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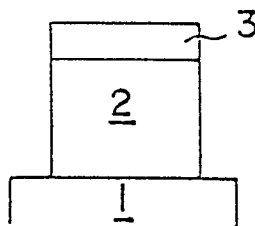
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54 **Photosensitive member comprising charge generating layer and charge transporting layer.**

57 A photosensitive member of the present invention comprises an electrically conductive substrate (1), a hydrogenated and/or halogenated amorphous silicon:germanium charge generating layer (3) and a hydrogen-containing amorphous carbon charge transporting layer (2) containing boron atoms or phosphorus atoms. The charge generating layer (3) may further contain various elements such as boron or phosphorus, oxygen, nitrogen and carbon as a chemical modifier.

FIG.1



PHOTOSENSITIVE MEMBER COMPRISING CHARGE GENERATING LAYER AND CHARGE TRANSPORTING LAYER

BACKGROUND OF THE INVENTION

Field of the Invention:

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The present invention relates to a photosensitive member of the function-separated type comprising an amorphous silicon:germanium layer as a charge generating layer and a hydrogen-containing amorphous carbon layer as a charge transporting layer.

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Description of the Prior Art:

Remarkable progress has been made in the application of electrophotographic techniques since the invention of the Carlson process. Various materials have also been developed for use in electrophotographic photosensitive members.

Conventional photoconductive materials chiefly include inorganic compounds such as amorphous selenium, selenium-arsenic, selenium-tellurium, zinc oxide, amorphous silicon and the like, and organic compounds such as polyvinylcarbazole, metal phthalocyanine, dis-azo pigments, tris-azo pigments, perillene pigments, triphenylmethanes, triphenylamines, hydrazones, styryl compounds, pyrazolines, oxazoles oxadiazoles and the like. The structures of photosensitive members include, for example, those of the single-layer type wherein such a material is used singly, the binder type wherein the material is dispersed in a binder, and the function-separated type comprising a charge generating layer and a charge transporting layer.

However, conventional photoconductive materials have various drawbacks. For example, the above-mentioned inorganic materials except for amorphous silicon (a-Si) are harmful to the human body.

The electrophotographic photosensitive member, when employed in a copying apparatus, must always have stabilized characteristics even if it is subjected to the severe environmental conditions of charging, exposure, developing, image transfer, removal of residual charges and cleaning, whereas the foregoing organic compounds have poor durability and many unstable properties.

In order to eliminate these drawbacks, progress has been made in recent years in the application of a-Si formed by the glow discharge process to electrophotographic photosensitive members as a material with reduced harmfulness, higher sensitivity, higher hardness such as more than 7H level of the JIS standards for pencil lead hardness and higher durability. Nevertheless, a-Si is hazardous to manufacture since it requires highly ignitable silane gas as its starting material. Moreover, a-Si requires a large quantity of silane gas which is expensive, rendering the resulting photosensitive member exceedingly more costly than conventional photosensitive members. The manufacture of photosensitive members of a-Si involves many disadvantages. For example, a-Si is low in film-forming speed and releases a large amount of explosive undecomposed silane products in the form of particles when forming a film. Such particles, when incorporated into the photosensitive member being produced, gives a seriously adverse influence on the quality of images to be obtained. Further, a-Si has a low chargeability due to its original high relative dielectric constant. This necessitates the use of a charger of higher output for charging the a-Si photosensitive member to a predetermined surface potential in the copying apparatus.

On the other hand, it has been proposed in recent years to use amorphous carbon films as plasma-polymerized organic films for photosensitive members.

Plasma-polymerized organic films per se have been well-known for a long time. In Journal of Applied Polymer Science, Vol. 17, pp. 885-892, 1973, for example, M. Shen and A.T. Bell state that a plasma-polymerized organic film can be produced from the gas of any organic compound. The same authors discuss film formation by plasma polymerization in "Plasma Polymerization," published by the American Chemical Society in 1979.

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However, the plasma-polymerized organic films prepared by the conventional process have been used only as insulating films. They are thought to be insulating films having a specific resistivity of about 10^{16} ohm-cm like usual polyethylene films, or are used as recognized at least as such. The use of the film for electrophotographic photosensitive members is based also on the same concept; the film has found limited use only as an undercoat or overcoat serving solely as a protective layer, adhesion layer, blocking layer or insulating layer.

For example, Unexamined Japanese Patent Publication SHO 59-28161 discloses a photosensitive member which comprises a plasma-polymerized high polymer layer of reticular structure formed on a substrate and serving as a blocking-adhesion layer, and an a-Si layer formed on the polymer layer. Unexamined Japanese Patent Publication SHO 59-38753 discloses a photosensitive member which comprises a plasma-polymerized film having a thickness of 10 to 100 angstroms and formed over a substrate as a blocking-adhesion layer, and an a-Si layer formed on the film, the plasma-polymerized film being prepared from a gas mixture of oxygen, nitrogen and a hydrocarbon and having a high resistivity of 10^{13} to 10^{15} ohm-cm. Unexamined Japanese Patent Publication SHO 59-136742 discloses a photosensitive member wherein an aluminum substrate is directly coated with a carbon film having a thickness of about 1 to about 5 microns and serving as a protective layer for preventing aluminum atoms from diffusing through an a-Si layer formed over the substrate when the member is exposed to light. Unexamined Japanese Patent Publication SHO 60-63541 discloses a photosensitive member wherein a diamond-like carbon film, 200 angstroms to 2 microns in thickness is interposed between an aluminum substrate and an overlying a-Si layer to serve as an adhesion layer to improve the adhesion between the substrate and the a-Si layer. The publication says that the film thickness is preferably up to 2 microns in view of the residual charge.

These disclosed inventions are all directed to a so-called undercoat provided between the substrate and the a-Si layer. In fact, these publications mention nothing whatever about charge transporting properties, nor do they offer any solution to the foregoing substantial problems of a-Si.

Furthermore, U.S. Patent No. 3,956,525, for example, discloses a photosensitive member of a the polyvinylcarbazole-selenium type coated with a polymer film having a thickness of 0.1 to 1 microns and formed by glow discharge polymerization as a protective layer. Unexamined Japanese Patent Publication SHO 59-214859 discloses a technique for protecting the surface of an a-Si photosensitive member with an approximately 5-micron-thick film formed by plasma-polymerizing an organic hydrocarbon monomer such as styrene or acetylene. Unexamined Japanese Patent Publication SHO 60-61761 discloses a photosensitive member having a diamond-like carbon thin film 500 angstroms to 2 microns in thickness and serving as a surface protective layer, it being preferred that the film thickness be up to 2 microns in view of transmittancy. Unexamined Japanese Patent Publication SHO 60-249115 discloses a technique for forming a film of amorphous carbon or hard carbon with a thickness of about 0.05 to about 5 microns for use as a surface protective layer. The publications states that the film adversely affects the activity of the protected photosensitive member when exceeding 5 microns in thickness.

These disclosed inventions are all directed to a so-called overcoat formed over the surface of the photosensitive member. The publications disclose nothing whatever about charge transporting properties, nor do they solve the aforementioned substantial problems of a-Si in any way.

Unexamined Japanese Patent Publication SHO 51-46130 discloses an electrophotographic photosensitive member of the polyvinylcarbazole type which has a polymer film 0.001 to 3 microns in thickness and formed on its surface by being subjected to glow discharge polymerization. Nevertheless, the publication is totally mute about charge transporting properties, further failing to solve the foregoing substantial problems of a-Si.

With respect to a-Si, W. E. Spear and P. G. LeComber state in Philosophical Magazine, Vol. 33, pp. 935-949, 1976, that a-Si can control polarities. Since then, progress has been made in the application of a-Si to various photosensitive devices.

For example, Unexamined Japanese Patent Publication No. SHO 56-62254 discloses a photosensitive member of a-Si containing carbon. This reference aims at adjusting photoconductivity of a-Si by incorporating carbon therein, and the a-Si layer is needed to form in a large thickness.

Thus, the conventional plasma-polymerized organic films for use in electrophotographic photosensitive members are used as undercoats or overcoats because of their insulating properties and need not have a carrier transporting function. Accordingly, the films used are limited in thickness to a very small value of up to about 5 microns if largest. Carriers pass through the film owing to a tunnel effect, while if the tunnel effect is not expectable, the film used has such a small thickness that will not pose problems actually as to the occurrence of a residual potential. Further, the conventional a-Si layer for use in electrophotographic photosensitive members are used in a large thickness, causing disadvantages in view of cost or productivity.

SUMMARY OF THE INVENTION

The main object of the present invention is to provide a photosensitive member excellent in electrophotographic characteristics and is capable of giving satisfactory images.

Another object of the invention is to provide a photosensitive member comprising a charge transporting layer which is excellent in charge transportability and in charging characteristics and a charge generating layer which exhibits distinct photoconductive properties.

Still another object of the invention is to provide a photosensitive member which is highly resistant to moisture and weather and excellent in transparency.

These and other objects of the invention can be accomplished by providing a photosensitive member comprising an electrically conductive substrate, a charge generating layer comprising hydrogenated amorphous silicon containing germanium or fluorinated amorphous silicon containing germanium, and a charge transporting layer comprising amorphous carbon containing hydrogen and boron atoms or phosphorus atoms.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 to 6 are diagrams showing photosensitive members embodying the invention; and
Figs. 7 and 8 are diagrams showing apparatus for preparing photosensitive members of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The photosensitive member embodying the present invention is characterized in that the member comprises a hydrogenated or fluorinated amorphous silicon:germanium layer as a charge generating layer (hereinafter referred to as a-Si layer) and an amorphous carbon layer containing hydrogen and boron or phosphorous prepared by applying a glow discharge with plasma polymerization as a charge transporting layer (hereinafter referred to as "a-C layer").

We have conducted research on the application of hydrogen-containing amorphous carbon layers to photosensitive members of function-separated type and found that a hydrogenated amorphous carbon layer containing boron or phosphorus, which is originally thought to be an insulating layer, exhibits ability to transport charges, readily showing satisfactory electrophotographic characteristics, when laminated to a hydrogenated or fluorinated amorphous silicon:germanium layer. Although much still remains to be clarified in detail for the theoretical interpretation of this finding, the result will presumably be attributable to the following reason. The band structure formed by electrons in a relatively unstable state, such as π -electrons, unpaired electrons, remaining free radicals and the like, which are captured in the hydrogenated amorphous carbon layer containing boron or phosphorus has, at the conduction band or charge electron band, an energy level close to that of the band formed by the hydrogenated or fluorinated amorphous silicon:germanium, so that the carriers produced in the hydrogenated or fluorinated amorphous silicon:germanium layer can be readily injected into the hydrogenated amorphous carbon layer containing boron or phosphorus, which further permits satisfactory travel of the carriers therethrough by the action of the above-mentioned electrons of relatively unstable energy state.

The carbon and hydrogen contents of the a-C layer of the invention can be determined by a usual method of elementary analysis, for example, by organic elementary (CHN) analysis.

The charge generating layer exhibits distinct photoconductive properties when exposed to visible light in the vicinity of semiconductor laser beams in wavelength and can be of an exceedingly smaller thickness than in the case of conventional amorphous silicon photosensitive members in serving its function. The charge transporting layer does not exhibit distinct photoconductive properties when exposed to visible light or light in the vicinity of semiconductor laser beams in wavelength, but has suitable ability to transport charges and is excellent in characteristics for use in electrophotographic photosensitive members, e.g. in chargeability, durability and resistance to moisture, weather and environmental pollution, and also in transmittance. The layer therefore affords a high degree of freedom also in providing laminate structures for use as photosensitive members of the function-separated type.

According to the present invention, hydrocarbons are used as organic gases for forming the a-C layer. These hydrocarbons need not always be in a gaseous phase at room temperature at atmospheric pressure but can be in a liquid or solid phase insofar as they can be vaporized on melting, evaporation or sublimation, for example, by heating or in a vacuum. Examples of useful hydrocarbons are saturated hydrocarbons, unsaturated hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons and the like. Such hydrocarbons are usable in combination.

A wide variety of hydrocarbons are usable. Examples of useful saturated hydrocarbons are normal paraffins such as methane, ethane, propane, butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane, eicosane, heneicosane, docosane, tricosane, tetracosane, pentacosane, hexacosane, heptacosane, octacosane, nonacosane, triacontane, dotriacontane, pentatriacontane, etc., isoparaffins such as isobutane, isopentane, neopentane, isohexane, neohexane, 2,3-dimethylbutane, 2-methylhexane, 3-ethylpentane, 2,2-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, tributane, 2-methylheptane, 3-methylheptane, 2,2-dimethylhexane, 2,2,5-dimethylhexane, 2,2,3-trimethylpentane, 2,2,4-trimethylpentane, 2,3,3-trimethylpentane, 2,3,4-trimethylpentane, isononane, etc., and the like.

Examples of useful unsaturated hydrocarbons are olefins such as ethylene, propylene, isobutylene, 1-butene, 2-butene, 1-pentene, 2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 1-hexene, tetramethylethylene, 1-heptene, 1-octene, 1-nonene, 1-decene and the like; diolefins such as allene, methylallene, butadiene, pentadiene, hexadiene, cyclopentadiene and the like; triolefins such as ocimene, alloocimene, myrcene, hexatriene and the like; acetylene, butadiyne, 1-pentadiyne, 2,4-hexadiyne, methylacetylene, 1-butyne, 2-butyne, 1-pentyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, 1-decyne and the like.

Examples of useful alicyclic hydrocarbons are cycloparaffins such as cyclopropane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclononane, cyclodecane, cycloundecane, cyclododecane, cyclotridecane, cyclotetradecane, cyclopentadecane, cyclohexadecane and the like; cycloolefins such as cyclopropene, cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclononene, cyclodecene and the like; terpenes such as limonene, terpinolene, phellandrene, sylvestrene, thujene, carene, pinene, bornylene, camphene, fenchene, cyclofenchene, tricyclone, bisabolene, zingiberene, curcumene, humulene, cadinenesquisibienihene, selinene, caryophyllene, santalene, cedrene, camphorene, phyllocladene, podocarpene, mirene and the like; steroids; etc.

Examples of useful aromatic hydrocarbons are benzene, toluene, xylene, hemimellitene, pseudocumene, mesitylene, prehnitene, isodurene, durene, pentamethylbenzene, hexamethylbenzene, ethylbenzene, propylbenzene, cumene, styrene, biphenyl, terphenyl, diphenylmethane, triphenylmethane, dibenzyl, stilbene, indene, naphthalene, tetralin, anthracene, phenanthrene and the like. In addition to hydrocarbons, also usable are compounds, such as alcohols, ketones, ethers and esters, which can be converted to carbon.

While the amount of hydrogen atoms to be contained in the a-C layer of the present invention is invariably dependent on the process by which the layer is prepared, i.e. the glow discharge process, the hydrogen content is generally 30 to 60 atomic % based on the combined amount of carbon and hydrogen atoms present. The carbon and hydrogen contents of the a-C layer can be determined by a usual method of organic elementary analysis, for example, by ONH analysis.

The hydrogen content of the a-C layer of the invention is variable in accordance with the film forming apparatus and film forming conditions. The hydrogen content can be decreased, for example, by elevating the substrate temperature, lowering the pressure, reducing the degree of dilution of the starting materials, applying a greater power, decreasing the frequency of the alternating electric field to be set up, increasing the intensity of a d.c. electric field superposed on the alternating electric field or desired combination of such procedures.

It is suitable that the a-C layer serving as the charge transporting layer of the invention be 5 to 50 microns, preferable 7 to 20 microns, in thickness for use in the usual electrophotographic process. Thicknesses smaller than 5 microns result in a lower charge potential, failing to give a sufficient copy image density, whereas thicknesses larger than 50 microns are not desirable in view of productivity. The a-C layer is high in transmittancy, dark resistivity and charge transportability, traps no carriers even when not smaller than 5 microns in thickness as mentioned above and contributes to light decay.

According to the present invention, the gases of starting materials are made into an a-C layer, most preferably via a plasma which is produced by d.c. low-or high-frequency, microwave or like plasma process. Alternatively, the layer may be formed via ions which are produced by the ionization deposition, ion-beam deposition or like process, or via neutral particles produced by the vacuum evaporation process, sputtering process or the like. These processes may be used in combination.

According to the present invention, boron atoms or phosphorus atoms may be incorporated into the a-C layer as a chemically modifying substance. The amount of phosphorus atoms or boron atoms to be incorporated into the a-C layer is up to 20,000 atomic ppm based on all the constituent atoms of the layer. The phosphorus or boron content of the layer can be determined by a usual method of elementary analysis, e.g. Auger electron spectroscopy or IMA analysis. The incorporation of boron or phosphorus enables the polarity adjustment of the member and assures high transportability. When containing no boron or phosphorus atoms, the layer obtained fails to exhibit satisfactory transportability and is liable to deteriorate with time. Whereas boron or phosphorus atoms assure suitable transportability when present in a small amount, the boron or phosphorus content, if exceeding 20,000 atomic ppm, conversely gives reduced resistivity to the layer to result in impaired chargeability. According to the invention, therefore, the boron or phosphorus content is critical.

The amount of boron atoms or phosphorus atoms to be contained in the a-C layer as a chemically modifying substance according to the invention is controllable chiefly by varying the amount of boron compound or phosphorus compound, such as one exemplified above, to be introduced into the reactor for plasma polymerization. The use of an increased amount of boron or phosphorus compound gives a higher boron or phosphorus content to the a-C layer of the invention, while a decreased amount of such a compound supplied results in a lower boron or phosphorus content.

According to the present invention, silane gas, disilane gas or silane fluoride gas is used for forming the a-Si layer. Further, a germane gas is used for incorporating germanium atoms into the layer.

The amount of germanium atoms to be contained in the a-Si layer of the invention is preferably up to 30 atomic % based on the combined amount of silicon atoms and germanium atoms. The germanium and silicon contents of the layer can be determined by a usual method of elementary analysis, e.g., Auger electron spectroscopy. The content of germanium atoms can be increased by supplying the germane gas at an increased flow rate for the formation of the layer. As the germanium content increases, the photosensitive member of the invention improves in long-wavelength sensitivity, making it possible to select the light source from among those widely ranging from short to long wavelengths, hence desirable. However, if the germanium content exceeds 30 atomic %, reduced chargeability will result, so that presence of an excess of germanium atoms is undesirable. Accordingly, the amount of germanium atoms to be contained in the a-Si layer of the invention is critical.

The a-Si layer of the present invention may further contain boron atoms or phosphorus atoms. The incorporation of boron atoms or phosphorus atoms in the a-Si layer improves charge transportability and assures polarity adjustment. More specifically, by doping boron in the a-Si layer, charges of positive polarity serve as the majority carrier in the a-Si layer (P-type) and become readily movable. On the other hand, by doping phosphorus in the a-Si layer, charges of negative polarity serve as the majority carrier in the a-Si layer (N-type) and become readily movable. Consequently, the photosensitive member exhibits improved chargeability and transportability.

A phosphine gas, diborane gas or the like is used as a material gas for incorporating phosphorus atoms or boron atoms into the layer as a chemically modifying substance. The amount of phosphorus atoms or boron atoms to be present in the a-Si layer as a chemically modifying substance according to the invention is up to 20,000 atomic ppm, preferably up to 150 atomic ppm, most preferably up to 100 atomic ppm based on all the constituent atoms of the layer. The phosphorus or boron content of the layer can be determined by a usual method of elementary analysis, e.g. Auger electron spectroscopy or IMA analysis. Whereas phosphorus atoms or boron atoms assure appropriate transportability or polarity control effect when present in a suitable amount, the phosphorus or boron content, if exceeding 20,000 atomic ppm, conversely gives reduced resistivity to the layer to result in impaired chargeability.

The a-Si layer of the present invention may contain oxygen, nitrogen and carbon atoms as a chemically modifying substance. These atoms can be incorporated into the a-Si layer singly or in combination of more than two atoms. The incorporation of these atoms in the a-Si layer suitably increases the electric resistivity of the a-Si layer so that high chargeability is obtained. Further, the member exhibits small dark decay. The above effects can be obtained even if the a-Si layer contains only one atoms among oxygen, nitrogen and carbon.

According to the present invention, oxygen gas or an oxygen compound gas, such as nitrous oxide gas, ozone gas or carbon monoxide gas, is used as a material gas for incorporating into the layer oxygen atoms serving as a chemically modifying substance. Examples of useful material gases for incorporating nitrogen atoms into the layer are nitrogen gas and nitrogen compound gases such as ammonia gas, nitrous oxide gas and nitrogen dioxide gas. Examples of material gases useful for incorporating carbon atoms into the layer are methane, ethane, ethylene, acetylene, propane, propylene, butane, butadiene, butadiyne, butene, carbon monoxide, carbon dioxide and like carbon compounds.

The amounts of oxygen, nitrogen and carbon atoms to be present as a chemically modifying substance in the invention are 0.001 to 1 atomic % for oxygen atoms, 0.001 to 3 atomic % for nitrogen atoms and 0.001 to 5 atomic % for carbon atoms respectively based on all constituent atoms of the a-Si layer. The contents of these atoms in the a-Si layer can be determined by a usual method of elementary analysis, e.g. Auger electron spectroscopy of IMA analysis. Although, oxygen, nitrogen and carbon atoms assure suitable chargeability when present in a very small amount, the contents of oxygen, nitrogen and carbon atoms, if exceeding 1 atomic %, 3 atomic % and 5 atomic % respectively, increases the electric resistivity of the a-Si layer to excess to entail inefficient generation of optically excited carriers and impaired carrier mobility, thereby entailing lower sensitivity.

While the amount of hydrogen or fluorine atoms to be incorporated into the a-Si layer of the invention is invariably dependent on the process by which this layer is prepared, i.e. the glow discharge process, the hydrogen or fluorine content is generally 10 to 35 atomic % based on the combined amount of silicon atoms and hydrogen atoms or of silicon atoms and fluorine atoms in the layer. The hydrogen or fluorine content of the layer can be determined by a usual method of elementary analysis, e.g. ONH analysis in metal or Auger electron spectroscopy.

It is suitable that the a-Si layer serving as the charge generating layer of the invention be 0.1 to 5 microns in thickness for use in the usual electrophotographic process. The thickness, if smaller than 0.1 micron, fails to fully absorb light and to generate a sufficient amount of charges, resulting in lower sensitivity, whereas thicknesses larger than 5 microns are undesirable in view of productivity. The a-Si layer has high ability to generate charges, and when forming a laminate structure along with the a-C layer as the most distinct feature of the invention, the a-Si layer assures efficient injection of the resulting carriers into the a-C layer, contributing to satisfactory light decay.

According to the present invention, the a-Si layer is prepared from the desired gaseous materials by the same process as the a-C layer.

The quantities of oxygen atoms, nitrogen atoms, carbon atoms, and phosphorus or boron atoms to be incorporated into the a-Si layer as chemically modifying substances according to the invention are respectively controllable primarily by varying the amounts of oxygen gas or oxygen compound gas, nitrogen gas or nitrogen compound gas, carbon compound gas, and phosphine gas or diborane gas to be introduced into the reactor for plasma polymerization. The use of increased amounts of oxygen gas or oxygen compound gas, nitrogen gas or nitrogen compound gas, carbon compound gas, and phosphine gas or diborane gas gives the a-Si layer of the invention higher oxygen, nitrogen, carbon, and phosphorus or boron contents, respectively, whereas use of a decreased amount of such a gas gives the layer a lower content of the element concerned.

The photosensitive member of the present invention comprises a charge generating layer and a charge transporting layer of the type described above, which are formed in a superposed structure suitably determined as required.

Fig. 1 shows a photosensitive member of one type comprising an electrically conductive substrate 1, a charge transporting layer 2 formed on the substrate and a charge generating layer 3 formed on the layer 2. Fig. 2 shows another type comprising an electrically conductive substrate 1, a charge generating layer 3 on the substrate and a charge transporting layer 2 on the layer 3. Fig. 3 shows another type comprising an electrically conductive substrate 1, and a charge transporting layer 2, a charge generating layer 3 and another charge transporting layer 2 formed over the substrate and arranged one over another.

These sensitive members are used, for example, by positively charging the surface with a corona charger or the like and exposing the charged surface to an optical image. In the case of Fig. 1, the holes then generated in the charge generating layer 3 travel through the charge transporting layer 2 towards the substrate 1. In Fig. 2, the electrons generated in the charge generating layer 3 travel through the charge transporting layer 2 toward the surface of the photosensitive member. In Fig. 3, the holes generated in the charge generating layer 3 travel through the lower charge transporting layer 2 toward the substrate 2, and at the same time, the electrons generated in the charge generating layer 3 travel through the upper transporting layer 2 toward the surface of the member. Consequently, an electrostatic latent image is formed, with satisfactory light decay assured. Conversely, when the surface of the photosensitive member is negatively charged and then exposed, the electron and the hole may be replaced by each other in respect of the above behaviour for the interpretation of the travel of carriers. With the structures of Figs. 2 and 3, the image projecting light passes through the charge transporting layer, which nevertheless has high transmittancy, permitting satisfactory formation of latent image.

Fig. 4 shows another type comprising an electrically conductive substrate 1, and a charge transporting layer 2, a charge generating layer 3 and a charge transporting layer 4 provided over the substrate and arranged one over another. Thus, the illustrated structure corresponds to the structure of Fig. 1 provided with a surface protective layer. Since the outermost surface of the structure of Fig. 1 is provided by a charge generating of a-Si having poor humidity resistance in the present invention, it is generally desirable that the surface be covered with a protective layer for assuring stability toward humidity. With the structures of Figs. 2 and 3, the charge transporting layer embodying the invention and having high durability provides the outermost surface, so that the surface protective layer need not be provided. However, such a photosensitive member can be formed with a surface protective layer as another type so as to be compatible with various other elements within the copying machine, for example, to be free from surface soiling deposition of developer.

Fig. 5 shows another type comprising an electrically conductive substrate 1, and an intermediate layer 5, a charge generating layer 3 and a charge transporting layer 2 which are formed over the substrate and arranged one over another. Thus, this structure corresponds to the structure of Fig. 2 provided with an intermediate layer. Since a charge generating layer of a-Si is joined to the substrate in the structure of Fig. 2, it is generally desirable to interpose an intermediate layer therebetween to assure good adhesion and an injection inhibitory effect. With the structures of Figs. 1 and 3, the charge transporting layer of the invention which is excellent in adhesion and injection inhibitory effect is joined to the substrate, so that no intermediate layer may be provided. However, the photosensitive member of either of these types can be formed with an intermediate layer in order to render the transporting layer to be formed compatible with the preceding fabrication step, such as pretreatment of the conductive substrate. Another type of photosensitive member is then available.

Fig. 6 shows still another type comprising an electrically conductive substrate 1, and an intermediate layer 5, a charge transporting layer 2, a charge generating layer 3 and a surface protective layer 4 which are formed over the substrate and superposed one over another. Thus, this structure corresponds to the structure of Fig. 1 provided with an intermediate layer and a surface protective layer. The intermediate and protective layers are formed for the same reasons as already stated. Thus, the provision of these two layers in the structure of Fig. 2 or 3 affords another type.

According to the present invention, the intermediate layer and the surface protective layer are not limited specifically in material or fabrication process. Any material or process is suitably selectable provided that the contemplated object can be achieved. The a-C layer of the invention may be used. However, if the material to be used is an insulating material such as one already mentioned, the thickness of the layer needs to be up to 5 microns to preclude occurrence of residual potential.

The charge transporting layer of the photosensitive member embodying the present invention is produced by so-called plasma polymerization wherein molecules in a vapor phase are subjected to discharge decomposition in a vacuum phase, and the active neutral seeds or charge seeds contained in the resulting atmosphere of plasma are led onto a substrate by diffusion or an electric or magnetic force and accumulated into a solid phase on the substrate through a rebinding reaction.

Fig. 7 shows an apparatus for preparing the photosensitive member of the invention. First to sixth tanks 701 to 706 have enclosed therein starting material compounds which are in gas phase at room temperature and a carrier gas and are connected respectively to first to sixth regulator valves 707 to 712 and first to sixth flow controllers 713 to 718. First to third containers 719 to 721 contain starting material compounds which are liquid or solid at room temperature, can be preheated by first to third heaters 722 to 724 for vaporizing the compounds, and are connected to seventh to ninth regulator valves 725 to 727 and seventh to ninth flow controllers 728 to 730, respectively. The gases to be used as selected from among these gases are mixed together by a mixer 731 and fed to a reactor 733 via a main pipe 732. The interconnecting piping can be heated by a pipe heater 734 which is suitably disposed so that the material compound, in a liquid or solid phase at room temperature and vaporized by preheating, will not condense during transport. A grounded electrode 735 and a power application electrode 736 are arranged as opposed to each other within the reactor 733. Each of these electrodes can be heated by an electrode heater 737. The power application electrode 736 is connected to a high-frequency power source 739 via a high-frequency power matching device 738, to a low-frequency power source 741 via a low-frequency power matching device 740 and to a d.c. power source 743 via a low-pass filter 742. Power of one of the different frequencies is applicable to the electrode 736 by way of a connection selecting switch 744. The internal pressure of the reactor 733 is adjustable by a pressure control valve 745. The reactor 733 is evacuated by a diffusion pump 747 and an oil rotary pump 748 via an exhaust system selecting valve 746, or by a cooling-removing device 749, a mechanical booster pump 750 and an oil rotary pump 748 via another exhaust system selecting valve 746. The exhaust gas is further made harmless by a suitable removal device 753 and then released to

the atmosphere. The evacuation piping system can also be heated by a suitably disposed pipe heater 734 so that the material compound which is liquid or solid at room temperature and vaporized by preheating will not condense during transport. For the same reason, the reactor 733 can also be heated by a reactor heater 751. An electrically conductive substrate 752 is placed on the electrode 735 in the reactor. Although Fig. 7 shows that the substrate 752 is fixed to the grounded electrode 735, the substrate may be attached to the power application electrode 736, or to both the electrodes.

Fig. 8 shows another type of apparatus for preparing the photosensitive member of the invention. This apparatus has the same construction as the apparatus of Fig. 7 with the exception of the interior arrangement of the reactor 833. The numerals shown by 700 order in Fig. 7 are replaced by the numerals at 800 order in Fig. 8. With reference to Fig. 8, the reactor 833 is internally provided with a hollow cylindrical electrically conductive substrate 852 serving also as the grounded electrode 735 of Fig. 7 and with an electrode heater 837 inside thereof. A power application electrode 836, similarly in the form of a hollow cylinder, is provided around the substrate 852 and surrounded by an electrode heater 837. The conductive substrate 852 is rotatable about its own axis by motor from outside.

The reactor for preparing the photosensitive member is first evacuated by the diffusion pump to a vacuum of about 10^{-4} to about 10^{-6} torr, whereby the adsorbed gas inside the reactor is removed. The reactor is also checked for the degree of vacuum. At the same time, the electrodes and the substrate fixedly placed on the electrode are heated to a predetermined temperature. To obtain a photosensitive member of the desired one of the foregoing structures, an undercoat layer or a charge generating layer may be formed on the substrate before the charge transporting layer is formed when so required. The undercoat or charge generating layer may be formed by the present apparatus or by some other apparatus. Subsequently, material gases are fed into the reactor from the first to sixth tanks and the first to third containers (i.e. from those concerned), each at a specified flow rate, using the flow controllers concerned, i.e. first to ninth flow controllers and the interior of the reactor is maintained in a predetermined vacuum by the pressure control valve. After the combined flow of gases has become stabilized, the high-frequency power source, for example, is selected by the connection selecting switch to apply a high-frequency power to the power application electrode. This initiates discharge across the two electrodes, forming a solid layer on the substrate with time. The thickness of the layer is controllable by varying the reaction time, such that the discharge is discontinued upon the thickness reaching the desired value.

Any a-Si layer or a-C layer can be formed as desired by using suitable selected material gases. The layers, which are different in composition, can be formed as a laminate structure by temporarily discontinuing the discharge after forming one of the layers to change the composition of material gases, and then restarting the discharge to form the other layer over the first layer. Further, it is possible to form the layers having different in the form of a laminate structure having a gradient composition by gradually changing only the flow rates of material gases with continued discharge. The thickness of each layer is controlled by varying the reaction time. Then, the photosensitive member of the present invention is prepared by discontinuing the discharge when the desired laminate structure is obtained with the thickness of each layer thus controlled.

Next the regulator valves concerned are closed, and the reactor is thoroughly exhausted. When a photosensitive member of the desired structure has been formed according to the invention, the vacuum within the reactor is vitiated and the member is removed from the reactor. If another charge generating layer or overcoat layer are to be superposed on the above structure, such a layer is formed using the present apparatus as it is. Or the photosensitive member formed by the above process is taken out from the reaction chamber after destroying the vacuum, and is then transferred to another apparatus to form such a layer. Thus, the photosensitive member of the present invention can be obtained which has a charge transporting layer and a charge generating layer and, if necessary, an overcoat layer.

The present invention will be described with reference to the following examples.

Example 1

Using an apparatus for practicing the present invention, a photosensitive member was prepared, the member comprising an electrically conductive substrate, a charge transporting layer and a charge generating layer provided in this order as shown in Fig. 1.

Charge Transporting Layer Forming Step (CTL):

The glow discharge decomposition apparatus shown in Fig. 7 was used. First, the interior of the reactor 733 was evacuated to a high vacuum of about 10^{-6} torr, and the first, second and fourth regulator valves 707, 708 and 710 were thereafter opened to introduce hydrogen gas from the first tank 702 into the first flow controller 713, butadiyne gas from the second tank 702 into the second flow controller 714 and diborane gas which was diluted to the concentration of 12 % by hydrogen gas into the fourth flow controller 716, each at an output pressure of 1.0 kg/cm². The dials on the flow controllers were adjusted to supply the hydrogen gas at a flow rate of 60 sccm, butadiyne gas at 60 sccm and the diborane gas at 20 sccm to the reactor 733 through the main pipe 732 via the intermediate mixer 731. After the flows of the gases were stabilized, the internal pressure of the reactor 733 was adjusted to 1.9 torr by the pressure control valve 745. On the other hand, the substrate 752, which was an aluminum substrate measuring 50 mm in length, 50 mm in width and 3 mm in thickness, was preheated to 220°C. With the gas flow rates and the pressure in stabilized state, 160-watt power with a frequency of 400KHz was applied to the power application electrode 736 from the low-frequency power source 741 preconnected thereto by the selecting switch 744 to conduct plasma polymerization for 45 minutes, forming an a-C layer, 15 microns in thickness, as a charge transporting layer on the substrate, whereupon the power supply was discontinued, the regulator valves were closed, and the reactor 733 was fully exhausted.

When subjected to CHN quantitative analysis, the a-C layer thus obtained was found to contain 40 atomic % of hydrogen atoms based on the combined amount of carbon atoms and hydrogen atoms. Further, when subjected to IMA analysis, the a-C layer thus obtained was found to contain 2 atomic % of boron atoms based on all the constituent atoms therein.

Charge Generating Layer Forming Step (CGL):

Next, the tanks were partly exchanged and the first, second, third and sixth regulator valves 707, 708, 709 and 712 were opened to introduce hydrogen gas from the first tank 701 into the first flow controller 713, tetrafluorosilane gas from the second tank 702 into the second flow controller 714, germane gas from the third tank 703 into the third flow controller 715 and silane gas from the sixth tank 706 into the sixth flow controller 718, each at an output pressure of 1.0 kg/cm². The dials on the flow controllers were adjusted to supply the hydrogen gas at a flow rate of 200 sccm, tetrafluorosilane gas at 50 sccm, germane gas at a flow rate of 6 sccm and the silane gas at 50 sccm to the reactor 733. After the flows of the gases stabilized, the internal pressure of the reactor 733 was adjusted to 0.9 torr by the pressure control valve 745. On the other hand, the substrate 752 formed with the a-C layer was preheated to 230°C. With the gas flow rates and the pressure in stabilized state, 35-watt power with a frequency of 13.56 MHz was applied to the power application electrode 736 from the high-frequency power source 739 to effect glow discharge for 5 minutes, whereby a charge generating a-Si:H layer was formed with a thickness of 0.3 microns.

When subjected to ONH quantitative analysis (EMGA-1300 manufactured by Horiba Seisakusho) and Auger electron spectroscopy, the a-Si layer thus obtained was found to contain 18 atomic % of hydrogen atoms, 5 atomic % of fluorine atoms and 11 atomic % of germanium atoms based on all the constituent atoms therein.

Characteristics:

When the photosensitive member obtained was used for the usual Carlson process with negative charging and positive charging, the member showed a maximum charge potential (hereinafter referred to as Vmax) of -770V (+340V). (The obtained values at positive charging were shown in parenthesis hereinafter). Specifically, the chargeability per 1 micron (hereinafter referred to as C.A.) was 50V/micron (22V/micron) by calculating from the entire thickness of the member, i.e. 15.3 microns, indicating that the member had satisfactory charging properties.

The period of time required for dark decay from Vmax to the potential corresponding to 90 % of Vmax (hereinafter referred to as DDR) was about 34 seconds (9 seconds), showing that the member has satisfactory charge retentivity.

The amount of light required for the light decay from Vmax to the potential corresponding to 20 % of Vmax with white light (hereinafter referred to as E1/2) was about 5.8 lux-sec (1.8 lux-sec), showing that the member was satisfactory in photosensitive characteristics.

These results indicate that the photosensitive member prepared in the present example according to the invention exhibits outstanding performance. When the member was used in the Carlson process for forming images thereon, followed by image transfer, sharp copy images were obtained.

5

Examples 2 to 32

Photosensitive members were prepared as similarly as with Example 1, each member comprising an electrically conductive substrate (1), a charge transporting layer (2) and a charge generating layer (3) provided in this order as shown in Fig. 1.

Table 1 shows the various condition values for forming a charge transporting layer, Table 2 shows the various condition values for forming a charge generating layer and Table 3 shows the results of the evaluation of each member.

Table 1 and Table 2 show the conditions different from Example 1 for forming a charge transporting layer and charge generating layer and classified into 34 items (1) to (34). These items are described at the top column of each Table. Some condition values shown at each item are common to each example, while others are varying in each example.

Table 1 shown the items (1) to (16) as follows:

- (1) flow rate of hydrogen gas from the first tank (701) (sccm)
- (2) flow rate of material gas from the second tank (702) (sccm)
- (3) flow rate of dopant gas from the third tank (703) (sccm)
- (4) flow rate of dopant gas from the fourth tank (704) (sccm)
- (5) flow rate of dopant gas from the first container (719) (sccm)
- (6) temperature of the first heater (722) (°C)
- (7) pressure (Torr)
- (8) temperature of the substrate (°C)
- (9) dimension of the substrate (length x width x thickness) (unit: mm)
- (10) frequency from the power source (Hz)
- (11) time for plasma polymerization (hour)
- (12) thickness of the layer (micron)
- (13) power (watt)
- (14) hydrogen content (atomic %)
- (15) and (16) content of the dopant contained in the charge transporting layer (atomic %)

Table 2 shows the items (17) to (34) as follows:

- (17) flow rate of hydrogen gas from the first tank (701) (sccm)
- (18) flow rate of dopant gas from the second tank (702) (sccm)
- (19) flow rate of dopant gas from the third tank (703) (sccm)
- (20) flow rate of dopant gas from the fourth tank (704) (sccm)
- (21) flow rate of dopant gas from the fifth tank (705) (sccm)
- (22) flow rate of dopant gas from the sixth tank (706) (sccm)
- (23) pressure (Torr)
- (24) temperature of the substrate (°C)
- (25) frequency from the power source (Hz)
- (26) time for plasma polymerization (minute)
- (27) thickness of the layer (micron)
- (28) power (watt)
- (29) hydrogen content (atomic %)
- (30) to (34) content of the dopant contained in the charge generating layer (atomic %)

The result of the evaluation shown in Table 3 is classified into 7 items (35) to (41) as follows:

- (35) initial charging potential (V)
- (36) thickness of the entire member (micron)
- (37) chargeability per 1 micron (V/micron)
- (38) DDR (sec.)
- (39) $E(1/2)$ (lux-sec.)
- (40) light quantity required for light decay to a potential corresponding to 20 % of the V_{max} potential after the initial charging by using a semiconductive laser having a wavelength of 780 nm (erg/cm²)
- (41) clearness of the image

The level of the clearness of the image is represented by o (clear) and x (unclear). More specifically, the photosensitive members marked with x are not satisfactory in performance. When such members were used in the Carlson process for forming images thereon, followed by image transfer, fogged copy images only were obtained.

5 Table 4 shows the outline of the photosensitive members obtained at Examples 1 to 32.

Table 4

10

Ex. No.	CTL	CGL
1 - 5	a-C:H:B	a-Si:Ge:(H, Hal)
15 7 - 11	ditto	a-Si:Ge:(H, Hal):(B, P)
13, 14	ditto	a-Si:Ge:(H, Hal):(B, P):O:N
20 16 - 18	ditto	a-Si:Ge:(H, Hal):(B, P):O
19, 20, 22-24	ditto	a-Si:Ge:(H, Hal):(B, P):N
25 - 29	ditto	a-Si:Ge:(H, Hal):(B, P):C
25 31	ditto	a-Si:Ge:(H, Hal):(B, P):N:C
6	a-C:H:P	a-Si:Ge:(H, Hal)
30 12	ditto	a-Si:Ge:(H, Hal):(B, P)
15	ditto	a-Si:Ge:(H, Hal):(B, P):O:N
21	ditto	a-Si:Ge:(H, Hal):(B, P):N
35 30	ditto	a-Si:Ge:(H, Hal):(B, P):C
32	ditto	a-Si:Ge:(H, Hal):(B, P):C:O

40 From the results shown in Table 3, it is understood that the photosensitive member according to the present invention has improved chargeability and high sensitivity.

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50

55

Table 1

Charge Transporting Layer Forming Step

Ex No.	(1) (sc cm)	(2) (sccm)	※ 2 (3) (sccm)	(4) (sc cm)	(5) (sccm)	(6) (°C)	(7) (Torr)	(8) (°C)	(9) (mm)	(10) (Hz)	(11) (Hr)	(12) (μm)	(13) (watt)	(14) (at.%)	※ 1 (15) (at.%)	(16) (at.%)
2	105	C ₂ H ₂ 45	4500P B 80	—	—	—	2.0	200	50× 50× 3	1356 M	2.5	15	150	34	B	8000P
3	60	C ₂ H ₆ 60	1.2% B 9	—	—	—	2.1	170	50× 50× 3	400K	0.6	15	130	56	B	900P
4	60	C ₂ H ₆ 60	60 P B 20	—	—	—	1.8	220	50× 50× 3	400K	9	15	150	41	B	21P
5	40	—	0.16% B 10	—	C ₈ H ₈ 40	35	2.0	200	50× 50× 3	30K	1.5	15	150	47	B	98P
6	20	—	2000P P 30	—	C ₁₀ H ₁₆ 20	48	1.2	200	50× 50× 3	40K	3.25	15	150	43	P	290P
7	same as Example 5															
8	same as Example 4															
9	same as Example 3															
10	same as Example 2															
11	same as Example 1															
12	same as Example 6															
13	same as Example 5															
14	same as Example 2															
15	same as Example 6															
16	same as Example 3															
17	same as Example 1															
18	same as Example 4															
19	same as Example 5															
20	same as Example 4															
21	same as Example 6															
22	same as Example 4															
23	same as Example 1															
24	same as Example 2															
25	same as Example 5															
26	same as Example 4															
27	same as Example 3															
28	same as Example 2															
29	same as Example 1															
30	same as Example 6															

Table 1

Charge Transporting Layer Forming Step

Ex	(1)	(2)	※2 (3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	※1 (15)	(16)
No.	(sc cm)	(sccm)	(sccm)	(sc cm)	(sccm)	(°C)	(Torr)	(°C)	(mm)	(Hz)	(Hr)	(μm)	(watt)	(at. %)	(at. %)	(at. %)
31	200	C ₄ H ₂ 45	10% B 15	—	—	—	1.5	150	50× 50× 3	400K	1.16	15	160	42.5B	1.3	
32	200	C ₄ H ₂ 45	10% P 17	—	—	—	1.5	150	50× 50× 3	400K	1.08	15	140	41.0P	1.4	

※1 For example, 8000 P represents 8000 atomic ppm.

※2 For example, 4500P B and 2000P P mean the diborane gas and phosphine gas diluted to the concentration of 4500 ppm and 2000 ppm with hydrogen gas respectively. Similarly, 1.2% B means the diborane gas diluted to the concentration of 1.2% with the hydrogen gas.

Table 2

Charge Generating Layer Forming Step

Ex No	(17) (sc cm)	(18) (sc cm)	(19) (sc cm)	※3 (20) (sc cm)	(21) (sc cm)	(22) (sc cm)	(23) Torr	(24) (°C)	(25) (Hz)	(26) min.	(27) μ m	(28) watt	(29) (at. %)	※1 (30) (at. %)	(31) (at. %)	(32) (at. %)	(33) (at. %)	(34) (at. %)
2	200	GeH ₄ 0.6	GeH ₄ 6	—	—	SiH ₄ 100	0.8	250	13.56	5	0.3	35	20	Ge 1				
3	200	GeH ₄ 2	—	—	—	SiH ₄ 100	0.8	250	13.56	5	0.3	35	20	Ge 3				
4	200	GeH ₄ 6	—	—	—	SiH ₄ 100	0.9	250	13.56	5	0.3	40	20	Ge 10				
5	200	GeH ₄ 20	—	—	—	SiH ₄ 100	1.0	250	13.56	5	0.3	45	20	Ge 30				
6	Same as Example 4																	
7	200	GeH ₄ 6	—	B ₂ H ₆ 10	—	SiH ₄ 100	1.0	240	13.56	5	0.3	40	18	Ge 9.7	B10P			
8	200	GeH ₄ 6	—	PH ₃ 10	—	SiH ₄ 100	0.8	250	13.56	5	0.3	40	20	Ge 10P	11P			
9	200	SiF ₄ 50	GeH ₄ 6	B ₂ H ₆ 10	—	SiH ₄ 50	0.9	230	13.56	5	0.3	35	24	Ge 10.5	B10P			F 5
10	200	SiF ₄ 50	GeH ₄ 6	PH ₃ 10	—	SiH ₄ 50	0.8	240	13.56	5	0.3	40	26	Ge 9.8	F13P			F5.6
11	Same as Example 9																	
12	Same as Example 7																	
13	200	GeH ₄ 6	—	B ₂ H ₆ 10	N ₂ O 0.01	SiH ₄ 100	0.9	230	13.56	5	0.3	45	22	Ge 10.1	B10PC	0.001	N0.002	
14	200	GeH ₄ 6	—	B ₂ H ₆ 10	N ₂ O 3	SiH ₄ 100	1.0	240	13.56	5	0.3	45	21	Ge 9.7	B11PC	0.31	N 0.53	
15	200	GeH ₄ 10	SiF ₄ 50	B ₂ H ₆ 10	N ₂ O 1	SiH ₄ 50	0.9	250	13.56	5	0.3	35	22	Ge 17	B10PC	0.1	N 0.17	
16	200	GeH ₄ 10	—	B ₂ H ₆ 10	O ₂ 0.5	SiH ₄ 100	0.8	250	13.56	5	0.3	35	20	Ge 16	B12PC	0.1		
17	200	GeH ₄ 6	—	B ₂ H ₆ 50	O ₂ 5	SiH ₄ 100	0.8	250	13.56	5	0.3	40	24	Ge 11	B45PC	1		
18	200	GeH ₄ 10	—	B ₂ H ₆ 10	O ₂ 0.5	SiH ₄ 100	0.8	250	13.56	5	0.3	35	20	Ge 16	B12PC	0.1		
19	200	GeH ₄ 6	SiF ₄ 50	B ₂ H ₆ 100	N ₂ 1.0	SiH ₄ 50	0.9	250	13.56	5	0.3	35	22	Ge 10.3	B95PN	0.1		F 5
20	200	GeH ₄ 8	—	B ₂ H ₆ 10	NH ₃ 2	SiH ₄ 100	0.9	240	13.56	5	0.3	45	21	Ge 13.2	B11PN	0.3		
21	200	GeH ₄ 10	—	B ₂ H ₆ 50	N ₂ 10	SiH ₄ 100	0.8	250	13.56	5	0.3	40	24	Ge 15.8	B30PN	1.0		
22	200	GeH ₄ 6	—	B ₂ H ₆ 10	N ₂ 0.01	SiH ₄ 100	0.8	250	13.56	5	0.3	35	23	Ge 11	B10PN	0.001		

Table 2

Charge Generating Layer Forming Step

Ex	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)	(25)	(26)	(27)	(28)	(29)	(30)	(31)	(32)	(33)	(34)
No	(sc cm)	(sc cm)	(sc cm)	(sc cm)	(sc cm)	(sc cm)	Torr	(°C)	(Hz)	min.	μ m	watt	(at. %)	(at. %)	(at. %)	(at. %)	(at. %)	(at. %)
23	Same as Example 20																	
24	200 6	GeH ₄	—	PH ₃ 10	N ₂ 3	SiH ₄ 200	0.9	250	13.56	5	0.3	35	18	Ge	P12PC	0.3		
25	200 10	GeH ₄	—	B ₂ H ₆ 10	C ₂ H ₆ 3	SiH ₄ 100	0.9	240	13.56	5	0.3	45	21	Ge	B11PC	0.3		
26	200 6	GeH ₄	—	B ₂ H ₆ 10	CH ₄ 0.01	SiH ₄ 100	0.8	250	13.56	5	0.3	35	20	Ge	B9PC	0.001		
27	200 6	GeH ₄	—	B ₂ H ₆ 100	CH ₄ 10	SiH ₄ 100	0.8	250	13.56	5	0.3	40	24	Ge	B95PC	1.0		
28	200 3	GeH ₄	SiF ₄ 50	B ₂ H ₆ 10	CF ₄ 0.1	SiH ₄ 50	0.9	250	13.56	5	0.3	35	22	Ge	B11PC	0.1		F4.8
29	200 6	GeH ₄	—	PH ₃ 10	CH ₄ 3	SiH ₄ 200	1.0	230	13.56	5	0.3	35	18	Ge	P12PC	0.3		
30	Same as Example 27																	
31	200 8	GeH ₄	SiF ₄ 50	PH ₃ 10	C ₂ H ₆ 5	N ₂ 4	SiH ₄ 50	0.95	245	13.56	5.6	0.3	40	19.9	Ge	P10PC	0.4	N0.35 F6.2
32	200 8	GeH ₄	SiF ₄ 50	B ₂ H ₆ 10	C ₂ H ₆ 4	SiH ₄ 50	1.0	250	13.56	5.7	0.3	38	20.1	Ge	B	0.35	0	0.4 F5.4

※1 Same as Table 1

※3 B₂H₆ and PH₃ at this column are diluted to the concentration of 100 ppm with hydrogen gas.

※4 The seventh tank was added to the apparatus to introduce the seventh gas.

Table 3

Result of Evaluation

Ex.No.	(35) (V)		(36) (μm)	(37) (V/ μm)		(38) (sec.)		(39) (E 1/2)		(40) (erg/ cm^2)		(41)
	-	+		-	+	-	+	-	+	-	+	
2	710	500	15.3	47	33	25	10	2.8	1.1	13.5	7.2	○
3	530	480	15.3	35	31	18	11	1.8	1.3	11.5	7.8	○
4	430	530	15.3	28	35	10	13	1.2	1.5	—	—	○
5	450	380	15.3	28	25	11	8	2.1	1.9	—	—	○
6	380	610	15.3	25	40	9	16	1.2	3.3	—	—	○
7	590	430	15.3	39	23	15	10	1.5	1.1	8.2	6.8	○
8	400	590	15.3	26	39	10	15	1.0	2.2	6.5	16.3	○
9	590	440	15.3	39	29	29	20	2.1	1.2	11.0	7.6	○
10	630	530	15.3	41	35	21	10	1.8	2.6	10.3	14.1	○
11	860	310	15.3	56	21	35	10	8.2	1.4	—	—	○
12	440	540	15.3	29	35	11	15	2.6	1.2	13.2	7.0	○
13	610	460	15.3	40	30	15	10	1.5	1.1	8.1	7.8	○
14	840	490	15.3	55	32	28	10	3.3	1.3	—	—	○
15	440	580	15.3	29	38	11	16	3.3	1.3	—	—	○
16	590	420	15.3	39	27	20	9	1.6	1.5	9.4	8.2	○
17	960	340	15.3	63	22	44	11	7.8	1.7	—	—	○
18	550	520	15.3	36	34	14	13	1.2	1.1	8.6	7.7	○
19	720	590	15.3	47	39	15	10	1.8	1.3	11.6	8.1	○
20	550	530	15.3	36	35	14	13	2.3	1.2	—	—	○
21	540	680	15.3	35	44	12	17	4.0	1.2	—	—	○
22	520	480	15.3	34	31	13	12	1.3	1.2	7.1	6.7	○
23	860	310	15.3	56	20	38	9	5.2	1.4	—	—	○
24	670	570	15.3	44	38	24	11	2.3	2.4	—	—	○
25	680	500	15.3	45	33	16	13	1.5	1.3	8.9	7.7	○
26	490	500	15.3	32	33	1.4	1.2	8.1	6.7	—	—	○
27	730	500	15.3	47	33	25	11	2.7	2.3	—	—	○
28	840	480	15.3	55	31	24	8	3.3	1.5	—	—	○
29	770	410	15.3	50	27	33	9	1.9	4.5	—	—	○
30	590	710	15.3	39	47	14	18	6.3	1.6	—	—	○
31	790	360	15.3	51.6	23.5	35	12	3.7	1.9	—	—	○
32	420	810	15.3	27.5	52.9	40	18	1.8	4.0	—	—	○

Comparative Examples 1 to 9

Photosensitive members were prepared, the members comprising an electrically conductive substrate (1), a charge transporting layer (2) and a charge generating layer (3) provided in this order as shown in Fig. 1.

The respective condition values for forming a charge transporting layer and a charge generating layer are shown in Table 5 and Table 6. Table 7 indicates the results of the evaluation of each member.

The items shown in Tables 5, 6 and 7 are respectively the same as those in Tables 1, 2 and 3.

As apparent from Table 7, the comparative photosensitive members are not satisfactory in electrophotographic performance.

Table 5

Charge Transporting Layer Forming Step

Com No.	(1) (sc cm)	(2) (sccm)	※2 (3) (sccm)	(4) (sccm)	(5) (sc cm)	(6) (°C)	(7) (Torr)	(8) (°C)	(9) (mm)	(10) (Hz)	(11) (Hr)	(12) (μm)	(13) (watt)	(14) (at. %)	※1 (15) (at.%)	(16) (at. %)
1	same as Example 1															
2	same as Example 1															
3	same as Example 13															
4	same as Example 19															
5	same as Example 25															
6	same as Example 1															
7	same as Example 6															
8	200	C ₄ H ₆ 50	10% B 35	—	—	—	1.9	170	50× 50× 3	800K	1.75	15	150	38.4B	2.9P	
9	250	C ₄ H ₆ 50	10% F 40	—	—	—	1.8	170	50× 50× 3	800K	1.8	15	150	37.2P	3.1P	

※1 same as Table 1

※2 same as Table 1

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Table 6

Charge Generating Layer Forming Step

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Co m. Ex No	(17) (sc cm)	(18) (sc cm)	※2 (19) (sc cm)	(20) (sc cm)	(21) (sc cm)	(22) (sc cm)	(23) Torr	(24) (°C)	(25) (Hz)	(26) min.	(27) μ m	(28) watt	(29) (at. %)	(30) (at. %)	※1 (31) (at. %)	(32) (at. %)	(33) (at. %)	(34) (at. %)
1	200	GeH ₄	SiF ₄	—	—	SiH ₄	0.9	240	13.56	5.8	0.3	35	9.8	Ge	F2.8			
	38		27			30			M				30.4					
2	220	—	SiF ₄	—	—	SiH ₄	0.85	240	13.56	5.4	0.3	35	23	F				
			50			50			M				5.0					
3	210	GeH ₄	100	N ₂ O	—	SiH ₄	0.85	245	13.56	5.8	0.3	40	18.5	Ge	B 9PC	1.2		
	8		ppmB	12		100			M				9.2					
			10															
4	220	GeH ₄	100	SiF ₄ N ₂	—	SiH ₄	0.95	245	13.56	5.8	0.3	37	16.1	Ge	B94FN	3.4	F	3.2
	8		ppmB	32	37	32			M				8.4					
			100															
5	210	GeH ₄	100	C ₂ H ₆	—	SiH ₄	0.85	240	13.56	5.8	0.3	38	17.4	Ge	B	C	5.7	
	8		ppmB	58		100			M				10.1	19.7P				
			10															
6	200	GeH ₄	10%	C ₂ H ₆	O ₂	SiH ₄	1.0	255	13.56	5.9	0.3	40	19.5	B	00.2C	0.28	Ge	7.8
	8		39	3	2	100			M				3.0					
7	250	GeH ₄	10%	C ₂ H ₄	N ₂	SiH ₄	1.0	255	13.56	5.9	0.3	40	19.0P	N0.2C	0.3	Ge	7.5	
	8		39	3	2	100			M				3.1					
8	same as Example 6																	
9	same as Example 1																	

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※1 Same as Table 1

※2 Same as Table 1

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Table 7

Result of Evaluation

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Com. Ex. No.	(35) (V)		(36) (μm)	(37) (V/ μm)		(38) (sec.)		(39) (E 1/2)		(40) (erg/ cm^2)		(41)
	-	+		-	+	-	+	-	+	-	+	
1	990	1000	15.3	64.7	65.4	49	52	21.6	25.7	—	—	×
2	530	560	15.3	34.6	36.6	61	72	2.5	2.9	—	—	×
3	960	980	15.3	62.7	64.1	51	57	23.2	26.7	—	—	×
4	950	1010	15.3	62.1	66.0	51	59	21.6	25.4	—	—	×
5	940	1050	15.3	61.4	68.6	50	60	22.3	24.8	—	—	×
6	190	220	15.3	12.4	14.4	0.3	0.4	18.4	19.2	—	—	×
7	170	160	15.3	11.1	10.5	0.4	0.3	17.3	14.9	—	—	×
8	230	99	15.3	15	6.5	45	0.5	53	19.5	—	—	×
9	87	200	15.3	5.7	13.1	0.4	47	20.4	49	—	—	×

Claims

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1. A photosensitive member which comprises an electrically conductive substrate, a charge generating layer and a charge transporting layer, said photosensitive member characterized in that the charge generating layer comprises amorphous silicon as a matrix and contains germanium, hydrogen and/or halogen, and the charge transporting layer comprises amorphous carbon containing hydrogen and boron or phosphorus.

2. A photosensitive member as claimed in Claim 1 wherein the amount of hydrogen contained in the charge transporting layer is about 30 to about 60 atomic % based on the combined amount of hydrogen atoms and carbon atoms.

3. A photosensitive member as claimed in Claim 1 wherein the amount of boron or phosphorus atoms contained in the charge transporting layer is less than about 20,000 atomic ppm based on all the constituent atoms contained therein.

4. A photosensitive member as claimed in Claim 1 wherein the amount of germanium contained in the charge generating layer is up to about 30 atomic % based on the combined amount of silicon atoms and germanium atoms.

5. A photosensitive member as claimed in Claim 1 wherein the charge generating layer contains hydrogen and/or halogen in an amount of about 10 to about 35 atomic % based on the combined amount of silicon atoms and hydrogen atoms or of silicon atoms and halogen atoms.

6. A photosensitive member as claimed in Claim 1 wherein the charge transporting layer further contains halogen atoms in an amount of about 0.1 to about 25 atomic % based on all the constituent atoms therein.

7. A photosensitive member as claimed in Claim 1 wherein the charge generating layer further contains boron or phosphorus atoms in an amount of less than about 20,000 atomic ppm based on all the constituent atoms therein.

8. A photosensitive member as claimed in Claim 7 wherein the amount of the boron or phosphorus atoms is preferably up to about 150 atomic ppm based on all the constituent atoms therein.

9. A photosensitive member as claimed in Claim 1 wherein the charge generating layer further contains oxygen in an amount of about 0.001 to about 1 atomic % based on all the constituent atoms therein.

10. A photosensitive member as claimed in Claim 1 wherein the charge generating layer further contains nitrogen in an amount of about 0.001 to about 3 atomic % based on all the constituent atoms therein.

11. A photosensitive member as claimed in Claim 1 wherein the charge generating layer further contains carbon in an amount of about 0.001 to about 5 atomic % based on all the constituent atoms therein.

FIG.1

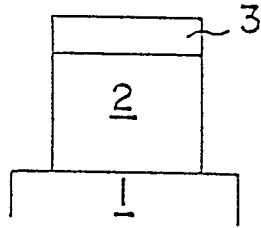


FIG.2

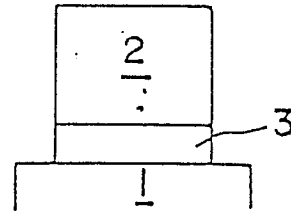


FIG.3

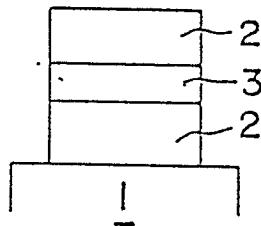


FIG.4

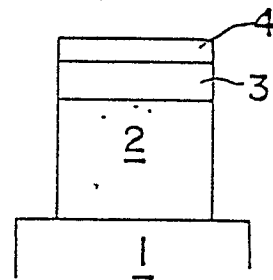


FIG.5

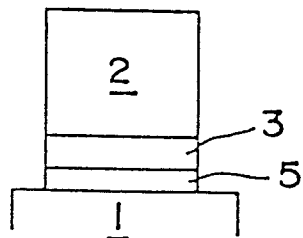


FIG.6

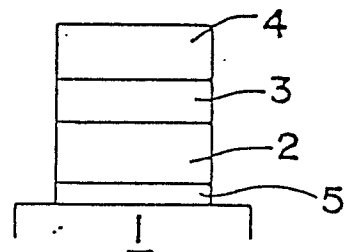


FIG. 8

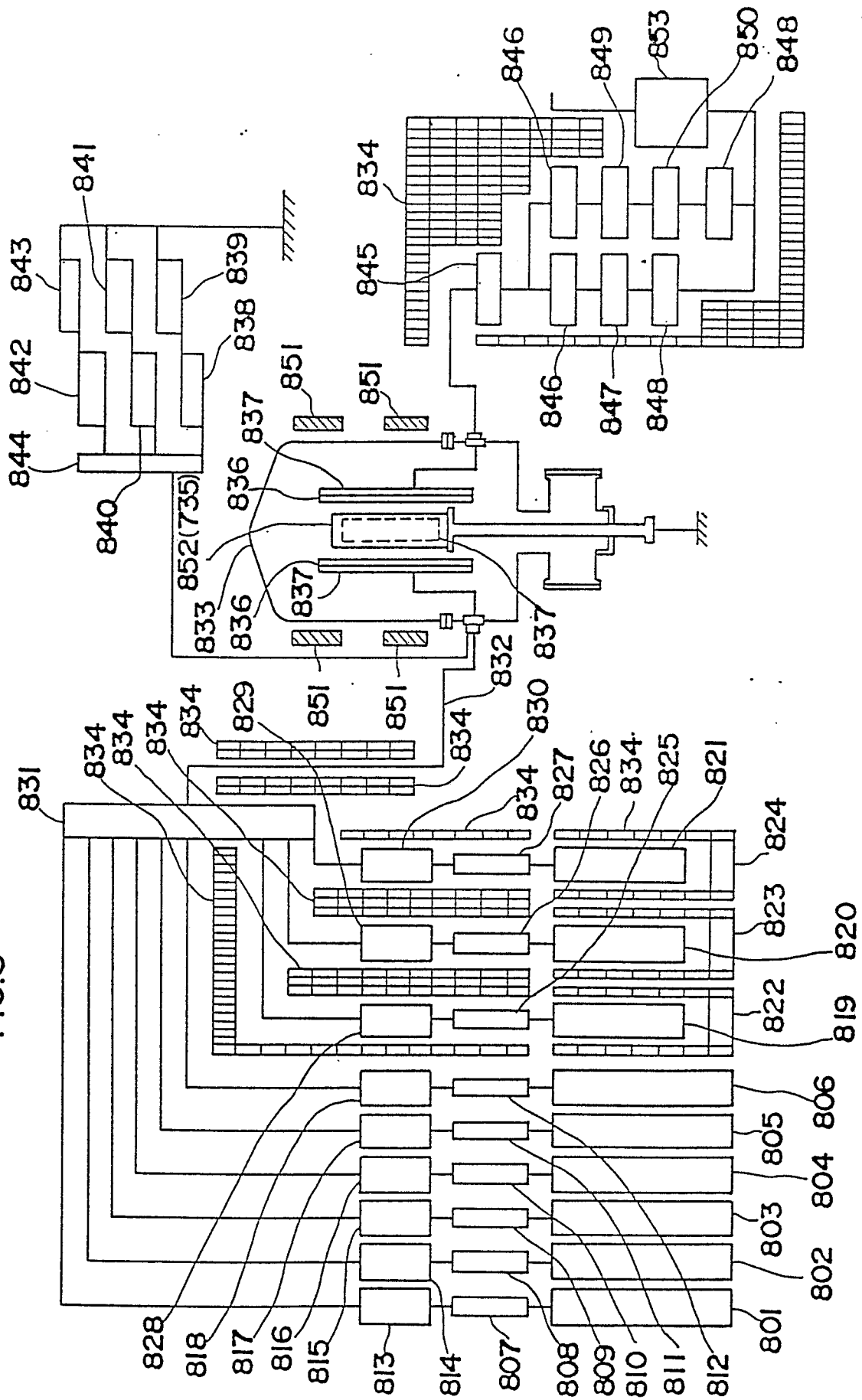
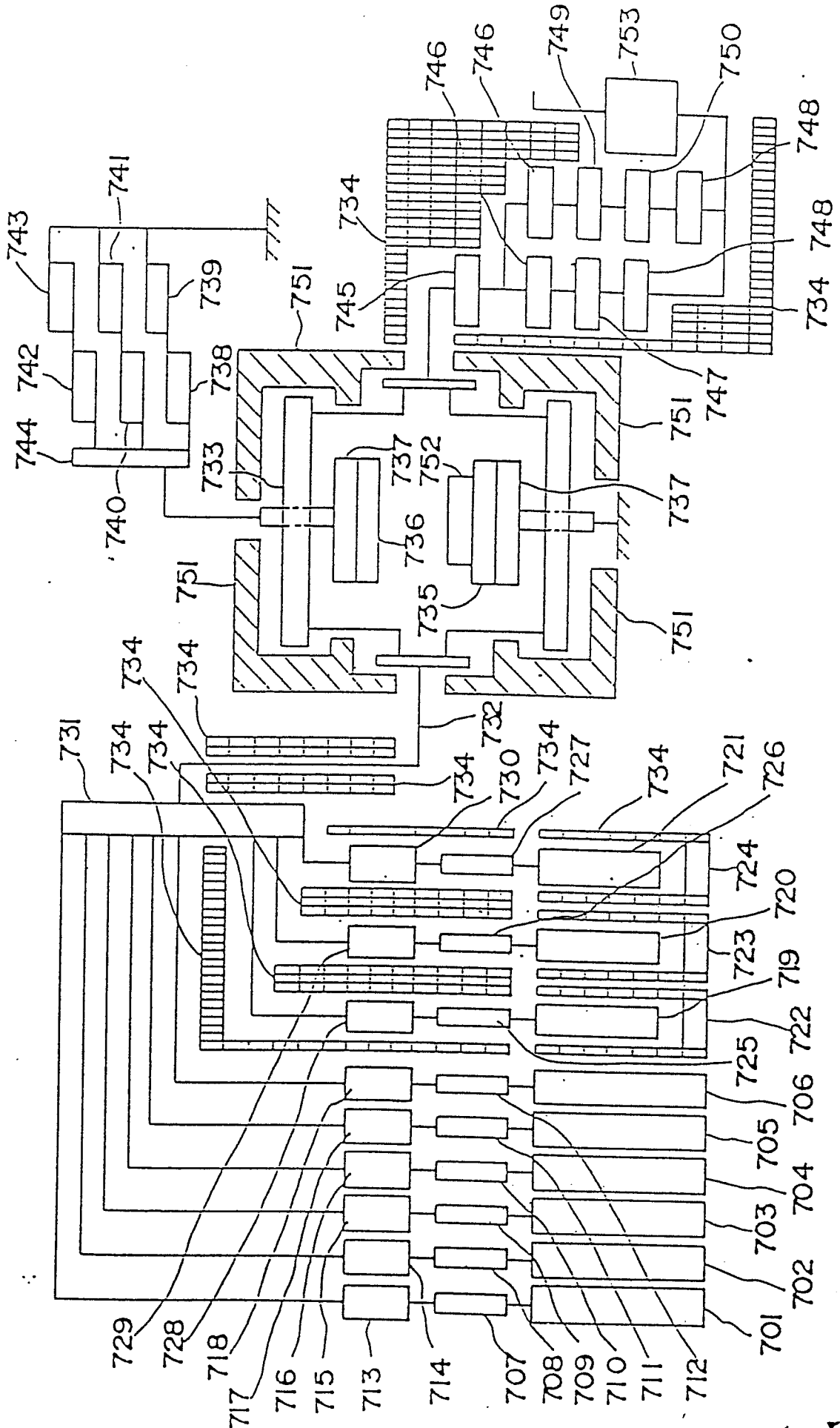


FIG.7





DOCUMENTS CONSIDERED TO BE RELEVANT			EP 87113879.8
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D, A.	PATENT ABSTRACTS OF JAPAN, unexamined applications, section P, vol. 8, no. 137, June 26, 1984 THE PATENT OFFICE JAPANESE GOVERNMENT page 128 P 282 * Kokai-no. 59-38 753 (TOKYO SHIBAURA DENKI K.K.) *	1	
A	EP - A2 - 0 151 754 (ENERGY CONVERSION DEVICES, INC.) * Claims 1-3,5,7-17 *	1,2,5, 6,9- 11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 14-12-1987	Examiner BÖHM
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	



EP 87113879.8

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE - A1 - 3 201 146 (CANON) * Claims 1,4,5,7-19,21-24, 41,42,57-59,61-66; page 20, lines 18-22; page 61, lines 29-35 *	1,5,7, 8,10, 11	G 03 G 5/08
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A	US - A - 4 491 626 (KAWAMURA) * Claims 1-6 *	1,4,5, 7-9	
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A	EP - A2 - 0 141 664 (XEROX) * Claims 1,3-5,7,8; page 9, lines 4-13; page 12, lines 29-35 *	1,3,4, 7,8, 10,11	
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A	DE - A1 - 3 303 700 (CANON) * Claims 1-6; page 26, lines 17-21; page 39, line 28 - page 40, line 29 *	1,2,5- 8,10	TECHNICAL FIELDS SEARCHED (Int. Cl.4) G 03 G
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D,A	JOURNAL OF APPLIED POLYMER SCIENCE, vol. 17, 1973, New York H. KOBAYASHI et al. "Formation of an Amorphous Powder During the Polymerization of Ethylene in a Radio-Frequency Discharge" pages 885-892 * Page 887, Synopsis *	1	
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The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 14-12-1987	Examiner BÖHM
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	