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(54) A PHOTOCONDUCTIVE COMPOSITION FOR USE IN THE PREPARATION OF AN ELECTROPHOTOGRAPHIC MATERIAL

(71) We, KONISHIROKU PHOTO INDUSTRY CO. LTD., a Japanese Company of 1—10, 3-chome, Nihonbashi-Muro-Machi, Chuo-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a photoconductive composition for use in the preparation of an electrophotographic material which is particularly suitable for a method of forming an electrostatic image in which an exposure by activation light is effected prior to an imagewise exposure on the electrophotographic (photoreceptor) material. Such materials generally comprise a conductive support and a photosensitive layer supported thereon which includes a resin and fine photoconductive powder dispersed therein.

In a widely known prior art electrophotographic process a photoreceptor material is provided with photosensitivity by charging by means of known methods, and then directly formed thereon with an electrostatic image by effecting an imagewise exposure. Alternatively, the electrostatic image is electrostatically transferred on a sheet of transfer paper, then developed by means of a dry or wet developer and fixed to produce a visible image. Recently, however, an electrophotographic process has been developed in which the electrostatic image formed on the photoreceptor material is developed by a developer to produce a powdered image, which is electrostatically transferred on a sheet of transfer paper and then fixed to form the visible image.

To produce the visible image with the aid of such electrophotographic process, it is first of all necessary to form an electrostatic image which is excellent in characteristics with respect to charging, dark decay and light decay.

Further, a photoreceptor material particularly for use in an electrophotographic copying machine of the repeated transfer type is required to have characteristics in which it is free from wear or degradation without any reduction in quality of an image even after the repetitive use thereof for a great number of copies.

A photoconductive material preferably used in electrophotography is, for example, an inorganic photoconductive material such as selenium, xinc oxide, zinc sulphide, cadmium sulphide, cadmium selenide, cadmium sulphide selenide, mercury sulphide, titanium oxide or lead oxide; a photoconductive pigment such as metalfree phthalocyanine, copper phthalocyanine, cobalt phthalocyanine, nickel phthalocyanine, zinc phthalocyanine or lead phthalocyanine; or an organic photoconductive material such as poly-N-vinylcarbazole, anthracene or triallylamine derivatives. The inorganic photoconductive powder and the photoconductive pigment are particularly suitable for a photoreceptor material containing a binder resin and a powdered photoconductive material, i.e., photoconductive powder dispersed therein. The photoconductive powder usually used in electrophotography is on average more than 0.3 micron in grain size and thus relatively large. A photoreceptor material is further preferably used which contains as little resin relative to the photoconductive powder as possible in order to provide an efficient photoconductivity in the photoconductive powder. In other words, the photoreceptor material contains a small amount of resin and a relatively large-grain photoconductive powder dispersed therein because a photoreceptor with a rapid light decay is required in view of the fact that a high-speed reproduction capable of reproducing a great number of copies in a short time is commercially demanded because of a preferred tendency to the reproduction by means of an electrophotographic copying machine of the repeated transfer type. Such a photoreceptor indeed has the required rapid light decay, but poor characteristics with respect to charging, dark decay, image quality and wear resistance.

On the other hand, many efforts have been made to use a photoreceptor containing small grain photoconductive powder. Such a photoreceptor has excellent characteristics with respect to the charging, dark decay, image quality and wear resistance, but disadvantageously very poor with respect to the light decay. To overcome the drawbacks, proposals have been made in which a photoconductive powder having a large grain size is suitably mixed with a photoconductive powder having a small grain size, or a photosensitive layer dispersively containing the photoconductive powder of large granularity is combined in overlaid relationship with a photosensitive layer dispersively containing a photoconductive powder of small grain size, thereby providing a laminated photoreceptor. These proposals, however, do not produce a superimposed effect of the good properties of each, but only averaged properties. A protective layer is also often provided to protect the surface of the photoreceptor because it suffers from electric impact or mechanical wear in view of the fact that little resin is contained therein. This, on the contrary, causes the degradation of the light decay property and an increase in residual charges with the result of no achievement of a practically preferable photoreceptor.

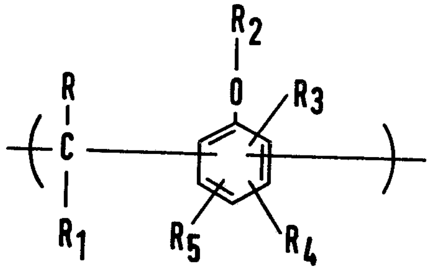
In published examined Japanese patent applications Sho 42—5912 and Sho 51-39538 or published unexamined Japanese patent application Sho 48—54946 there is, for example, already disclosed a method in which an overall exposure is performed on the photoreceptor prior to the charging and imagewise exposure steps to improve the wear resistance, i.e., one of the properties in the photoreceptor used in an electrophotographic copying machine of the repeated transfer type. Such a method is, however, intended to weaken a reduction in charge potential and an increase in dark decay caused by the repetition of the charging and exposure in the electrophotographic photoreceptor, and not to provide a positive improvement in properties of the light decay and image quality.

Further there is known a method of making an overall irradiation on a residual toner image by means of a cleaning lamp for easy cleaning prior to the removal of the toner by means of a cleaning brush and a method of making an overall exposure prior to the charging step to restore a memory in the photoreceptor. This method is particularly adapted for use in an electrophotographic copying machine of the repeated transfer type in which the photoreceptor is subjected to the charging and exposure steps to prepare an electrostatic image, which is developed by the developer to produce a toner image transferred onto paper with these steps repeated to reproduce a great number of images. This method is also primarily intended to clean the toner image, and not to improve various characteristics, particularly with respect to the light decay in the electrophotographic photoreceptor.

The present invention seeks, therefore, to provide a photoreceptor which is suitable for use in a method for forming an electrostatic image free from the above-mentioned drawbacks.

A photoreceptor formed according to the present invention is excellent in charging properties, mechanical wear resistance and electric impact resistance.

According to the present invention, there is provided a photoconductive composition for use in the preparation of an electrophotographic material, comprising a photoconductive phthalocyanine pigment dispersed in a phenol resin having the following general formula



where R and R_1 are a hydrogen atom or methyl radical; R_2 a hydrogen atom or epoxy radical; and R_3, R_4 and R_5 are a hydrogen atom, halogen atom or alkyl or alkoxy radical having 1 to 20 carbon atoms, at least one of R_3, R_4 and R_5 being an alkyl or alkoxy radical having 4 to 20 carbon atoms.

The photoreceptor defined above is particualrly suitable for use in a method of forming an electrostatic image comprising the steps of charging the photoreceptor, which is subjected to a dark decay after the charging step, effecting an exposure by activation light on the photoreceptor, and effecting an imagewise exposure on the photoreceptor. The exposure by activation light is effected prior to the imagewise exposure.

The activation light, originating from a halogen lamp, fluorescent lamp, tungsten lamp, mercury lamp or xenon lamp, has a spectral range including at least a portion of an absorption wavelength range in the photoconductive powder. The activation light exposure, which may be effected by the use of an electrostatic image cleaning lamp, is preferably 0.1 to 10 times as great in quantity of light as the imagewise exposure.

The photoconductive phthalocyanine pigment most suitably used in combination with the phenol resin in the photoreceptor of the present invention preferably is one containing metalfree phthalocyanine, copper phthalocyanine, cobalt phthalocyanine, lead phthalocyanine or zinc phthalocyanine, which is preferably 0.01 to 0.3 micron average grain size. The photoconductive powder of phthalocyanine pigments is blended with the resin in a ratio of from 1:3 to 1:20 by weight.

Thus, in the preferred method of using the photoreceptor of the present invention, this latter is subjected to the activation light exposure for activation and sensitization prior to the imagewise exposure and in a step including at least a portion of the charging step or dark decay. This allows the rapid light decay and thus high-speed reproduction of images in the electrophotographic copying machine of the repeated transfer type. Further, the use of a photoreceptor material, for example, containing a photoconductive phthalocyanine pigment and a phenol resin allows a high-speed reproduction of images and preparation of a lithographic plate by means of a laser beam.

The activation and sensitization of the photoreceptor according to this method makes it possible to use fine photoconductive powder, which is preferably from 0.01 to 0.3 micron in average grain size. This allows the formation of an electrostatic image which is excellent in properties with respect to charging and light decay. The electrostatic image is developed by a developer to form a visible image, which is very fine and has a high resolution because of the use of fine photoconductive powder.

The use of the fine photoconductive powder, on the other hand, allows the use of much resin with the result that a photoreceptor is obtained which is excellent in the charging property, mechanical wear resistance and electric impact resistance, and thus has a great resistance against an electrical impact such as corona discharge in an electrophotographic copying machine of the repeated transfer type.

Thus, it will be understood that the above method of operating with the photoreceptor of the present invention is quite superior to the methods in the prior art, for example, a method of operation in the known electrophotographic copying machine of the repeated transfer type, in which an overall exposure is effected by a cleaning lamp prior to the charging step to clean a residual toner image or restore the memory of the photoreceptor.

In a photoreceptor material containing fine photoconductive powder preferably 0.01 to 0.3 micron in average grain size, or having relatively much resin, the photoconductive powder is coated with the resin to a great extent. In this case, however the light decay is prevented by resins between the photoconductive particles with the result of low sensitivity. The previous exposure to activation light, however, causes the acceleration of the light decay with the result of high sensitivity. The reason why it is so is not apparent, but it is believed that carriers are produced depending on the number of photons and sufficiently captured in the trap (in this case, in the resin between the photoconductive particles) within the photoconductive layer, and the imagewise exposure causes the contribution of the carriers to the efficient light decay without any capture in the trap or causes the release of the carriers already captured by the imagewise exposure with the superimposing effect on the light decay.

Other objects and advantages will be apparent when reading the following detailed description made by way of examples in conjunction with the accompanying drawings in which:—

Fig. 1 is a graph showing electrostatic characteristics of photoreceptor materials formed as embodiments of the invention, in which an exposure by activation light is effected thereon at various times;

Figs. 2*a* to 2*d* are sectional views showing the construction of photoreceptors according to the invention and the steps by which a visible image is formed;

Fig. 3 is an absorption spectrum of a photoreceptor material incorporating ε-type copper phthalocyanine by means of a xenon lamp;

Fig. 4*a* is a graph showing the electrostatic characteristic of a sample of the photoreceptor material of example 1 described below; and

Fig. 4*b* is a graph showing the electrostatic characteristic of a sample photoreceptor for comparison in the example 1;

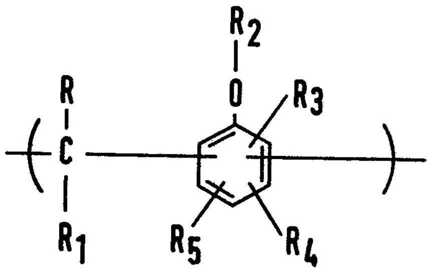
Fine photoconductive powder used in the present invention is, for example, made of a photoconductive phthalocyanine pigment disclosed in published examined Japanese patent specifications Sho 48—34189, 49—4338, 49—17535 and published unexamined Japanese patent specifications Sho 47—30328, 47—30329, 50—38543, 51—23738.

The phthalocyanine pigment used in the present invention is indicated by the general formula $(C_8H_4N_2)_4Rn$, where R is an hydrogen atom, deuterium, lithium, sodium, potassium, copper, silver, beryllium magnesium, calcium, zinc, cadmium, barium, mercury, aluminum, gallium, indium, lanthanum, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, titanium, tin, hafnium, lead, thorium, vanadium, antimony, chromium, molybdenum, uranium, manganese, iron, cobalt, nickel, rhodium, palladium, osmium or platinum, and n is 0 to 2.

It is preferable to select α, β, γ, π, χ or ε-type (crystalline form) metalfree phthalocyanine or metallic phthalocyanine such as copper, cobalt, lead or zinc phthalocyanine, which is preferably 0.01 to 0.3 micron in average grain size. A greater grain size is not suitable for the present invention because the powder is liable to wear or degradation upon exposure to light and/or corona discharge. A smaller grain size is, on the other hand, also not suitable because of degraded photoconductivity.

The resin (serving as a binder) used in a photoreceptor material according to the present invention is a phenol resin.

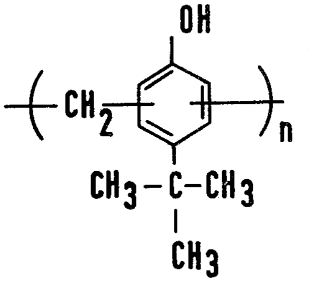
As mentioned above, according to the invention the phenol resin in which the photoconductive phthalocyanine pigment is dispersed has the following general formula:—



where R, R_1 are a hydrogen atom or methyl radical, R_2 a hydrogen atom or epoxy radical, and R_3, R_4, R_5 a hydrogen atom, halogen atom or alkyl or alkoxy radical having 1 to 20 carbon atoms, at least one of R_3, R_4, R_5 being an alkyl or alkoxy radical having 4 to 20 carbon atoms.

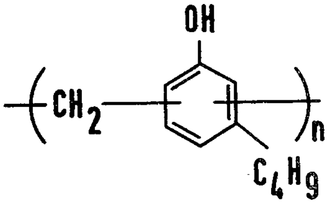
Particular examples of the phenol resin indicated by the above general formula are as follows:

(1)



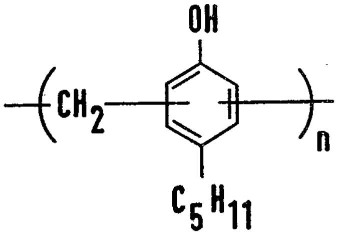
$n \fallingdotseq 10$

(2)



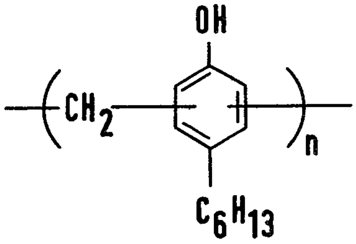
$n \fallingdotseq 10$

(3)



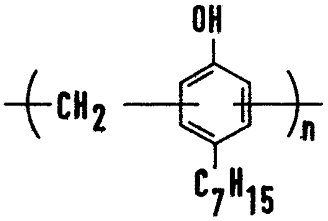
$n \fallingdotseq 15$

(4)



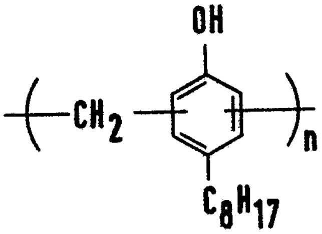
$n \fallingdotseq 15$

(5)



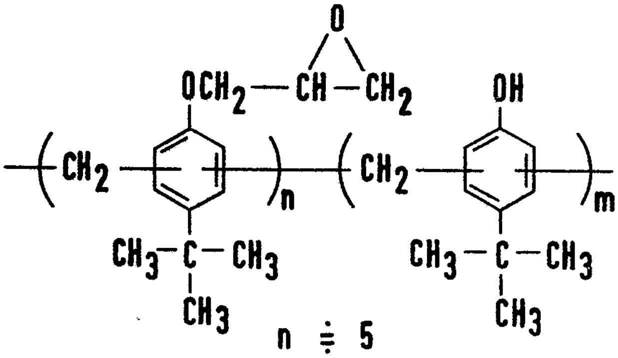
$n \doteqdot 15$

(6)



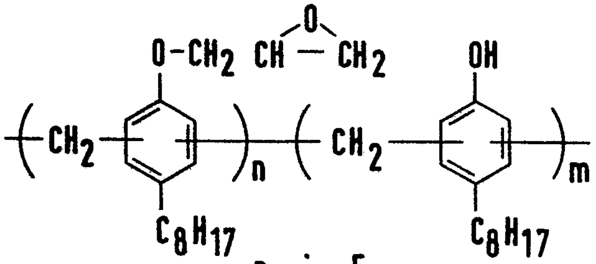
$n \doteqdot 15$

(7)



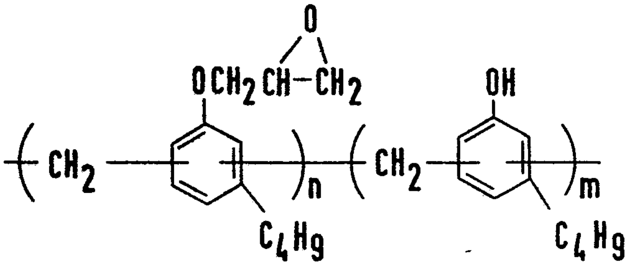
$n \doteqdot 5$ $m \doteqdot 5$

(8)



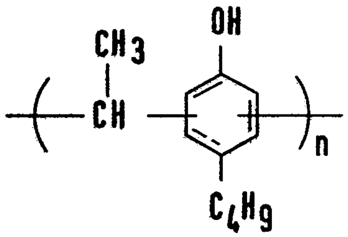
$n \doteqdot 5$ $m \doteqdot 10$

(9)



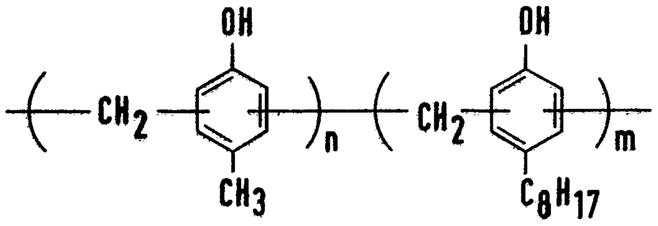
$n \doteqdot 5$ $m \doteqdot 10$

(10)



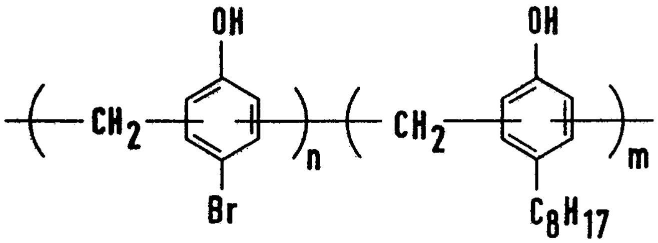
$n \doteqdot 20$

(11)



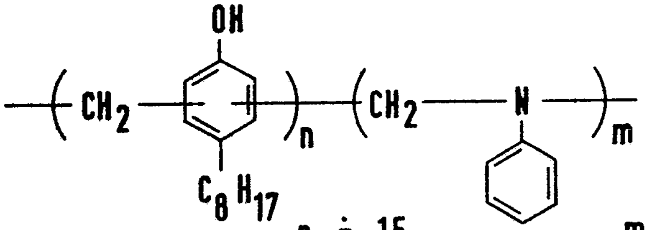
$n \doteqdot 5$ $m \doteqdot 15$

(12)



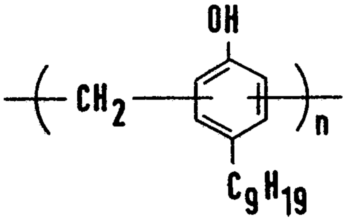
$n \doteqdot 5$ $m \doteqdot 15$

(13)



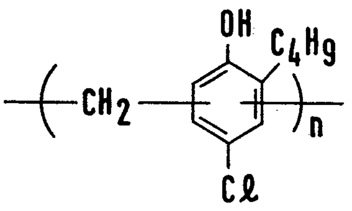
$n \doteqdot 15$ $m \doteqdot 5$

(14)



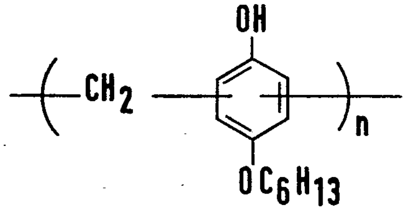
$n \doteqdot 40$

(15)



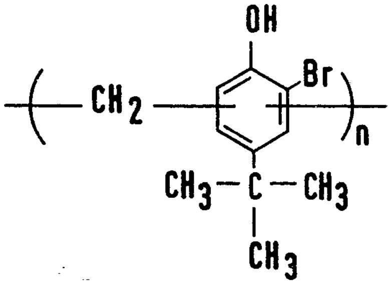
n ≑ 18

(16)



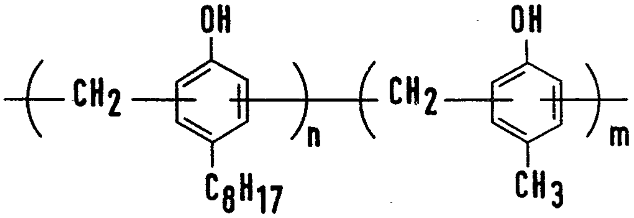
n ≑ 25

(17)



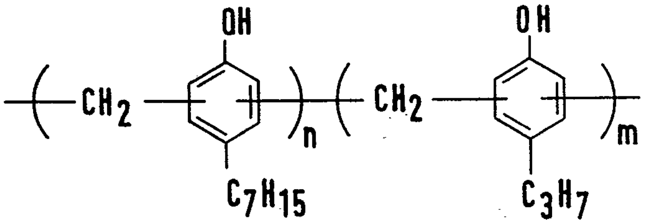
n ≑ 20

(18)



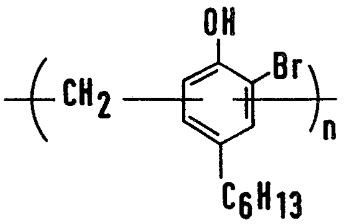
n ≑ 55 m ≑ 5

(19)



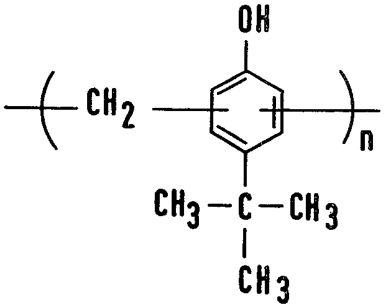
n ≑ 67 m ≑ 3

(20)



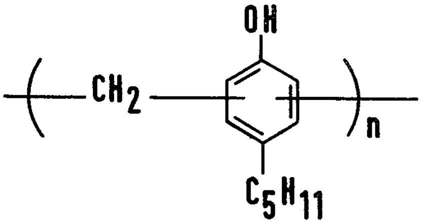
$n \doteqdot 50$

(21)



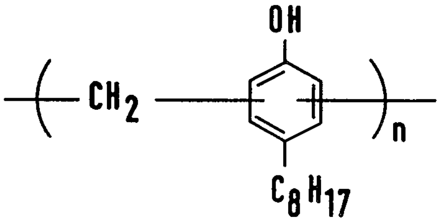
$n \doteqdot 75$

(22)



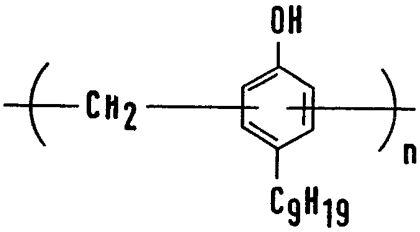
$n \doteqdot 80$

(23)



$n \doteqdot 3$

(24)



$n \doteqdot 5$

In the chemical formulae, *m* and *n* means a polymerization degree, and the polymerization degree of these resins amounts to between 2 and 10,000, preferably from 2 to 100.

Other examples of phenol resin within the previous general formula are resins of melamine, lignin, cumarone, aniline, indene, hydrocarbon, polyvinyl alcohol, fatty acid amide having 12 to 20 carbon atroms, acetate, lactone, acetal, chlorophenol, thiophene or styrenated phenol, or also substances modified by these monomers.

The phenol resin of the above general formula may be used in mixture with another resin compatible therewith such as acrylic resin, epoxy resin, styrene maleic anhydride copolymer, polyvinyl acetate, vinylidene chloride-acrylonitrile copolymer, or in mixture with phenol resins not covered by the present invention.

The photoreceptor material of the present invention incorporates a phenol resin having at least one alkyl or alkoxy radical of 4 to 20 carbon atoms. A phenol resin having an alkyl or alkoxy radical with less than three carbon atoms results in reduced sensitivity of the electrophotographic photoreceptor and poor sensitization effect due to an activation light exposure, and a phenol resin having an alkyl or alkoxy radical with more than twenty one carbon atoms, on the other hand, has remarkably reduced solvability to a solvent so that the photoreceptor material cannot be formed.

In the preparation of a photoreceptor 1 according to the present invention as shown in Fig. 2a, a photosensitive solution is first prepared by preparing a mixture of 100 parts by weight of photoconductive powder, 15 to 2000 parts by weight of a phenol resin and, if necessary, 0.05 to 10 parts by weight of sensitizing dye and dispersively mixing the mixture with 50 to 10000 parts by weight of an organic solvent. The sensitizing dye is, for example, such as rose bengal, auramine, bromophenol blue, bromothymol blue, fuchsine or the like, or 2,4,7-trinitro-9-fluorene, or 2,4,5,7-tetranitro-fluorene. The organic solvent is such as benzene, toluene, xylene, trichloethylene, ethyl-acetate, acetone, methyl-ethyl-keton or the like. The photosensitive solution is then applied on a conductive support 2 such as a metallic plate of copper, iron, nickel, aluminium or stainless steel; a support prepared by evaporating or laminating on paper or plastic film a metal such as aluminum, gold, silver, copper or nickel, or metallic oxide such as tin oxide; or a support coated with a layer comprising a resin and powder dispersed in the resin such as powder of the above metal or metallic oxide or powder of carbon black. The photosensitive solution is applied so as to be 1 to 50 microns thick after it has been dried. Thus, a photosensitive layer 3 is prepared. Between the photosensitive layer 3 and the support 2 there is, if necessary, provided an intermediate layer 4 made of a high molecular organic compound or semiconductor layer having a rectifying characteristic.

A ratio of the photoconductive powder to resin in the photosensitive layer is preferably 6:1 to 1:2 by weight for the inorganic photoconductive powder. The increase of the photoconductive powder above this ratio results in degraded wear resistance and electrical impact resistance as well as poor sensitization effect due to the activation light exposure. The increase of the resin leads to the remarkable degradation of photosensitivity with the result of no practicability. For the photoconductive phthalocyanine, the ratio is preferably 1:3 to 1:20 by weight. The increase of the photoconductive phthalocyanine disadvantageously causes the degradation of the charging characteristic with the result of the difficult charging and increase in dark decay. The increase of the resin, on the other hand, causes the remarkable degradation of the photosensitivity, thus no practicability for the photosensitive layer.

In the method described above of employing the photoreceptor in electrophotography the photoreceptor 1 is irradiated all over the surface with activation light 12 prior to an imagewise exposure as shown in Fig. 2, i.e., simultaneously with the corona discharge 6, 7 as shown in Fig. 2c or at a time during an interval between the corona discharge 6, 7 and the imagewise exposure 8 as shown in Fig. 2d, thereby forming an electrostatic image 9. In other words, the activation light 12 is radiated on the overall surface of the photoreceptor 1 prior to the imagewise exposure 8 and in a step including at least a portion of the charging step or dark decay to activate the fine photoconductive powder. The imagewise exposure is then effected through a pattern 11 prior to the disappearance of the activation of the powder to accelerate the light decay, thereby rapidly forming the electrostatic image 9 with the result of rapid formation of a visible image 10.

A light source usually used for the imagewise exposure is such as a halogen lamp, tungsten lamp, xenon lamp, fluorescent lamp, mercury lamp or incandescent lamp. A halogen lamp or tungsten lamp is preferably used. Further a laser beam source can be particularly efficiently used.

A light source for the activation light of the invention is substantially the same as that for the imagewise exposure. The fluorescent lamp used as a cleaning lamp in electrophotographic copying machines of the repeated transfer type may be effectively used other than the halogen or tungsten lamp. Where a laser beam is used to effect the imagewise exposure, another laser beam can be used to generate the activation light. The quantity of light in the imagewise exposure usually amounts to 5 to 40 lux-seconds for a photoreceptor of phthalocyanine. The quantity of activation light is, on the other hand, 0.01 to 100, preferably 0.1 to 10 times as great as the quantity of imagewise exposure light for each photoreceptor. The activation light has a spectrum substantially the same as that of the light for the imagewise exposure, or a narrow spectrum corresponding to a strong absorption wavelength region in the photoreceptor. For this purpose, a tungsten lamp of 2854°K is used, for example, in combination with an interference filter KL 45, 50, 55, 60, 65, 70 or 80 manufactured by Toshiba Kasei Industrial Co. Ltd., and further in combination with colored glass to derive therefrom a narrow spectrum of wavelength corresponding to the absorption spectrum in the photoreceptor, thereby generating activation light.

The activation light is radiated prior to the imagewise exposure as mentioned above, and preferably in a step including the charging step during which the activation light effectively acts upon the photoreceptor.

The cleaning lamp usually provided in the electrophotographic copying machine may be used as a light source for the activation exposure through light guide means such as an optical fiber or lens system. This allows the cleaning of residual toners, and the prevention of potential decay and increase of a fog, and further causes the acceleration of the light decay with the copying machine thus improved in capability, construction and costs.

Various photoreceptor materials have been measured with respect to their electrostatic characteristics by means of an electrostatic paper analyzer SP—428 manufactured by Kawaguchi Electric Co. Ltd., in the order of processes 1 to 6 in the following table 1, with the result of electrostatic characteristics (for process 1 to 4) as shown by *a* to *d* in Fig. 1.

TABLE 1

L = lux(es)

Process	Steps			
1		Charging 10 sec (5KV)	Dark Decay 5 sec	Imagewise Exp. (Light of W, 3L)
2	Activation Exp. (Light of W, 3L)	Charging 10 sec (5KV)	Dark Decay 5 sec	Imagewise Exp. 6 (Light of W, 3L)
3		Activation Exp. (Light of W, 3L) Charging 10 sec (5KV)	Dark Decay 5 sec	Imagewise Exp. (Light of W, 3L)
4		Activation Exp. (Light of W, 3L) Charging 10 sec (5KV)		Imagewise Exp. (Light of W, 3L)

TABLE 1 (continued)

L = lux(es)

Process	Steps		
5	Charging 5 sec (5.8KV)	Dark Decay 5 sec	Imagewise Exp. (Light of W, 5L
6	Activation Exp. 5 sec. (Light of W, 5L) Charging 5 sec (5.8 KV)	Dark Decay 5 sec	Imagewise Exp. (Light of W, 5L)

From Fig. 1 it will be understood that the charging characteristics *b, c, d* of the photoreceptor material subjected to the activation exposure exhibit higher sensitivity than the conventional characteristic *a* not subjected to the activation exposure. The comparison of saturated potentials shows that they are substantially 650V with no remarkable difference recognized therebetween. The observation of light decay curves in Fig. 1 further reveals that the activation light exposure improves the light decay.

In the measurements using the above-mentioned electrostatic paper analyzer SP—428, it has been found that the activation light exposure helps the acceleration of the light decay in the photoreceptor material. It has also been found in the following measurement that the method described herein, employing an activation light exposure, is quite suitable for electrophotographic copying machines of the repeated transfer type.

A metallic drum of 30 cm in diameter was provided at its circumference with a fluorescent lamp of 10 watts for the activation exposure, a corotoron charging device for positive charging, a halogen lamp of 750 watts for the imagewise exposure, a powder developer, an electrostatic transfer device and a cleaning brush. The photoreceptor of a size B4 was mounted on the drum, which was rotated at a speed of 100 cm per minute for copying at every transfer. The copying was effected twenty times at every 10-lux increment of the imagewise exposure in the range of an illumination intensity of 10 to 200 luxes on the sample surface obtained by moving the exposure device. The copying was then similarly performed twenty times without the activation exposure at every 10-lux increment. The comparison of the visible images with and without the activation exposure showed that, for the formation of a proper visible image, the quantity of light required with the activation light exposure was about one-third as little as the quantity of light required without it. Further, the copying was effected 500 times without any interruption with the proper imagewise exposure by means of a copying machine equipped with an activation exposure lamp with the result of production of a visible image having excellent image quality. In this case, the photoreceptor was free from wear at least up to 5000 copies.

It has been found that the activation light exposure prior to the imagewise exposure causes the light decay to take place in the photoreceptor a few times as rapidly as the light decay without it, and that the nearer the spectrum of light for the imagewise exposure is to a strong absorption wavelength region in the photoreceptor, the more rapidly the light decay occurs, and the nearer the spectrum of activation light is to the strong absorption wavelength region therein, the greater sensitization efect is obtained. Thus, it will be understood that the light decay takes place most rapidly when the spectrum of light for both the imagewise and activation exposures is in the region of the strong absorption wavelength (for example, 800 millimicrons) of the photoreceptor. It has further been found that a photoreceptor containing ε-type phthalocyanine pigment is suitable for use with a He—Ne laser or semiconductor laser from the viewpoint of spectral sensitivity.

Thus an electrophotographic copying machine of the repeated transfer type which utilizes a photoreceptor of the binder type less than 0.3 micron (of the type in which the fine photoconductive powder is dispersed in the resin), particularly a photoreceptor containing copper phthalocyanine, has the advantages of being free from wear upon repeated transfer and capable of high-speed reproduction if a residual charge cleaning lamp is used as a light source for activation exposure, which selectively includes a spectrum at which copper phthalocyanine exhibits a strong absorption, or if light is used the spectrum of which includes the strong absorption wavelength region or a spectrum useful for cleaning the residual charges.

Examples of the present invention will now be described.

Example 1.

α-type copper phthalocyanine pigment, Fastgen Blue FSN (manufactured by Dainippon Ink chemical Industrial Co. Ltd.)	1 part by weight
phenol formaldehyde resin including a t-buthyl radical in para-position (compound example 1)	5 parts by weight
methyl-ethyl-ketone	40 parts by weight

The composition having the above weight ratio was dispersed at room temperature for 5 minutes by means of an ultrasonic dispersing device, and then applied on a conductive support comprising a polyester film 80 microns thick and laminated aluminum thereon 10 microns thick by means of a rotary application device, which was rotated 300 revolutions per minute so that it might be 7 microns after drying. The thus prepared photoreceptor material was heated for about one hour for drying in a drier heated to a temperature of 80°C to prepare a sample photoreceptor.

The thus prepared sample photoreceptor was measured with respect to its charging characteristics by means of an electrostatic paper analyzer SP—428 under the condition that the corona discharge of +6.0 KV was performed in a dark place for positive charging for 10 seconds and the tungsten light of 2854°K was radiated on the sample surface with an illumination intensity of 35 luxes.

The result was that the quantity of exposure required to attenuate the surface potential up to its half-value (the half-decay exposure) was 12 lux-seconds with an S-shaped light decay curve as shown in Fig. 4a. Another photoreceptor was prepared which, instead of the above binder (compound example 1), contains a phenol formaldehyde resin (compound example 1 for comparison to be described later) having 65% of methyl radical in the paraposition and about 35% of methyl radical in the meta-position and other substances which are the same as above. Similar measurements showed that the half-decay exposure was 40 lux-seconds and the light decay curve was L-shaped as shown in Fig. 4b.

The sample photoreceptor and the photoreceptor for comparison were then measured as to the electrostatic characteristics according to process 5 without the activation exposure and the process 6 with it. The condition was such that a voltage of 6 KV was applied to the corotorn changing device for positive charging with a gap of 9 mm between the discharging wire and the sample surface, and the activation and imagewise exposures were all effected by means of a tungsten lamp of 2854°K with an illumination intensity of 5 luxes on the sample surface. This gave the result that, for the sample photoreceptor, the saturated charging potential was 600 V and the rate of dark decay 20% in both the processes 5, 6 with the half-decay 20% in both the processes 5, 6 with the half-decay exposure being 12 lux-seconds in process 5, and 6 lux-seconds in process 6 with obvious sensitization obtained. For the photoreceptor for comparison, on the other hand, the half-decay exposure was 40 lux-seconds in process 5 and 35 lux-seconds in process 6 with less sensitization than the sample photoreceptor.

Example 2.

Various phenol resins and phthalocyanine pigments were used to prepare 15 kinds of sample photoreceptors according to the method in example 1.

Separately, resins of the following compounds for comparison were further used to prepare the photoreceptors for comparison similarly according to the method in the example 1 for 16 kinds of comparing measurements in combination with the sample photoreceptors. These sample photoreceptors and photoreceptors for comparison were measured with respect to their electrostatic characteristics by means of an electrostatic paper analyser 5P—428, under the condition that a voltage of 5 KV was applied to a corotoron corona discharging device for positive charging with a gap of 9 mm between the discharging wire and the sample surface. The imagewise and activation exposures were performed with an illumination intensity of 3 luxes on the sample surface by means of tungsten light of 2854°K.

The results of this measurement are shown in Table 2.

TABLE 2
X = Compound Example
Y = Compound Example for Comparison

No.	Resin	Phthalocyanine Pigments	Charging Polarity	Half-decay Exp. (L-Sec)	Electrostatic Characteristic
1	X No. 1	ε-type copper phthalocyanine	+	8.8	S-shaped
	Y No. 1	same as above	+	20	L-shaped
2	X No. 1	β-type copper phthalocyanine	+	21	S-shaped
	Y No. 1	same as above	+	70	L-shaped
3	X No. 6	ε-type copper phthalocyanine	+	8.6	S-shaped
	Y No. 1	same as above	+	20	L-shaped
4	X No. 2	same as above	+	9.0	S-shaped
	Y No. 2	same as above	+	22	L-shaped
5	X No. 3	α-type copper phthalocyanine	+	12	S-shaped
	Y No. 4	same as above	+	40	L-shaped
6	X No. 4	same as above	+	13	S-shaped
	Y No. 4	same as above	+	41	L-shaped
7	X No. 5	same as above	+	11	S-shaped
	Y No. 5	same as above	+	38	L-shaped
8	X No. 7	same as above	+	15	S-shaped
	Y No. 6	same as above	+	39	L-shaped
9	X No. 8	same as above	+	14	S-shaped
	Y No. 2	same as above	+	40	L-shaped
10	X No. 9	same as above	+	12	S-shaped
	Y No. 2	same as above	+	40	L-shaped
11	X No. 10	same as above	+	11	S-shaped
	Y No. 2	same as above	+	40	L-shaped
12	X No. 11	same as above	+	15	S-shaped
	Y No. 2	same as above	+	40	L-shaped
13	X No. 12	same as above	+	11	S-shaped
	Y No. 2	same as above	+	40	L-shaped

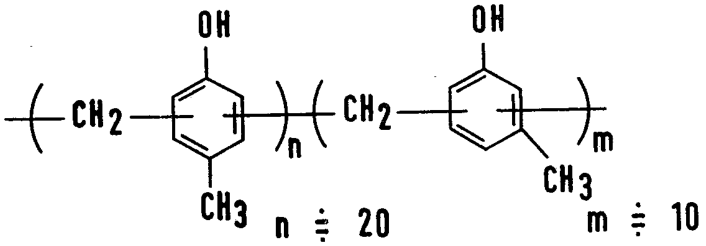
TABLE 2 (continued)

X = Compound Example
Y = Compound Example for Comparison

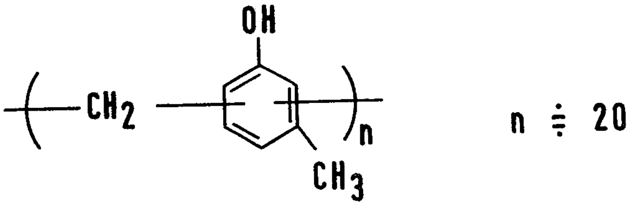
No.	Resin	Phthalocyanine Pigments	Charging Polarity	Half-decay Exp. (L-Sec.)	Electrostatic Characteristic
14	X No. 13	α-type copper phthalocyanine	+	14	S-shaped
	Y No. 2	same as above	+	40	L-shaped
15	X No. 14	same as above	+	10	S-shaped
	Y No. 2	same as above	+	40	L-shaped

Compound examples for comparison

(1)



(2)



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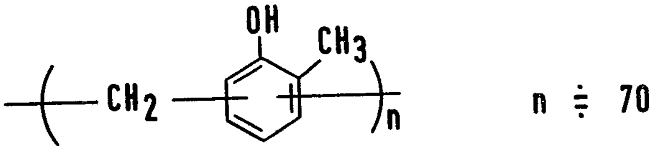
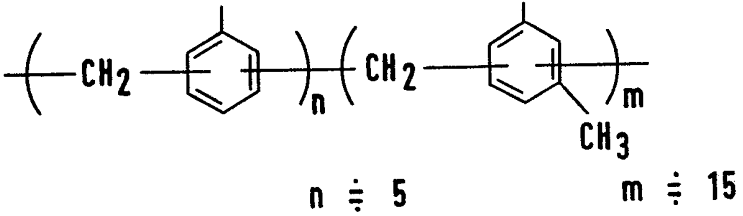


(4)



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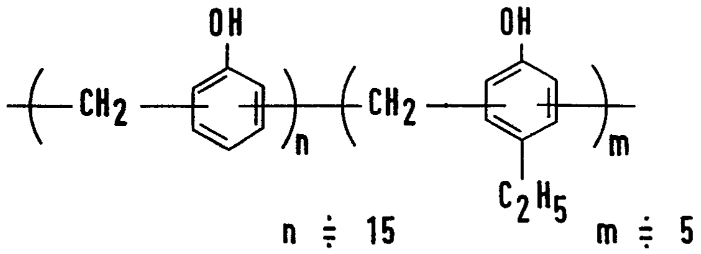
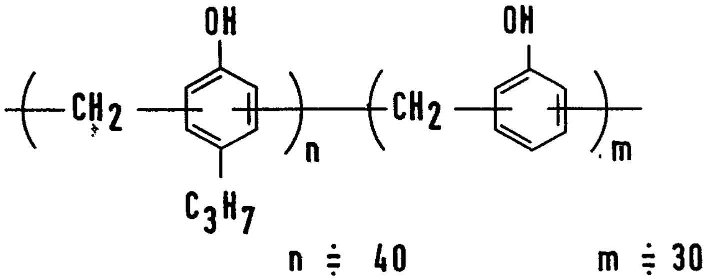


(6)



It is to be noted that, in Table 2, the α-type phthalocyanine is Fastgen Blue FNS manufactured by Dainippon Ink Chemical Industrial Co. Ltd.; β-type is Fastgen Blue FGF manufactured by the same; and ε-type is Lionol Blue ER (manufactured by Toyo Ink Co. Ltd.)

Table 2 reveals that the sample photoreceptor of the present invention comprising the phthalocyanine pigment and an binder resin of the compound examples generally exhibits an S-shaped light decay characteristic upon positive charging with greater sensitivity than the photoreceptor for comparison comprising the binder resin of the compounds for comparison, which generally exhibits an L-shaped light decay characteristic.

Further, the sample photoreceptor and the photoreceptor for comparison shown in Table 2 were measured with respect to their characteristics according to process 5 without the activation exposure and process 6 with it similarly as in example 1, with the result that the sample photoreceptor exhibiting the S-shaped light decay characteristic had a remarkable effect due to the activation light exposure with more than about twice as much sensitization as that in the photoreceptor for comparison.

The photoreceptor for comparison exhibiting the L-shaped light decay characteristic, on the other hand, indeed has a recognizable sensitization effect, but less than the sample photoreceptor. This would be due to the fact that the sample photoreceptor exhibiting the S-shaped light decay characteristic has many traps for capturing generated carriers in the photoreceptor, and the traps are effectively filled upon exposure by activation light.

Example 3.

ε-type copper phthalocyanine pigment, Lionol Blue ER (Manufactured by Toyo Ink Co. Ltd.)	1 part by weight
phenol formaldehyde having a t-buthyl radical in para-position (compound example 1)	6 parts by weight
methyl-ethyl-ketone	40 parts by weight

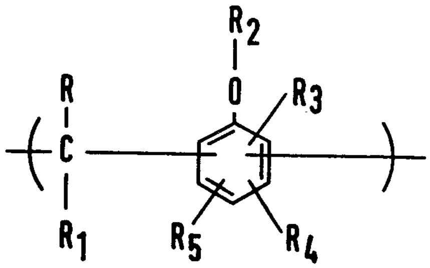
The composition having the above weight ratio was ultrasonically dispersed at room temperature for five minutes, and then applied on a rough-surface and anode-oxidised plate of aluminum by means of a rotary application device, which was rotated 500 revolutions per minute so that it might be 4 microns after drying. The thus prepared photoreceptor material was heated for drying for about three hours in a drier heated to a temperature of 60°C to prepare a sample photoreceptor.

The sample photoreceptor was subjected to the discharge of +6.0 KV in a dark place so that its surface potential might be about 300 V, and then simultaneously irradiated with activation light by an incandescent lamp of tungsten of 10 luxes. The photoreceptor was then imagewise exposed (20 lux-seconds) and developed by a magnetic brush method. As a result, a sharp toner image without any fog was formed on the photoreceptor. After the toner image was heated for fixing, the photoconductive layer was removed therefrom by an alkaline solution containing methyl-ethyl-ketone in order to prepare a lithographic plate.

Separately, another sample photoreceptor was prepared similarly, with the exception of no exposure by activation light, to form a toner image, which was, however, much fogged. The formation of the lithographic plate thus resulted in blurred image with its surface made dirty.

WHAT WE CLAIM IS:—

1. A photoconductive composition for use in the preparation of an electrophotographic material, comprising a photoconductive phthalocyanine pigment dispersed in a phenol resin having the following general formula



where R and R_1 are a hydrogen atom or methyl radical; R_2 a hydrogen atom or epoxy radical; and R_3, R_4 and R_5 are a hydrogen atom, halogen atom or alkyl or alkoxy radical having 1 to 20 carbon atoms, at least one of R_3, R_4 and R_5 being an alkyl or alkoxy radical having 4 to 20 carbon atoms.

2. A photoconductive composition according to claim 1, wherein said photoconductive phthalocyanine pigment contains metal free phthalocyanine, copper phthalocyanine, cobalt phthalocyanine, lead phthalocyanine or zinc phthalocyanine.

3. A photoconductive composition according to claim 2, wherein the metal free phthalocyanine and copper phthalocyanine are of an α, β, γ, χ, π or ε-type.

4. A photoconductive composition according to claim 1 or claim 2, wherein the photoconductive phthalocyanine pigment is blended with the said resin in a ratio of between 1:3 and 1:20 by weight.

5. A photoconductive composition as claimed in claim 1 and substantially as hereinbefore described with reference to the accompanying drawings.

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FIG. I

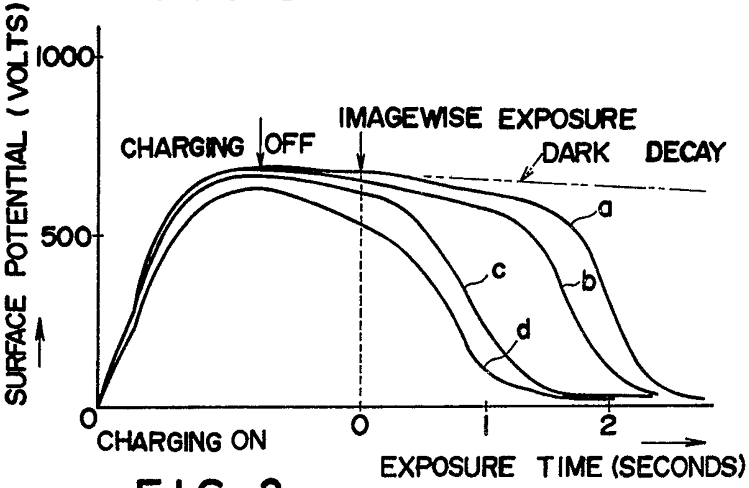

SURFACE POTENTIAL (VOLTS)
1000
500
0
CHARGING ON
CHARGING
OFF
IMAGEWISE EXPOSURE
DARK DECAY
a
b
c
d
0
1
2
EXPOSURE TIME (SECONDS)

FIG. 2

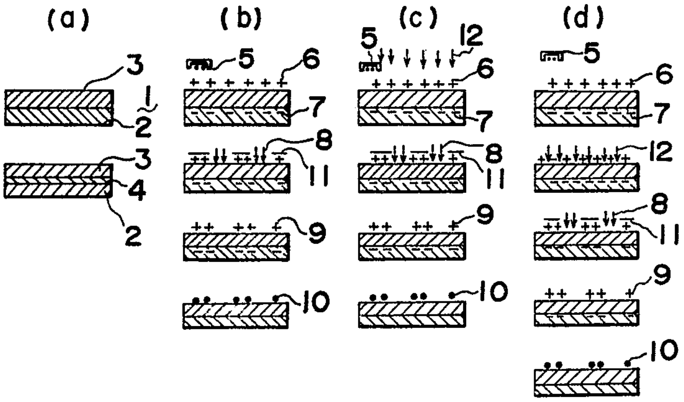

(a)
3
1
2
3
4
2
(b)
5
6
7
8
11
9
10
(c)
5
12
6
7
8
11
9
10
(d)
5
6
7
12
8
11
9
10

FIG. 3

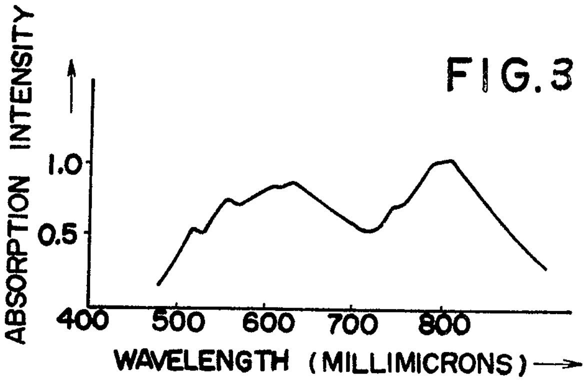

ABSORPTION INTENSITY
1.0
0.5
400
500
600
700
800
WAVELENGTH (MILLIMICRONS)

FIG.4a

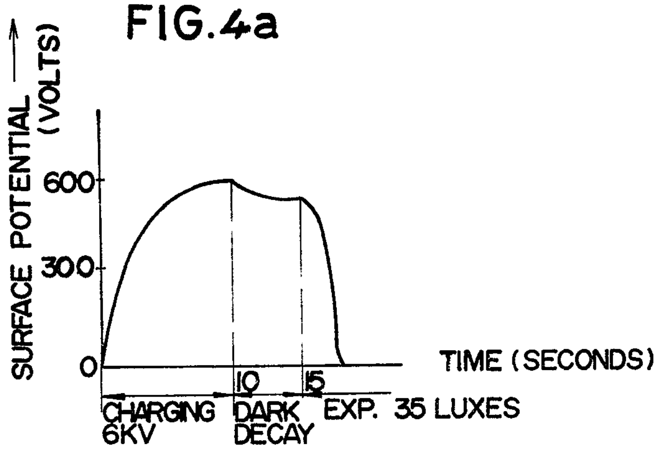
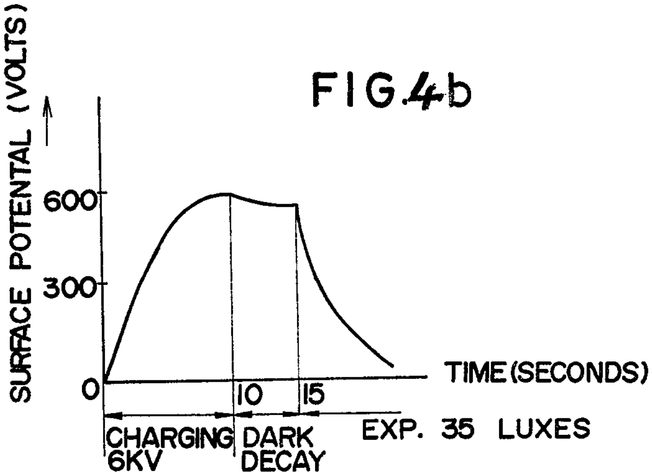

SURFACE POTENTIAL (VOLTS)
600
300
0
TIME (SECONDS)
10
15
CHARGING 6KV
DARK DECAY
EXP. 35 LUXES

FIG.4b


SURFACE POTENTIAL (VOLTS)
600
300
0
TIME (SECONDS)
10
15
CHARGING 6KV
DARK DECAY
EXP. 35 LUXES