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EUROPEAN PATENT APPLICATION

⑳ Application number : **90312847.8**

⑤① Int. Cl.⁵ : **G03G 5/06**

㉔ Date of filing : **27.11.90**

③① Priority : **28.11.89 JP 308716/89**
15.02.90 JP 34359/90
15.02.90 JP 34360/90

④③ Date of publication of application :
05.06.91 Bulletin 91/23

⑧④ Designated Contracting States :
DE FR GB

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⑤④ **Electrophotographic photoreceptor and method of forming images.**

⑤⑦ An electrophotographic photoreceptor comprising a conductive substrate and, provided thereon, a photoreceptive layer comprising a phthalocyanine pigment and a binder resin, wherein the phthalocyanine pigment has water molecules adsorbed thereon in a numerical amount greater than any other molecules, as measured by a vacuum method.

ELECTROPHOTOGRAPHIC PHOTORECEPTOR AND METHOD OF FORMING IMAGES

FIELD OF THE INVENTION

5 The present invention relates to an electrophotographic photoreceptor, more specifically to an electrophotographic photoreceptor using a specific phthalocyanine dye as a photoconductive material, useful to a printer and a copying machine, and suitable for forming latent images with a semiconductor laser ray or an LED ray.

BACKGROUND OF THE INVENTION

10 In recent years, organic photoconductive materials have come to be widely used instead of inorganic ones for the electrophotographic photoreceptors, because a wider freedom for selection of the raw materials for the organic photoconductive materials and a variety of the combinations of the raw materials and the synthesis conditions make it possible to obtain the various types of the organic photoconductive materials, which in turn makes it easy to prepare a desired photoreceptor for a specific purpose.

15 Further, a function separation type photoreceptor comprising an organic photoconductive material, in which there are provided a carrier generation layer and a carrier transfer layer both containing the different materials responsible for the respective functions, can have the further wider freedom of material selection and thereby an improvement in the electrophotographic properties such as electrification ability, sensitivity and durability can be expected.

20 On the other hand, a more improvement in image quality and an image edition function are demanded to a copying machine. To meet such requirements, development of a digital control copying machine or printer is under way, and improvement of a photoreceptor therefore is strongly desired. In the above digital recording equipment, dotted latent images are formed by a dotwise exposure with a laser ray modulated by an image signal, and then the latent images are developed by a reverse developing method to form images, wherein a semiconductor laser capable of providing a simpler, smaller and less expensive exposing unit is preferred. Its oscillation wavelength is in an infrared region of more than 750 nm. Therefore, a photoreceptor applied thereto is required to have a high sensitivity at least in a wavelength region of 750 to 850 nm.

25 Many organic dyes and pigments are proposed as a carrier generating substance for the foregoing function separation type photoreceptor, and there are used practically polycyclic quinone pigments such as dibromoanthanthrone, pyrylium dyes and eutectic complexes thereof with polycarbonate, squarium pigments, phthalocyanine pigments and azo pigments. Of them, phthalocyanine dyes are regarded to be the most fitted for an electrophotographic photoreceptor packaged with a light source of a semiconductor laser ray because of their higher quantum efficiency in photoelectric transfer and high spectral sensitivity extended to a near infrared region.

30 There are reported the photoreceptors using copper phthalocyanine, non-metallic phthalocyanine, chloroindium phthalocyanine and chlorogallium phthalocyanine. Recently, titanylphthalocyanine has come to attract an attention, and various photoreceptors using titanylphthalocyanines of different crystal forms are disclosed in Japanese patent Publication Open to Public Inspection Nos. 239248/1986, 670943/1987, 272272/1987 and 116158/1988 and 17066/1989.

35 It is well known that phthalocyanine has a crystal form of α , β , γ , X and Y types and that the characteristics of the photoreceptor are affected notably by the crystal form thereof, and phthalocyanine of a crystal form capable of providing stably a high sensitivity and an excellent electrification property is required. So far, however, there have been disclosed few titanylphthalocyanines having a high sensitivity and a good stability in a repetitive operation under high temperature, high humidity and high ozone conditions; α -type titanylphthalocyanine has high sensitivity but poor stability; β -type titanylphthalocyanine has poor sensitivity; and Y-type phthalocyanine disclosed in Japanese Patent Publication Open to Public Inspection has a deteriorated charging property in repeated use in a high ozone condition.

40 A contact developing method and a non-contact developing method are conventionally used in forming an image with an electrophotographic photoreceptor. The non-contact developing method, particularly the jumping developing method, is liable to be affected by environmental conditions. Particularly, repeated use of a photoreceptor under high temperature humidity conditions and lowering of electrification properties of corona electrodes owing to scattering of toners in a repetitive operation cause deterioration of image quality such as lowering of resolution and increase of fogging.

45 In the multi-color image forming method in which a plurality of overlapped toner images are formed on a photoreceptor and then transferred by only one transferring process to form the images, there are involved such

problems that an electrification property of an electrification electrode and luminous energy of a de-electrification lamp are liable to be lowered and as the results, surface voltage of a photoreceptor is lowered, which in turn results in causing fog, and that a ghost phenomenon in which an after-image is formed by a residual optical memory takes place.

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SUMMARY OF THE INVENTION

An object of the present invention is to provide an electrophotographic photoreceptor containing a specific phthalocyanine pigment and having excellent repeating properties and high sensitivity with less liability to be affected by environmental conditions.

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Another object of the present invention is to provide a method of forming images with the above photoreceptor.

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The above objects can be achieved by an electrophotographic photoreceptor comprising a conductive substrate and provided thereon a photoreceptive layer containing a phthalocyanine pigment and a binder resin, wherein the phthalocyanine pigment has a water molecule the most of the substances absorbed thereon, provided that the contents of the adsorbed substances are measured by a vacuum method.

BRIEF DESCRIPTION OF THE DRAWINGS

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Figs. 1 through 6 are cross-sectional drawings of the layer configuration of the photoreceptor according to the invention.

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- 1... a conductive support
- 2... a carrier generation layer
- 3... a carrier transfer layer
- 4, 4' and 4"... photoreceptive layers
- 5... an intermediate layer

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Fig. 7 shows a schematic cross-sectional drawing of an image forming equipment using the photoreceptor of the invention. Fig. 8 is a block diagram of copying operations of the equipment shown in Fig. 7. Fig. 9 is a cross-sectional drawing of the principal part of a developing device.

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- In Figs. 7 and 9,
- 1... a photoreceptor
- 2... an electrifier
- 5... a transfer electrode
- 8... a cleaning unit
- 9... a fixing roller
- 10... a laser optical system
- 17R, 17G and 17B... CCD image pick-up elements
- 18... an original copy
- 31, 32, 33 and 34... developing devices
- 41... a developing sleeve
- 42... a magnet
- 43... a developer reservoir
- 44... a layer thickness controlling blade
- 63... a transfer unit

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- L... image exposure
- E... developing area

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Fig. 10 shows a schematic cross-sectional drawing of a color copying machine.

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- 1... a photoreceptor
- 2... an electrifier
- 4... a transfer electrode
- 5... a separation electrode
- 6... a fixing device
- 8... a cleaning unit
- 10... a laser optical system
- 17R, 17G and 17B... CCD image pick-up elements
- 18... an original copy
- 31, 32, 33 and 34... developing devices
- 41... a developing sleeve

42... a magnet
 43... a developer reservoir
 44... a layer thickness controlling blade
 L... image exposure
 E... developing area
 T₁ and T₂... toners

Figs. 11 to 13 show the differential thermal curves of phthalocyanines of the invention. Fig. 14 shows a differential thermal curve of Y-type phthalocyanine and Fig. 15 shows a differential thermal curve of β -type titanylphthalocyanine.

DETAILED DESCRIPTION OF THE INVENTION

The phthalocyanine pigments of the invention have different crystal aggregation conditions from those of the titanylphthalocyanine pigments disclosed in the foregoing patent publications and are characterized by that they contain water molecules the most by number of the substances adsorbed thereon, of which contents are measured by a vacuum method, and that they have an aggregation condition in which their absorption spectra in the visible and near infrared regions have the maximum absorptions in 780 to 860 nm. They have a high sensitivity to a semiconductor laser ray.

The adsorbed substances are analyzed in the following manner :

Into a measuring chamber is placed a 3.0 cm³ glass ampul in which 0.5 g of a phthalocyanine pigment is sealed at an atmospheric pressure and 60% RH, and then the ampul is broken under a vacuum of 2×10^{-8} Torr to measure the molecular numbers of the substances desorbed from the phthalocyanine pigment by analyzing with a quadrupole mass spectrometer.

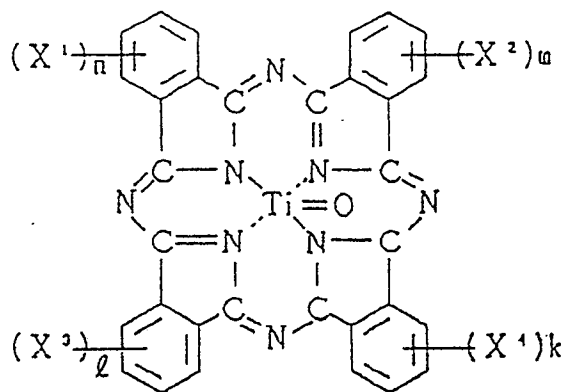
It has been found from the above analysis that the phthalocyanine pigment of the invention adsorbs water the most of hydrogen, nitrogen, carbon dioxide and water while a conventional phthalocyanine pigment adsorbs nitrogen the most.

The phthalocyanine pigment of the invention has an endothermic peak between 80°C and 120°C in a differential thermal analysis.

In the above differential thermal analysis, 10 mg of a sample are subjected to analysis at an atmospheric pressure and 60% RH with a temperature raised at a speed of 10°C/min. The above endothermic peak is defined by an endothermic peak having a half width of 30 degrees or more.

Examples of the phthalocyanine pigment according to the invention are non-metallic phthalocyanines, titanylphthalocyanines, vanadylphthalocyanines, lead phthalocyanines, chloroindium phthalocyanines and tin phthalocyanines. Of them, titanylphthalocyanine pigments and vanadylphthalocyanine pigments are preferred. Particularly preferred is a titanylphthalocyanine pigment of which X-ray diffraction spectrum with a Cu-K α ray has the peaks at Bragg angles (2 θ) of $9.5^\circ \pm 0.2^\circ$ and $27.2^\circ \pm 0.2^\circ$.

The basic structure of the titanylphthalocyanine pigment used in the invention is represented by the following formula :



wherein X¹, X², X³ and X⁴ independently represent a hydrogen atom, a halogen atom, an alkyl group and an alkoxy group ; and n, m, ℓ and k independently represent an integer of 0 to 4.

Next, an example of the manufacturing method of the titanylphthalocyanine used in the invention is described below. Titanium tetrapropoxide is added to the mixture of 1,3-diimino-isoindoline and sulfolane to react in a nitrogen atmosphere at 80 to 300°C, preferably 100 to 260°C. After completion of the reaction, the mixture

is allowed to cool, and then precipitated titaniumphthalocyanine is filtered. Subsequently, the product is subjected to mixed solvent treatment to obtain the phthalocyanine pigment of the invention. In the above procedure, it is important to treat the product in a mixed solvent comprising hydrophilic solvents such as alcohol and ketone. In the treatment, a homomixer, a disperser, an agitator, a ball mill, a sand mill or an attritor can be used as well as a conventional stirrer.

In the present invention, a carrier generation substance other than the phthalocyanine pigment of the invention may be jointly used, examples of which are β -type, mixture of α - and β -types, γ -type and amorphous titaniumphthalocyanines having different crystal forms from that of the phthalocyanine pigment of the invention; azo pigments; anthraquinone pigments; perylene pigments; polycyclic quinone pigments; and squarium pigments.

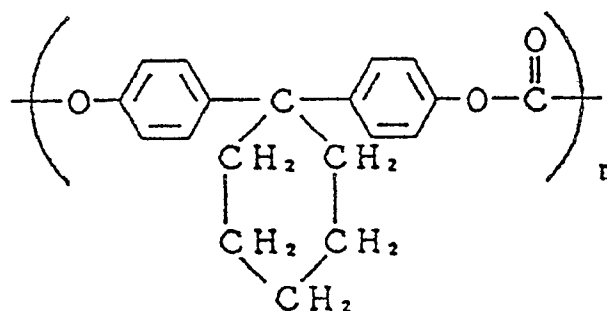
The photoreceptor of the invention can be prepared by dispersing the phthalocyanine pigment of the invention in a solution dissolving a binder resin in a solvent, dissolving therein a carrier transfer substance to prepare a coating solution and coating it on a conductive support, which may have thereon a subbing layer, by methods such as dip coating, spray coating and spiral coating. The photoreceptor prepared as above has a single-layered configuration shown in Fig. 1 or Fig. 2.

Function separation type photoreceptors shown in Figs. 3 through 6 are preferred to provide high sensitivity and durability, wherein a coating solution containing a binder resin and the pigment is coated on a conductive support 1 to form a carrier generation layer 2; then, a coating solution containing a carrier transfer substance is coated on the carrier generation layer 2 to form a carrier transfer layer 3, whereby a photoreceptive layer of double-layered configuration 4 (Fig. 3 or 5) or 4' (Fig. 4 or 6) is formed.

In forming the photoreceptive layer of a double-layered configuration, the carrier generation layer 2 and the carrier transfer layer 3 can be provided by dissolving or dispersing each of the carrier generation and transfer substances together with a binder resin in a solvent or dispersant coating the solutions or dispersions on a support, respectively.

Examples of the solvent and dispersant are butyl amine, N,N-dimethylformamide, acetone, methyl ethyl ketone, cyclohexanone, benzene, toluene, xylene, chloroform, 1,2-dichloroethane, dichloromethane, tetrahydrofuran, dioxane, methanol, ethanol, iso-propanol, ethyl acetate, butyl acetate, and dimethylsulfoxide. The binder used for the photoreceptive layer is preferably a hydrophobic polymer capable of forming an insulated film with a high dielectric constant. Examples of such a polymer are as follows:

- 1) polycarbonate
- 2) polyester
- 3) methacrylic resin
- 4) acrylic resin
- 5) polyvinyl chloride
- 6) polyvinylidene chloride
- 7) polystyrene
- 8) polyvinyl acetate
- 9) styrene-butadiene copolymer
- 10) vinylidene chloride-acrylonitrile copolymer
- 11) vinyl chloride-vinyl acetate copolymer
- 12) vinyl chloride-vinyl acetate-maleic anhydride copolymer
- 13) silicone resin
- 14) silicone-alkyd resin
- 15) phenol-formaldehyde resin
- 16) styrene-acryl copolymer
- 17) styrene-alkyd resin
- 18) poly-N-vinylcarbazole
- 19) polyvinyl butyral
- 20) polycarbonate resin
- 21) polycarbonate resin having the following structure:



These binder resins may be used singly or in combination.

The addition rate of the carrier generation substance to the binder resin is preferably 10 to 600 wt%, more preferably 50 to 400 wt%.

The thickness of the carrier generation layer is preferably 0.01 to 20 μm , more preferably 0.05 to 5 μm .

When the carrier generation layer 2 is formed by dispersing the carrier generation substance, the carrier generation substance is preferably a fine powder having an average particle size of 2 μm or less, preferably 1 μm or less. Too large particle size is liable to hinder particles from dispersing in the layer and form protrusions of particle on the surface to thereby deteriorate surface smoothness. In some cases, the protrusions cause electric discharge or adsorption of toner particles, which tends to form toner filming.

The examples of the carrier transfer substance are the compounds having a nitrogen-containing heterocyclic ring or a ring condensed therewith, such as oxazoles, oxadiazoles, thiazoles, thiadiazoles and imidazoles; polyarylethane compounds; pyrazoline compounds; hydrazone compounds, triarylamine compounds; styryl compounds; styryltriphenylamine compounds; α -phenylstyryltriphenylamine compounds, butadiene compounds, hexatriene compounds, carbazole compounds; and condensed polycyclic compounds.

These carrier transfer substances are described in Japanese Patent O.P.I. Publication No. 107356/1986.

These carrier transfer substances are used preferably in an amount of 10 to 500% by weight of the binder resin. The thickness of the carrier transfer layer is 1 to 100 μm , preferably 5 to 30 μm .

The photoreceptive layer on the photoreceptor of the invention may contain an electron acceptable substance so that sensitivity enhancement, minimization of residual voltage and lowering of fatigue in a repetitive operation can be expected. Examples of the electron acceptable substance are succinic anhydride, maleic anhydride, dibromosuccinic anhydride, phthalic anhydride, tetrachlorophthalic anhydride, tetrabromophthalic anhydride, 3-nitrophthalic anhydride, 4-nitrophthalic anhydride, pyromellitic anhydride, mellitic anhydride, tetracyanoethylene, tetracyanoquinodimethane, o-dinitrobenzene, m-dinitrobenzene, 1,3,5-trinitrobenzene, p-nitrobenzonitrile, picryl chloride, quinonechloroimide, chloranil, bromal, dichlorodicyano-p-benzoquinone, anthraquinone, dinitroanthraquinone, 9-fluorenylidene malonodinitrile, polynitro-9-fluorenylidene malonodinitrile, picric acid, o-nitrobenzoic acid, p-nitrobenzoic acid, 3,5-dinitrobenzoic acid, pentafluorosalicic acid, 5-nitrosalicic acid, 3,5-dinitrosalicic acid, phthalic acid, mellitic acid, and other electrophilic compounds. The addition amount of the electron acceptable substance is preferably 0.01 to 200 parts by weight per 100 parts of the carrier generation substance, more preferably 0.1 to 100 parts.

Further, the photoreceptive layer may contain a deterioration inhibitor such as an antioxidant and an optical stabilizer in order to improve preservability and durability.

The same materials as described above including the carrier generation and transfer substances and a binder resin can be applied to the photoreceptor of single-layered configuration shown in Figs. 1 and 2.

The conductive support used in the invention may be a metal plate, metal drum, and a paper or plastic film having conductivity which is provided by coating, vapor-depositing or laminating thereon a thin film of a conductive compound such as a conductive polymer, indium oxide and metal such as aluminum and palladium.

In the intermediate layer 5 which functions as an adhesive layer or a barrier layer, there can be used the high polymers described above as the binder resins, an organic polymer such as polyvinyl alcohol, ethyl cellulose, carboxymethylcellulose and polyamide, and aluminum oxide.

Next, an explanation will be given to an image-forming equipment which comprises a photoreceptor containing the phthalocyanine of the invention.

Fig. 7 is a schematic cross-sectional drawing of a copying machine. In an image reading section LE, an original copy 18 placed on an original copy stand 19 is exposed to a light source 13 movable in an X direction, and a reflected light 20 is imaged on each of CCD image pick-up elements 17R, 17G and 17B for red, green and blue colors, respectively, through a mirror 14, a lens 15 and a color separation filter 16. These CCD image pick-up elements convert optical information to time series electric signals and send them to an image data processing section TR₁ (see Fig. 8), where record image data are formed. In a laser optical system 10, a mod-

ulator MD modulates a laser ray from a semiconductor laser 21 in accordance with record image data from a video signal processing section TR₂ (22 Fig. 7 is a polygonal mirror). Meanwhile, the surface of an image carrier 1 (photoreceptor drum) is uniformly electrified by a scorotron electrification electrode 2. Subsequently, a modulated laser ray L from the laser optical system 10 is radiated on the image carrier 1, whereby an electrostatic latent image is formed. An electrostatic latent image formed through a blue color separation filter is subjected to reversal development by a yellow toner contained in a developing device 31. The image carrier 1 on which a toner image is formed is uniformly electrified once again by the scorotron electrification electrode 2. Similarly, the magenta and cyan toner images are formed on the image carrier. A recording paper P is fed to a drum-type transfer unit 63 through a feed roller 23 and gripped by a gripper 64 to be sent in a direction of an arrow with a rotation of the drum.

The developed toner image is then transferred onto the recording paper P with a transferring device 5 equipped in the transfer unit 63. In copying a monochromatic image, the recording paper P is immediately separated from the transfer unit 63 with a separation nail 66 and then sent to a heat-fixing roller 9 for fixing the toner image. In copying a multi-colored image, the separation nail 66 does not work immediately, and the recording paper P rotates while being fixed on the transfer unit 63. A transfer-accelerating exposure may be performed before transferring by the transferring device 5.

Residual toners on the surface of the image carrier 1 after transferring of a toner image of one color are removed by a cleaning device 8 (de-electrification may be carried out before cleaning, if necessary) in preparation for the following image forming procedure. Then, the above procedure is repeated to transfer, a toner image of the other colors over a preceding toner image fixed on the recording paper P held on the transfer unit 63. The above procedures are repeated to form a multi-colored image on the recording paper P, which is separated from the transfer unit 63 with the separation nail 66, followed by fixing similarly to the case of the monochromatic image.

Fig. 8 is a block diagram of copying operations of the copying machine shown in Fig. 7. In this diagram, an operation section OP actuates a control section CT, by which an image reading section LE is controlled to convert optical informations of the original copy to time series signals of respective colors. The data converted to the signals are processed in an image data processing section TR₁ and then converted to the data suitable for recording at an video signal processing section TR₂. In accordance with controlling signals, the image forming section RE performs the above image forming procedure to transfer a toner image on a copying paper and form a copied image. An electrophotography is used in the image forming section RE.

Various informations input in advance, copying magnifications and used colors can be memorized in an image memory ME such as a ROM (read only memory), a floppy disk and a magnetic tape, and can be taken out to send to the image forming section RE.

Fig. 9 is an enlarged figure of the developing devices 31 to 34, wherein a non-magnetic developing sleeve 41 which serves as a developer carrier rotates left while an internal magnet 42 rotates right, whereby a developer 50 in a developer reservoir 43 is adsorbed on the surface of the developing sleeve 41 and carried in a direction reverse to that of the rotation of a magnet 42. The developer carried on the developing sleeve 41 is regulated to a proper thickness in transit by a layer thickness regulating blade 44 to form a developer layer.

In the development, a DC bias voltage and/or an AC voltage are applied to the developing sleeve 41 by a bias power source 52 for developing in a developing area E. The developer layer passed through the developing area E is removed from the developing sleeve 41 by a cleaning blade 45 and returned to the developer reservoir 43. The toner is fed from a toner hopper to the developer reservoir 43 by a toner feeding roller, both of which are not illustrated. The developer 50 is stirred uniformly by stirring/carrying means 46, 47 and 48, and fully charged.

The developer layer may be carried with the developing sleeve 41 resting or rotating right, or with the magnet 42 resting or rotating left.

The developer 50 may be a one-component developer comprising magnetic toner particles but a two-components developer comprising magnetic carrier particles and non-magnetic toner particles is preferred in view of color sharpness and easiness in controlling electrification of toner particles.

Developing with the developing device of Fig. 9 is carried out by the non-contact developing method. Specific conditions of the development may be the same as those described in Japanese Patent O.P.I. Publication Nos. 147652/1982 or 181362/1984, both of which use two-component developers. When a one-component developer is used, the conditions may be the same as those described in Japanese Patent O.P.I. Publication No. 18656/1980 or Japanese Patent Examined Publication No. 9475/1966.

It is preferred that an alternating electric field applied between the image carrier 1 and the developing sleeve 41 be 100 Hz to 5 KHz and that the DC bias voltage applied to the developing sleeve 41 be 100 V to 2 KV. An opening 51 between the image carrier 1 and the developing sleeve 41 is controlled to the range of 10 to 2000 μ m. Therefore, it is preferred that the thickness of the developer layer regulated by the layer thickness regulating

blade 44 be thinner than the above opening.

In the two-component developer, the particle sizes of a carrier and a toner are preferably 5 to 100 μm and 20 μm or less, respectively. Useful carriers are a magnetic carrier and an insulating carrier coated with an insulating substance. In the one-component developer, a conventional insulating toner can be used.

5 Next, an image forming equipment capable of forming multi-colored images in one cycle of transfer process is explained in accordance with Fig. 10, in which a multi-color image forming equipment of a digital copying system is shown.

A four-colors toner image is formed on the image carrier 1 by repeating the procedures described in the above equipment. The four-colors toner image may be electrified with an electrification electrode in advance
10 of transfer. Then, it is transferred on the recording paper P by a transfer electrode 4, which is separated from the image carrier 1 by a separation electrode 5 and subjected to fixing by a fixing device 6. The image carrier 1 is cleaned by a cleaning device 8.

EXAMPLES

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The present invention will be described in more detail with the examples.

First, the synthetic examples of the various phthalocyanine pigments are described.

Synthesis 1

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To a mixture of 29.2 g of 1,3-diminoisoindoline and 200 ml of sulfolane were added 17.0 g of titanium tetraisopropoxide, and the mixture was heated at 140°C in a nitrogen atmosphere for 2 hours to complete reaction. After cooling, the deposit was filtered and washed in sequence with chloroform, 2% hydrochloric acid aqueous solution, water and methanol, followed by drying, to thereby obtain 25.5 g of titanylphthalocyanine (yield :
25 88.5%). Subsequently, 100 g of the product were dissolved in 2 kg of concentrated sulfuric acid, and the solution was poured into 20 l of water. The deposit was filtered to obtain an amorphous wet paste.

To 2 g of this wet paste was added a mixed solvent of 200 ml of 1,2-dichloroethane and 100 ml of methanol, and the mixture was stirred for 3 hours at a room temperature. After diluting with methanol, the product was filtered, washed with methanol and dried to obtain the crystals having the peaks at the Bragg angles (2θ) of
30 $9.5^\circ \pm 0.2^\circ$ and $27.2^\circ \pm 0.2^\circ$ in an X-ray diffraction spectrum. The X-ray diffraction spectrum was measured with an X-ray diffraction equipment model JDX-8200 made by JEOL, Ltd. under the following conditions :

X-ray source	Cu (Cu-K α ray)
Voltage	40.0 KV
Current	100.0 mA
35 Start angle	6.00 deg.
Stop angle	35.00 deg.
Step angle	0.020 deg.
Measuring time	0.50 deg.

A differential thermal analysis of this crystal gave a differential thermal curve shown in Fig. 7, which had
40 an endothermic peak at 99.6°C. The differential thermal analysis was carried out according to the method described previously.

Synthesis 2

45 Synthesis 1 was repeated to obtain the crystals having the peaks at the Bragg angles (2θ) of $9.5^\circ \pm 0.2^\circ$ and $27.2^\circ \pm 0.2^\circ$ in an X-ray diffraction spectrum, except that methanol used for treating the wet paste in the mixed solvent was replaced with acetone. A differential thermal analysis of this crystal gave a differential thermal curve shown in Fig. 8.

Synthesis 3

50 There were mixed 14.6 g (0.1 mol) of 1,3-diminoisoindoline and 7.95 g (0.03 mol) of vanadium oxide acetylacetonate in 100 ml of α -chloronaphthalene, and the mixture was heated at 190°C for 2 hours in a nitrogen stream to complete reaction. After cooling to a room temperature, the deposit was filtered and washed in sequence with α -chloronaphthalene, chloroform, 2% hydrochloric acid aqueous solution, water and methanol, followed by drying, to thereby obtain 11.0 g of vanadylphthalocyanine. Subsequently, the product was dissolved in concentrated sulfuric acid of 30 times the weight of the product, and then the solution was poured into water of 300 times the volume, and the deposit was filtered to obtain an amorphous wet paste.

To 2 g of this wet paste was added a mixed solvent of 200 ml of 2-dichloroethane and 100 ml of methanol, and the mixture was stirred for 3 hours at a room temperature. After diluting with methanol, the product was filtered off, washed with methanol and dried to obtain the crystals having the differential thermal curve shown in Fig. 13.

Comparative Synthesis 1

There were pulverized 10 parts of α -titanyl-phthalocyanine, 5 to 20 parts of sodium chloride as a pulverizing aid and 10 parts of polyethylene glycol as a dispersant for 7 to 15 hours at 60 to 120°C in a sand grinder. Grinding at a high temperature is liable to convert phthalocyanine to a β -type or easily decompose it.

The ground product taken out from the grinder was washed with water and methanol to remove the pulverizing aid and dispersant. Then, the product was refined with a 2% dilute sulfuric acid aqueous solution and filtered, followed by washing and drying, to obtain the crystals having the peaks at the Bragg angles of $9.5 \pm 0.2^\circ$ and $27.2 \pm 0.2^\circ$ in an X-ray diffraction spectrum. The differential thermal curve is shown in Fig. 14.

Comparative Synthesis 2

Synthesis 1 was repeated to obtain β -titanylphthalocyanine, except that the wet paste was stirred and heated in α -chloronaphthalene. An X-ray diffraction spectrum of the product had the peaks at the Bragg angles (2θ) of $9.3^\circ \pm 0.2^\circ$, $10.6^\circ \pm 0.2^\circ$, $13.2^\circ \pm 0.2^\circ$, $15.1^\circ \pm 0.2^\circ$, $15.7^\circ \pm 0.2^\circ$, $16.1^\circ \pm 0.2^\circ$, $20.8^\circ \pm 0.2^\circ$, $23.3^\circ \pm 0.2^\circ$, $26.3^\circ \pm 0.2^\circ$ and $27.1^\circ \pm 0.2^\circ$. The differential thermal curve thereof is shown in Fig. 15.

Then, the substances adsorbed on titanylphthalocyanine and vanadylphthalocyanine prepared in Syntheses 1 to 3 and Comparative syntheses 1 and 2 were analyzed in vacuum. The results were as follows :

		% by number of a molecule					
		H ₂	H ₂ O	CO	N ₂	O ₂	CO ₂
Synthesis 1	2.2	68.5	0.0	23.3	4.2	1.8	
Synthesis 2	2.0	59.3	0.0	31.3	5.6	1.8	
Synthesis 3	2.0	50.8	0.0	38.5	7.0	1.7	
Comparative Synthesis 1	1.1	15.7	0.0	69.1	12.1	2.0	
Comparative synthesis 2	0.0	2.6	0.0	79.5	13.9	4.0	

It is understood from the above analysis that titanylphthalocyanines and vanadylphthalocyanine prepared in Syntheses 1 to 3 contain water molecules at the largest percentage.

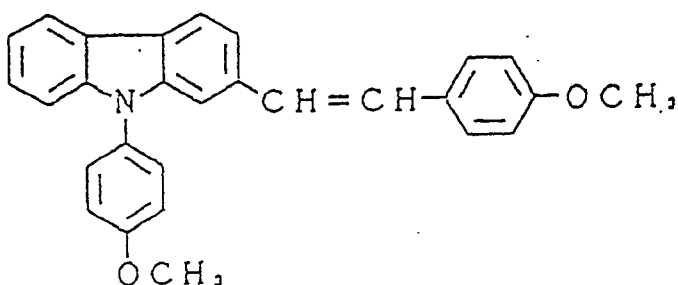
Example 1

Three parts (hereinafter, part means part by weight) of a copolymer polyamide (Luckamide 5003 made by Dainippon Ink & Chemicals, Inc.) was dissolved in 100 parts of methanol by heating. The solution was filtered with a 0.6 μ m filter and coated on an aluminum drum by the penetration coating method to form a subbing layer of 0.5 μ m thickness.

A dispersion was prepared by dispersing 3 parts of the inventive titanylphthalocyanine pigment prepared in Synthesis 1, 3 parts of a cellulose-modified silicone resin (KR 5240 made by Shin-Etsu Chemical Co.) as a binder resin, and 100 parts of methyl isobutyl ketone as a dispersant with a sand mill. Then, the dispersion was coated on the subbing layer by the penetration coating method to form a carrier generating layer of 0.2 μ m thickness. Next, there was coated thereon by the penetration coating method a solution prepared by dissolving 1 part of the carrier transfer substance T-1 shown below, 1.5 parts of a polycarbonate resin (Iupilon Z-200 made by Mitsubishi Gas Chemical Co.), and a small amount of a silicone oil (KF-54 made by Shin-Etsu Chemical Co.) in 10 parts of 1,2-dichloroethane to form a carrier transfer layer of 25 μ m thickness, whereby

the photoreceptor sample of the invention was prepared.

T-1



Example 2

A photoreceptor sample was prepared in the same manner as in Example 1, except that the titanylphthalocyanine pigment prepared in Synthesis 1 was replaced with what was prepared in Synthesis 2.

Example 3

A photoreceptor sample was prepared in the same manner as in Example 1, except that the titanylphthalocyanine pigment of Synthesis 1 was replaced with the vanadylphthalocyanine pigment prepared in Synthesis 3.

Example 4

Three parts of copolymer polyamide CM 8000 made by Toray was dissolved in 100 parts of methanol by heating. The solution was filtered with a 0.6 μm filter and coated on an aluminum drum by the penetration coating method to form a subbing layer of 0.5 μm thickness.

Next, the dispersion was prepared by dispersing 3 parts of the inventive titanylphthalocyanine pigment prepared in Synthesis 1, 3 parts of a polyvinylbutyral resin Eslec BHS made by Sekisui Chemical and 100 parts of methyl isobutyl ketone with a sand mill. The dispersion was coated on the subbing layer by the penetration method to form a carrier generating layer of 0.2 μm thickness, and a carrier transport layer was provided thereon in the same manner as in Example 1, whereby the photoreceptor sample of the invention was prepared.

Example 5

Example 4 was repeated to prepare the photoreceptor sample of the invention, except that the titanylphthalocyanine pigment prepared in Synthesis 1 was replaced with what was prepared in Synthesis 2.

Example 6

Example 4 was repeated to prepare the photoreceptor sample of the invention, except that the titanylphthalocyanine pigment prepared in Synthesis 1 was replaced with the vanadylphthalocyanine pigment prepared in Synthesis 3.

Comparison 1

Example 1 was repeated to prepare the photoreceptor sample of the comparison, except that the titanylphthalocyanine pigment prepared in Synthesis 1 was replaced with what was prepared in Comparative Synthesis 1.

Comparison 2

Example 1 was repeated to prepare the photoreceptor sample of the comparison, except that the titanylphthalocyanine pigment prepared in Synthesis 1 was replaced with what was prepared in Comparative Synthesis 2.

Comparison 3

Example 4 was repeated to prepare the photoreceptor sample of the comparison, except that the titanylphthalocyanine pigment prepared in Synthesis 1 was replaced with what was prepared in Comparative Synthesis 1.

Comparison 4

Example 4 was repeated to prepare the photoreceptor sample of the comparison, except that the titanylphthalocyanine pigment prepared in Synthesis 1 was replaced with what was prepared in Comparative Synthesis 2.

Evaluation

Each of the inventive and comparative samples was mounted in a modified model of U-Bix 1550 made by Konica Corp. (having a semiconductor laser light source). After adjusting in a grid voltage V_G to 600 [V], a potential V_H of an unexposed portion and a potential V_L of an exposed portion illuminated at 0.7 mW were measured. Further, V_H and V_L were also measured on the samples which were subjected to 50,000 cycles of copying operations at 33°C and 80%RH. The results are shown in Table 1.

Table 1

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	33°C 80%		33°C 80%		20°C 50%	
	Zero cycle		After 50,000 cycles		After 10,000 cycles at ozone conc. of 10 ppm	
	V _H (-V)	V _L (-V)	V _H (-V)	V _L (-V)	V _H (-V)	V _L (-V)
Example 1	585	49	582	51	570	48
Example 2	580	50	570	57	569	49
Example 3	581	61	563	75	567	55
Example 4	586	35	589	49	573	32
Example 5	583	39	585	55	572	35
Example 6	580	45	581	69	570	40
Comparison 1	580	49	581	58	439	39
Comparison 2	581	127	475	164	549	151
Comparison 3	585	37	579	48	421	35
Comparison 4	583	121	451	177	558	143

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As can be seen from the above results, the inventive photoreceptors have the high sensitivities and excellent stability in a repetitive use at a high temperature, high humidity and high ozone concentration, while the sensitivities of the comparative photoreceptors are deteriorated in a repetitive use at the above environment.

Example 7

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An aluminum drum coated with a polyamide resin layer of 0.3 μm thickness was coated by the dip coating method with a dispersion prepared by dispersing 3 parts of the titanylphthalocyanine pigment prepared in Synthesis 1 and 35 parts of a silicone resin (15% xylene-butanol solution of KR-5240 made by Shin-Etsu Chemical Co.) in 100 parts of methyl ethyl ketone with a sand mill to form a carrier generating layer of 0.2 μm thickness. Subsequently, the drum was coated by the blade coating method with a solution prepared by dissolving 1 part of the foregoing carrier transfer substance T-1, 1.3 parts of a polycarbonate resin (Iupilon Z200 made by Mithubishi Gas Chemical Co.), and a small amount of a silicone oil (KF-54 made by Shin-Etsu Chemical Co.) in 10 parts of 1,2-dichloroethane to form a carrier transfer layer of 20 μm thickness, whereby the photoreceptor sample of the invention was prepared.

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The sample was mounted in a modified model of a color copier DC-8010 (made by Konica Corp. ; two-component developer type) equipped with a 400 dpi optical system, and quality of copied images was evaluated, wherein a latent image was developed by the non-contact jumping method of a reversal system. The developing conditions are described below. The resolution and background fog were evaluated for the image quality of the sample at an initial stage and after 50,000 cycles of a copying operation at 33°C and 80% RH. The results are shown in Table 2. Developing conditions

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	Image carrier	150 ϕ drum
	Linear velocity	70 mm/sec
5	V_H	-600 V
	Sleeve linear velocity ($\phi 20$, 250 rpm)	260 mm/sec
10	Developing gap	500 μ m
	Thickness of developer layer	300 μ m
	Concentration of toner in developer	7 wt%
15	D C bias	350 V
	A C bias	1.2 KVp-p
20		(3 KHz)

Method of evaluation

25 Resolution : a resolution chart having vertical
 lines of 4, 5, 6, 7 and 8 lines/mm at
 equal spaces. The resolution is

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 indicated by a line density at which
 the respective vertical lines can be
 35 visually discriminated.

 Background fog: determined by visual observation of a
 40 sample obtained by copying white paper.

 o: no fog

 x: fog observed

45 Comparison 5

 A comparative photoreceptor sample was prepared and evaluated in the same manners as in Example 7,
 50 except that the titanylphthalocyanine pigment prepared in Comparative Synthesis 1 was used instead of the
 titanylphthalocyanine pigment of Synthesis 1.

 The results are shown in Table 2.

55 Comparison 6

 A comparative photoreceptor sample was prepared and evaluated in the same manners as in Example 7,
 provided that a developer layer was contacted to the photoreceptor. The results are shown in Table 2. The
 developing conditions were as follows :

Image carrier	150 ϕ drum
Linear velocity	70 mm/sec
5 Surface potential	$V_H = -600$ V
Sleeve linear velocity ($\phi 20$, 250 rpm)	260 mm/sec
10 Developing gap	500 μ m
Thickness of developer layer	600 μ m
D C bias	-560 V

Table 2

	33°C 80%RH Zero cycle		33°C 80%RH After 50,000 cycles	
	Resolution	Background fog	Resolution	Background fog
Example 7	8.0	o	8.0	o
30 Comparison 5	8.0	o	5.0	x
Comparison 6	7.0	x	6.0	x

As understood from Table 2, non-contact developing with the phthalocyanine photoreceptor of the invention makes it possible to provide a high resolution without causing background fog even after repeating 50,000 cycles of copying operation at such a high temperature and humidity as 33°C and 80% RH.

Example 8

The photoreceptor sample of the invention was prepared in the same manner as in Example 7.

The sample was mounted in an image forming equipment shown in Fig. 10, and quality of copied images was evaluated.

Method of evaluation

(a) Surface potential V_H :

Under environmental conditions of 33°C and 80%RH, the initial surface potential was set at - 600 V by adjusting a grid voltage.

(b) Background fog :

Same as in Example 7.

(c) Optical memory :

Is defined by $V_{H0} - V_{H1}$, wherein $-V_{H0}$ is an initial surface potential of an electrified photoreceptor and $-V_{H1}$ is a surface potential of the photoreceptor electrified once again after exposing to a laser ray.

(d) Ghost

Immediately after the same characters and charts are copied fifty times in succession, a halftone image is copied and it is visually observed whether or not the previous characters or charts appear on the halftone

image.

o : no ghost

x : ghost observed

5 Comparison 7

A comparative photoreceptor sample was prepared in the same manner as in Example 7, except that the titanylphthalocyanine pigment of Comparative Synthesis 1 was used instead of the titanylphthalocyanine pigment of Synthesis 1.

10 The sample was evaluated in the same manner as in Example 8. The results are shown in Table 3.

Table 3

	33°C, 80%RH, Zero cycle				33°C, 80%RH, After 50,000 cycles			
	V _H (V)	Optical memory (V)	Fog	Ghost	V _H (V)	Optical memory (V)	Fog	Ghost
20 Example 8	600	20	o	o	590	20	o	o
Comparison 7	600	60	o	o	487	95	x	x

25 It is understood from Table 3 that the photoreceptor of the invention has little degradation of a surface potential and causes substantially no fog, optical memory and ghost.

30 Claims

1. An electrophotographic photoreceptor comprising a conductive substrate and, provided thereon, a photoreceptive layer comprising a phthalocyanine pigment and a binder resin, wherein the phthalocyanine pigment has water molecules adsorbed thereon in a numerical amount greater than any other molecules, as measured by a vacuum method.
2. A photoreceptor according to claim 1, wherein the phthalocyanine pigment has an endothermic peak in a range of 80 to 120° in a differential thermal analysis.
3. A photoreceptor according to claim 1 or 2, wherein the phthalocyanine pigment is titanylphthalocyanine or vanadylphthalocyanine.
4. A photoreceptor according to claim 3, wherein the phthalocyanine pigment is titanylphthalocyanine having peaks at the Bragg angles (2θ) of $9.5^\circ \pm 0.2^\circ$ and $27.2^\circ \pm 0.2^\circ$.
5. A photoreceptor according to any one of the preceding claims, wherein the phthalocyanine pigment has been treated with a mixed solvent containing a hydrophilic solvent.
6. A photoreceptor according to claim 5, wherein the hydrophilic solvent is an alcohol or ketone.
7. A photoreceptor according to any one of the preceding claims, wherein the photoreceptive layer comprises a carrier generating layer comprising the phthalocyanine pigment and a carrier transport layer comprising a carrier transport material.
8. A photoreceptor according to claim 7, wherein the thickness of the carrier generating layer is 0.01 to 20 μm.
9. A photoreceptor according to claim 8, wherein the thickness is 0.05 to 5 μm.

10. A photoreceptor according to any one of claims 7 and 9, wherein the thickness of the carrier transport layer is 1 to 100 μm .

11. A photoreceptor according to claim 10, wherein the thickness is 5 to 30 μm .

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12. A method of forming an image comprising the steps of
forming an electrostatic latent image on a photoreceptor as defined in any one of the preceding claims by
exposure to a laser ray, and
developing the electrostatic latent image to a toner image with a toner, an alternating oscillation electric
field being applied to a developing area while maintaining a developer carrier and the photoreceptor in a
non-contact state,
transferring the toner image on a printing paper and fixing the toner image with a heat roller.

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13. A method of forming an image comprising the steps of
forming overlapped toner images on a photoreceptor as defined in any one of claims 1 to 11 by repeating
formation of an electrostatic latent image with digital exposure and development of the electrostatic latent
image with a toner,
transferring the overlapped toner images on a printing paper, and
fixing the toner images with a heat roller.

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FIG. 1

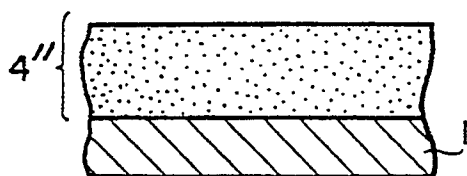


FIG. 2

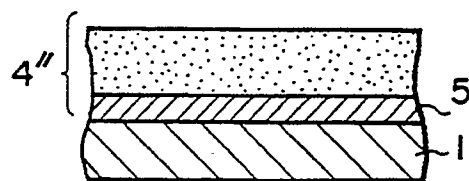


FIG. 3

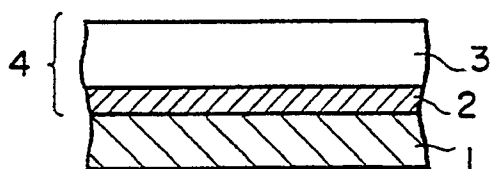


FIG. 4

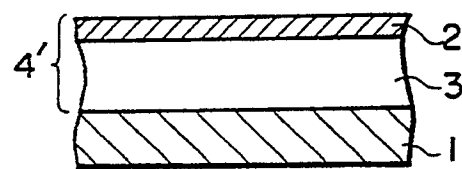


FIG. 5

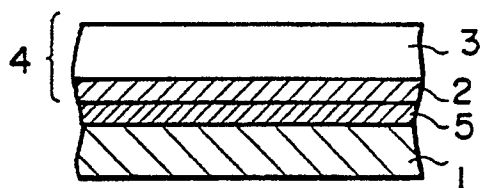


FIG. 6

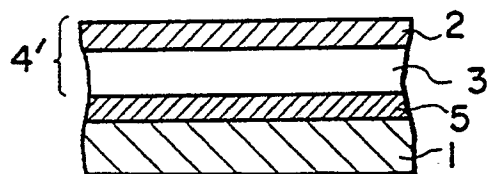


FIG. 8

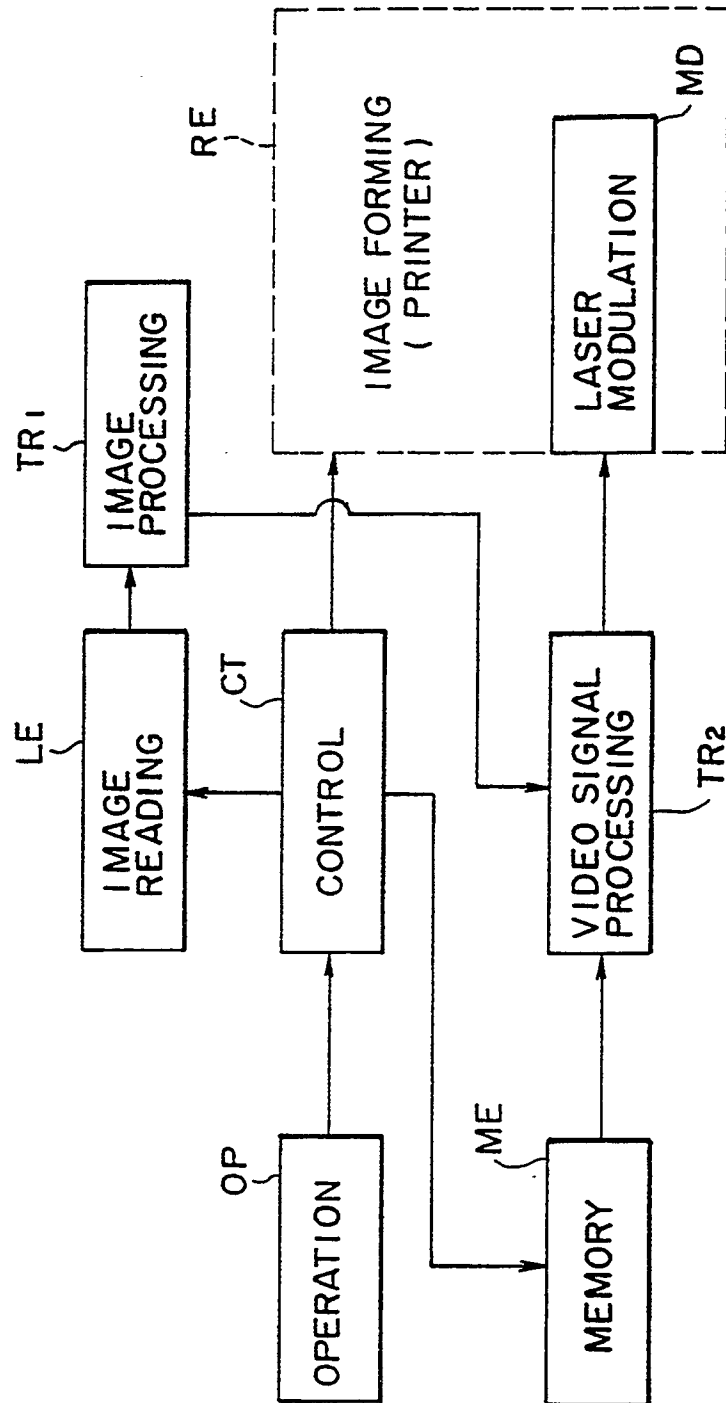


FIG. 9

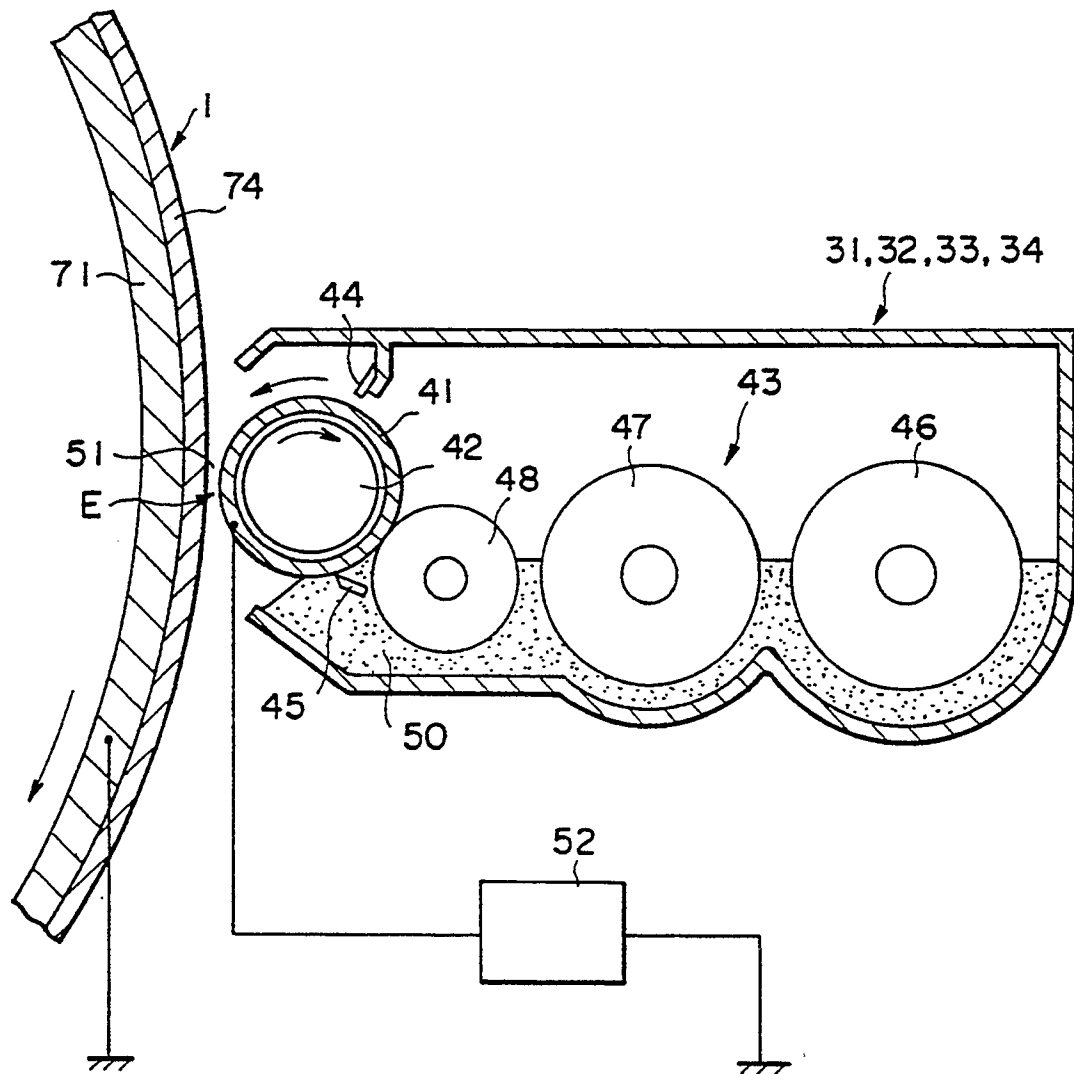


FIG. 10

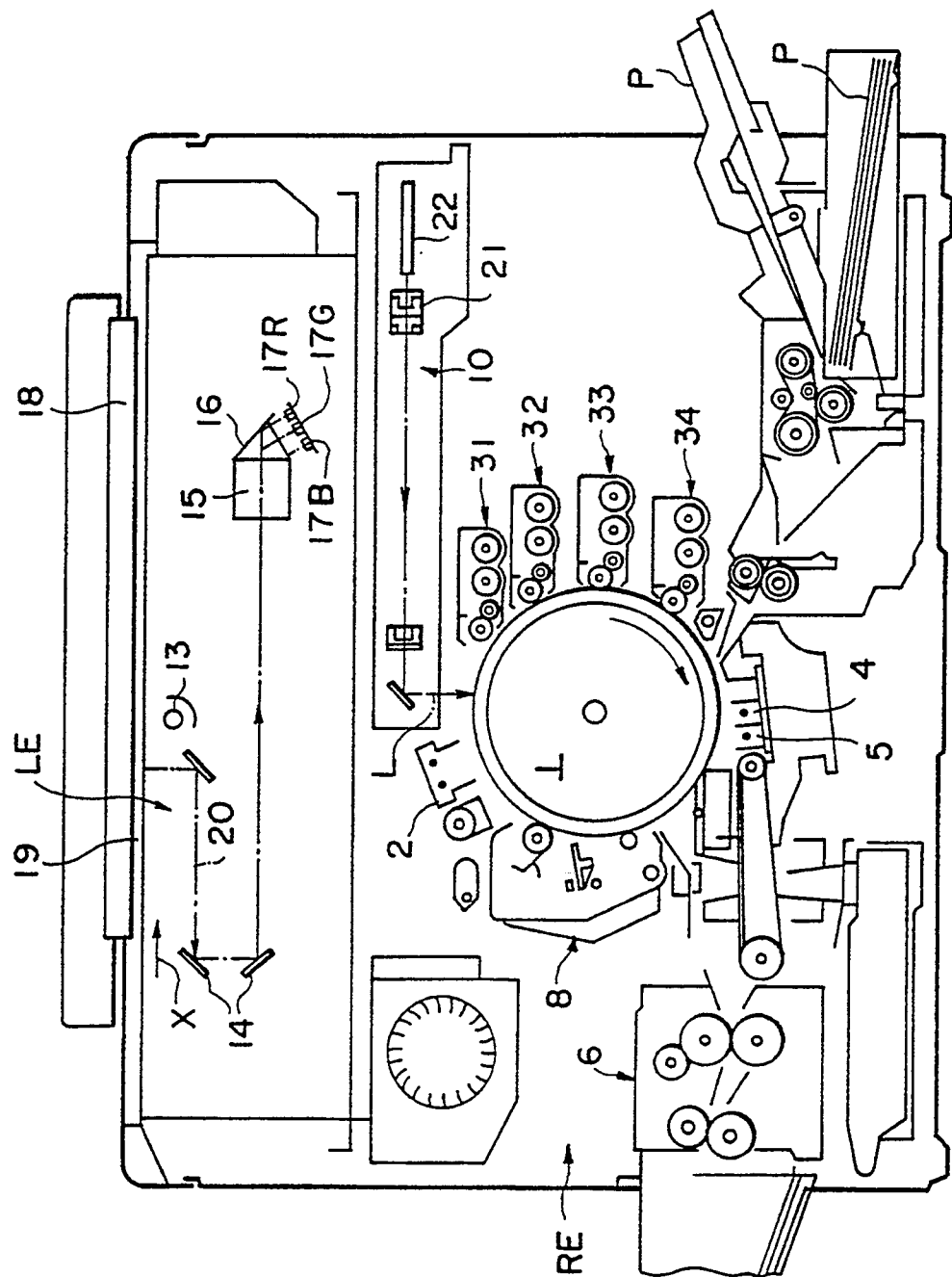


FIG. II

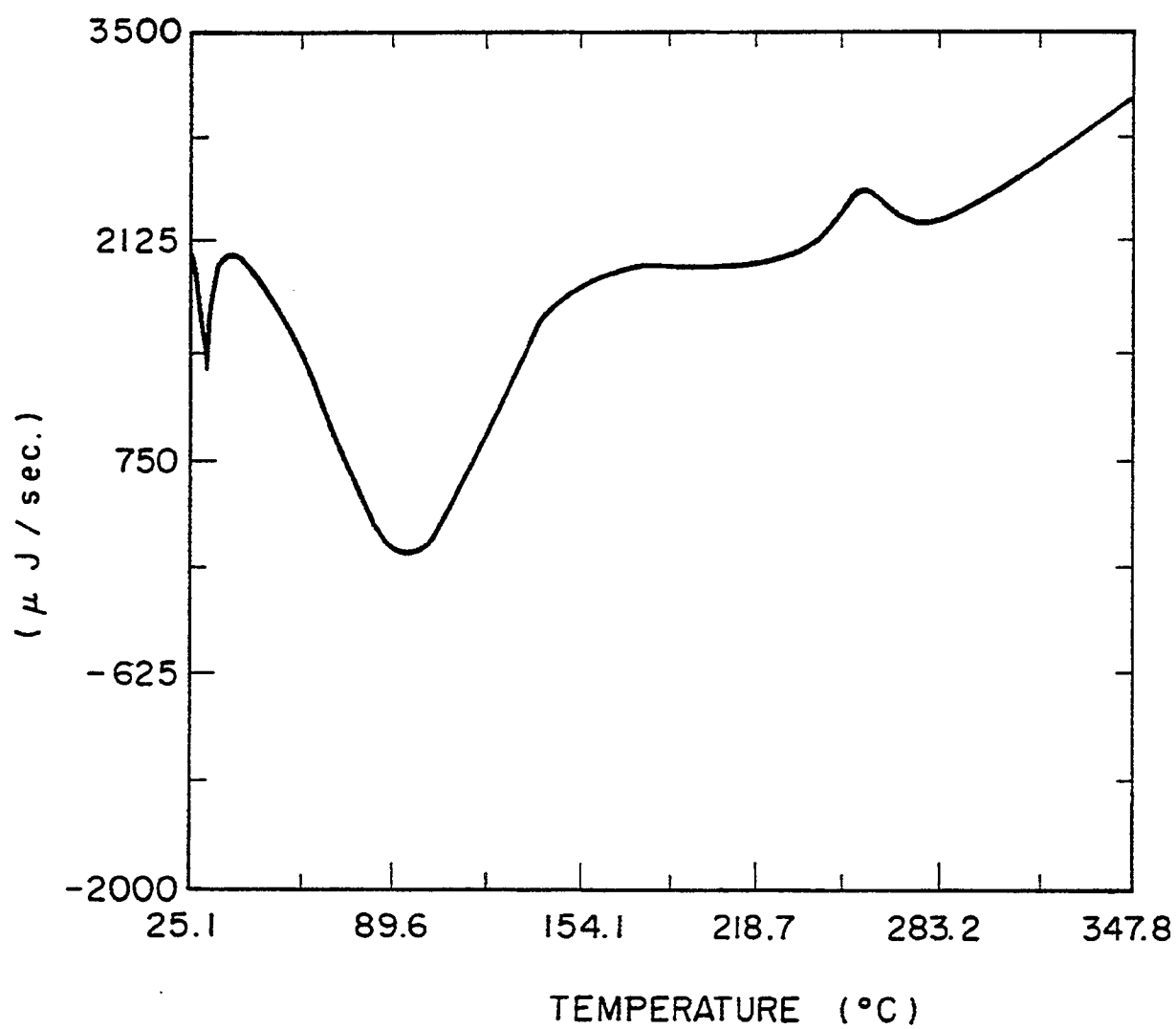


FIG. 12

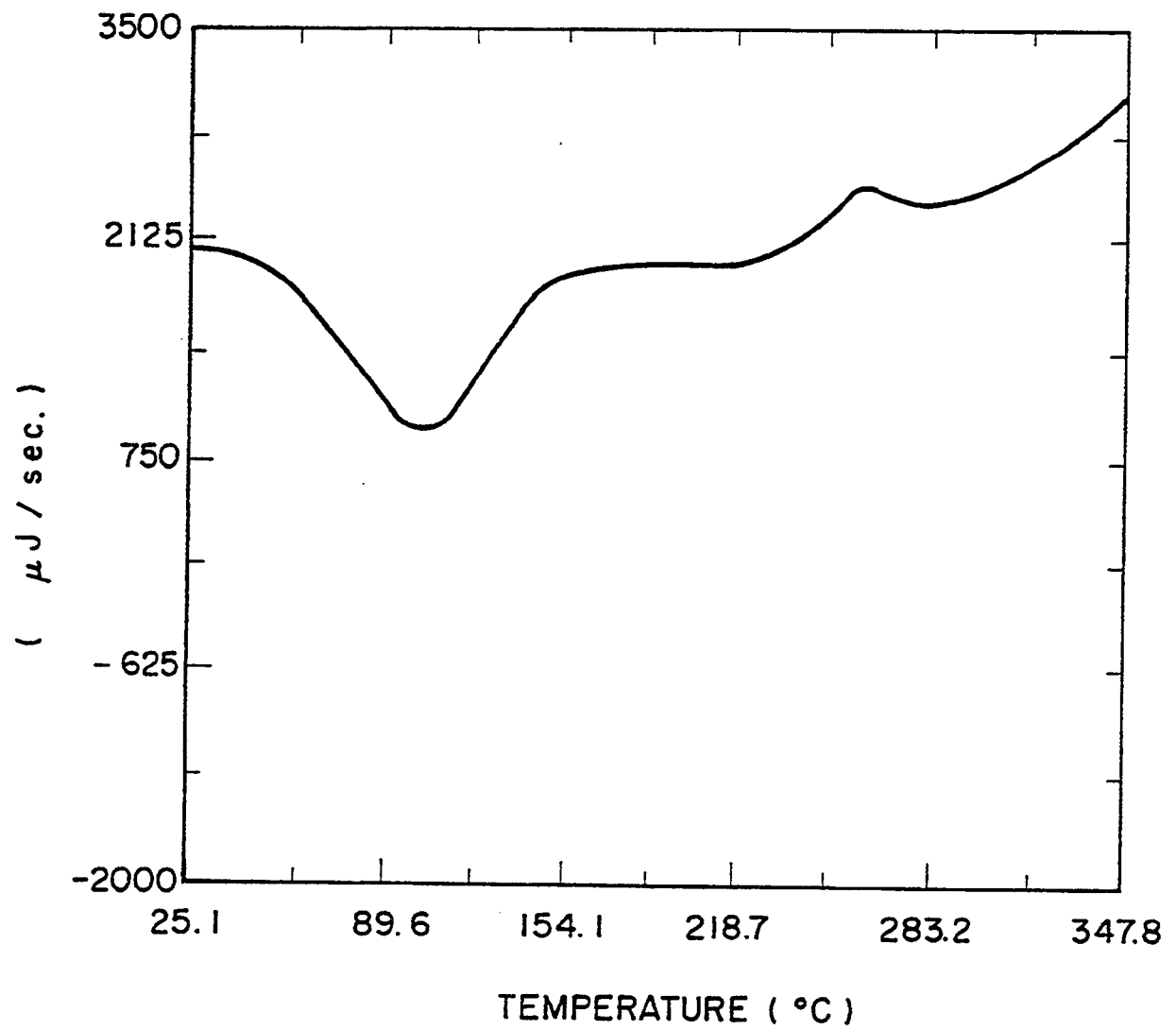


FIG. 13

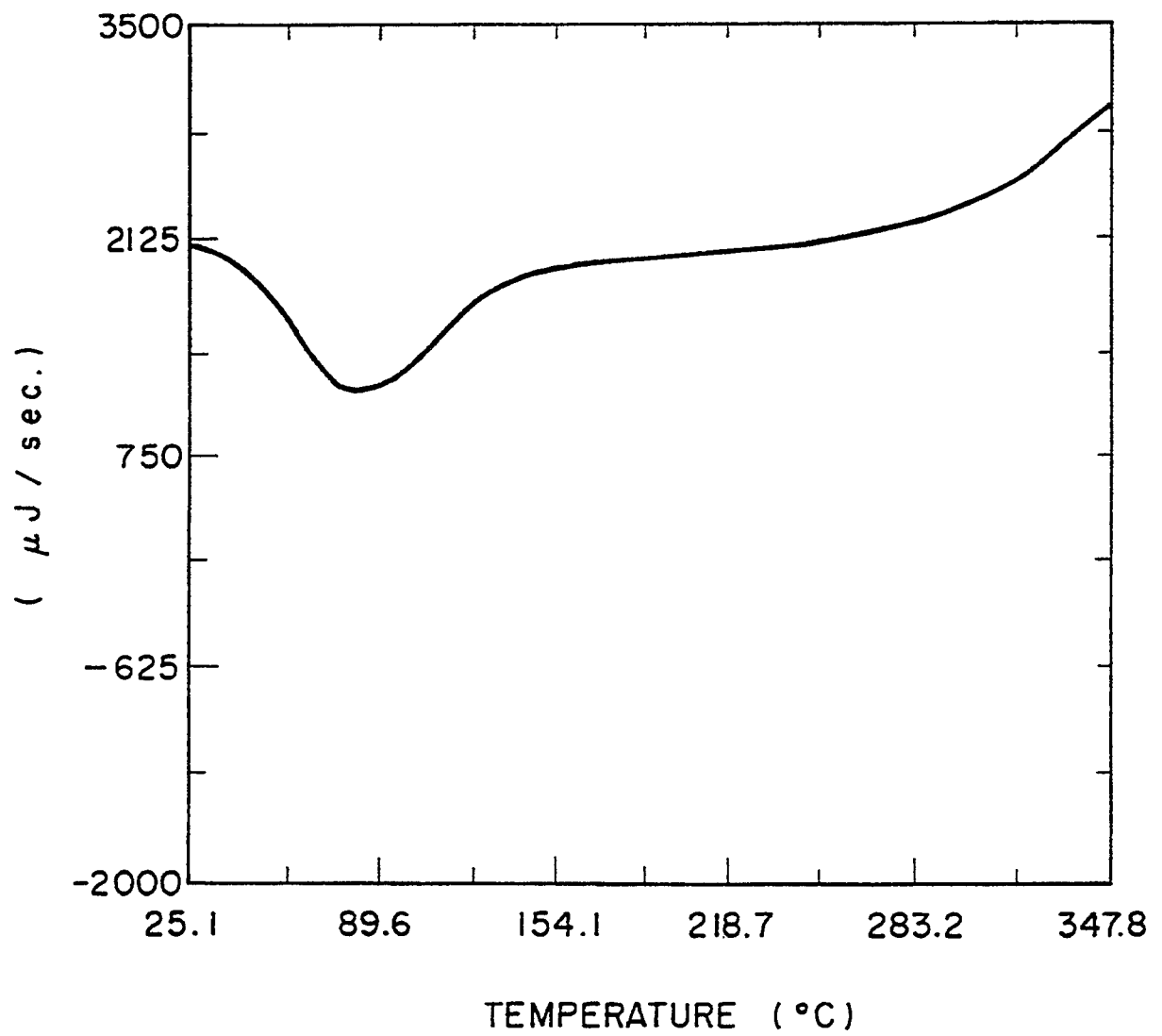


FIG. 14

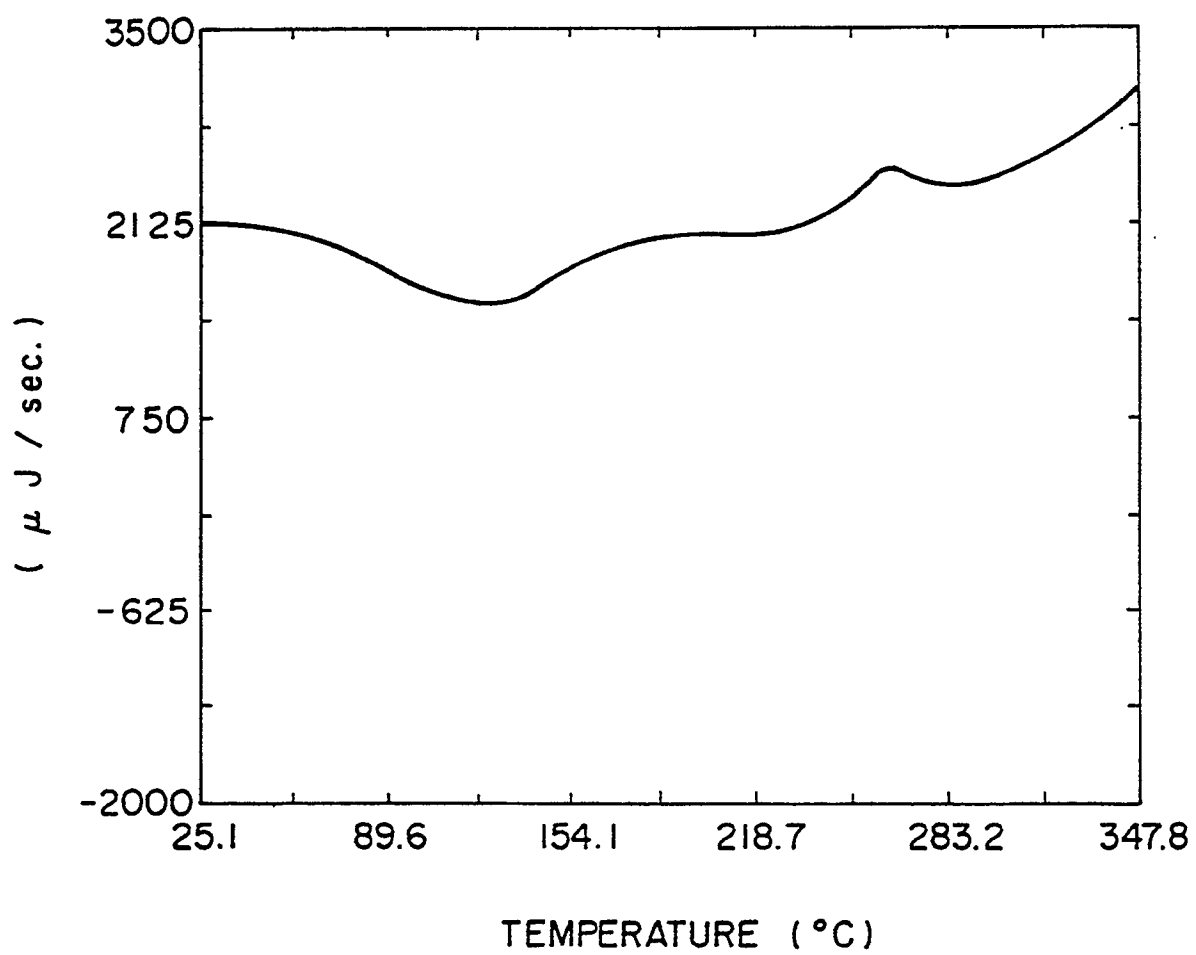


FIG. 15

