aluminum slide using a doctor blade set at a 7 mil wet gap. The prepared photoconductor was exposed to a 40 watt tungsten bulb for 2 seconds at a distance of 12 inches through a negative master. The exposed photoconductor was brought into contact with an insulated sheet of polyvinyl acetate. The two of them

passed between conductive rollers having applied voltage of 900 volts, the polarity of the roller in contact with the photoconductor being positive. Immediately after passing through the conductive rollers and with the voltage still applied, the photoconductor and the insulating sheet were separated and a positive electrostatic charge pattern was formed on the insulating sheet corresponding to the exposed area of the photoconductor. The electrostatic charge pattern was cascade developed with negative toner to form a positive copy of the negative master.

EXAMPLE XX

A photoconductor was prepared in the following manner: 40 mg. of 3,5-dinitrobenzoic acid was dissolved in 14.3 gms. of a 7% polyvinyl carbazole solution of 1,2-dichloroethane. To this was added 10 mg. of Malachite Green oxalate dye which was dissolved in 1 ml. of 50% each of methyl ethyl ketone and methyl alcohol. This prepared solution was coated on a stainless steel substrate using a doctor blade set at 7 mil wet gap. The prepared photoconductor was exposed to a 40 watt tungsten bulb at a distance of 14 inches to a positive master for 2 seconds. An insulating material of polyvinyl butyral having a high calender paper base and being part of a continuous roll was brought into contact with the exposed photoconductor and the two of them passed between a pair of conductive rollers having a 700 volt D.C. potential. The polarity of the roller in contact with the photoconductor was negative. Immediately after passing through the rollers and with the voltage still applied, the insulating material was separated from the photoconductor and a negative electrostatic charge pattern was formed on the insulating material corresponding to the exposed area of the photoconductor. The exposed photoconductor was brought into contact with other portions of the continuous roll of insulating material and passed through the rollers with the voltage applied (as stated above) until 5 negative electrostatic charge patterns were prepared. These charge patterns were developed with negative toner using a bias magnetic brush to yield 5 positive copies of the positive master. The quality of the fifth copy was excellent.

EXAMPLE XXI

A photoconductive composition was prepared by using 0.5 gm. 1-formyl-2,5-(bis-p-dimethylaminophenyl)-1,3,4-triazole, 5 gms. of 10% polyvinyl formal, 0.02 gm. 2,2',4,4',6,6'-hexanitrodiphenylamine, 0.005 gm. Malachite Green oxalate and 5 ml. of methanol. This photoconductive composition was coated on an aluminum slide using a doctor blade set at 7 mil wet gap. The prepared photoconductor was exposed for 0.5 second to a 250 watt photoflood lamp at a distance of 14 inches through a positive master. The exposed photoconductor was negatively electrostatically charged with a corona discharge unit having -6500 volt potential. The electrostatic charge pattern formed on the photoconductor was cascade developed with positively charged toner to yield a positive copy of the positive master.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that variations in form may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. In the process of forming a latent conductive pattern in an organic photoconductive layer and subsequently erasing said conductive pattern, the steps comprising:

selectively exposing an uncharged organic photoconductive layer comprising polyvinyl carbazole, a dye-stuff sensitizer, and a dinitro-substituted benzoic acid, to electromagnetic radiation to which said layer is sensitive, whereby a latent conductive pattern is produced in the exposed areas of said layer and remains after the electromagnetic radiation is removed;

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uniformly electrostatically charging said photoconductive layer to form an electrostatic charge pattern corresponding to the non-conductive areas of the photoconductive layer;

developing said photoconductive layer with a developer material to form a visible pattern;

transferring said visible pattern from said photoconductive layer and cleaning any residual developer material from the photoconductive layer; and

heating the photoconductive layer at a temperature within a range of about 100–150° C. and not longer than about 5 seconds whereby said latent conductive pattern is erased.

2. In the process of forming a latent conductive pattern in an organic photoconductive layer and subsequently erasing said conductive pattern, the steps comprising:

selectively exposing an organic photoconductive layer comprising polyvinyl carbazole, a dyestuff sensitizer, and a dinitro-substituted benzoic acid, to electromagnetic radiation to which said layer is sensitive, whereby a latent conductive pattern is produced in the exposed areas of said layer and remains after the electromagnetic radiation is removed;

bringing an insulating layer into contact with said photoconductive layer to induce an electrostatic charge pattern on the insulating layer corresponding to the conductive pattern in the photoconductive layer;

separating said insulating layer from said photoconductive layer and developing the insulating layer

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with a developing material to form a visible pattern; and

heating the photoconductive layer, in the absence of developer material on the surface of the photoconductive layer, at a temperature within a range of about 100–150° C. and not longer than about 5 seconds whereby said latent conductive pattern is erased.

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