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(54) An electrophotographic lithographic printing plate precursor.

(57) According to the present invention, there can be provided an electrophotographic lithographic printing plate precursor having an excellent image and high printing durability even under severer conditions. The feature of the photographic lithographic printing plate precursor consists in that it comprises a conductive support having provided thereon at least one photoconductive layer containing photoconductive zinc oxide and a binder resin, wherein the photoconductive layer contains resin grains containing at least one polymer component having at least one of functional groups represented by the following General Formula (I) and General Formula (II) and having an average grain diameter of same as or smaller than the maximum grain diameter of the photoconductive zinc oxide grains:

General Formula (I)

$$-W_1-(CH_2)_{n1}-CH=CH_2$$

General Formula (II)

$$-W_2-(CH_2)_{n2}-CH_2CH_2-X$$

wherein $-W_1-$ and $-W_2-$ represent respectively $-SO_2-$, $-CO-$ or $-OOC-$ and n_1 and n_2 represent respectively 0 or 1 and X represents a halogen atom.

EP 0 456 486 A2

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BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an electrophotographic lithographic printing plate precursor made by an electrophotographic system and more particularly, it is concerned with an improvement in a photoconductive layer forming composition for the lithographic printing plate precursor.

2. Description of the Prior Art

A number of offset masters for directly producing printing plates have hitherto been proposed and some of them have already been put into practical use.
Widely employed among them is a system in which a photoreceptor comprising a conductive support having provided thereon a photoconductive layer mainly comprising photoconductive particles, for example, of zinc oxide and a binder resin is subjected to an ordinary electrophotographic processing to form a highly lithographic toner image on the surface of the photoreceptor, followed by treating the surface with an oil-desensitizing solution referred to as an etching solution to selectively render non-image areas hydrophilic and thus obtain an offset printing plate.

Requirements of offset masters for obtaining satisfactory prints include: (1) an original should be reproduced faithfully on the photoreceptor; (2) the surface of the photoreceptor has affinity with an oil-desensitizing solution so as to render non-image areas sufficiently hydrophilic, but, at the same time, has resistance to solubilization; and (3) a photoconductive layer having an image formed thereon is not released during printing and is well receptive to dampening water so that the non-image areas retain the hydrophilic properties to be free from stains even upon printing a large number of prints.

It is known that these properties are affected by the ratio of zinc oxide to a resin binder in the photoconductive layer, For example, if the ratio of a binder resin to zinc oxide particles is decreased, oil-desensitivity of the surface of the photoconductive layer is increased to reduce background stains, but, on the other hand, the internal cohesion of the photoconductive layer per se is weakened, resulting in reduction of printing durability due to insufficient mechanical strength. If the ratio of a binder resin to zinc oxide particles is increased, on the other hand, printing durability is improved, but background staining becomes conspicuous. It is a matter of course that the background staining is a phenomenon associated with the degree of oil-desensitization achieved and it has been made apparent that the oil-desensitization of the photoconductive layer surface depends on not only the binder resin/zinc oxide ratio in the photoconductive layer, but also the kind of the binder resin used to a great extent.

For particular use as an offset master, occurrence of background stains due to insufficient oil-desensitivity presents a serious problem. In order to solve this problem, various resins for binding zinc oxide have been proposed, including resins having a weight average molecular weight Mw 1.8 - 10 x 10^{-4} and a glass transition point Tg 10 - 80°C, obtained by copolymerizing (meth)acrylate monomers and other monomers in the presence of fumaric acid in combination with copolymers of (meth)acrylate monomers and other monomers than fumaric acid, as described in Japanese Patent Publication No. 31011/1975; terpolymers each containing a (meth)acrylic acid ester unit having a substituent having carboxylic acid group at least 7 atoms distant from the ester linkage, as disclosed in Japanese Patent Laid-Open Publication No. 54027/1978; tetra- or pentamers each containing an acrylic acid unit and hydroxyethyl unit, as disclosed in Japanese Patent Laid-Open Publication Nos. 20735/1979 and 202544/1982; terpolymers each containing a (meth)acrylic acid ester unit having an alkyl group having 6 to 12 carbon atoms as a substituent and a vinyl monomer containing carboxylic acid group, as disclosed in Japanese Patent Laid-Open Publication No. 68046/1983; and the like. These resins function to improve the oil-desensitivity of photoconductive layers.

Nevertheless, evaluation of such resins as noted above for improving the oil-desensitization indicates that none of them is completely satisfactory in terms of stain resistance, printing durability and the like.

On the other hand, it has hitherto been studied to use resins having functional groups capable of forming hydrophilic groups through decomposition such as a binder resin, for example, those having functional groups capable of forming hydroxyl groups through decomposition as disclosed in Japanese Patent Laid-Open Publication Nos. 195684/1987, 210475/1987 and 210476/1987 and those having functional groups capable of forming carboxyl groups through decomposition as disclosed in Japanese Laid-Open Publication No. 212669/1987.

Furthermore, it has been studied to jointly use a small amount of resin grains of fine grain diameters, containing functional groups capable of forming hydrophilic groups through decomposition and a high network structure, in the photoconductive layer containing zinc oxide, for example, those having functional groups capable of forming carboxyl groups through decomposition as disclosed in Japanese Patent Laid-Open Publication

Nos. 261658/1989 and 266547/1989, those having functional groups capable of forming hydroxyl groups through decomposition and those having functional groups capable of forming sulfo groups and phosphono groups through decomposition as disclosed in Japanese Patent Laid-Open Publication No. 287571/1989.

These binder resins or resin grains are those which form hydrophilic groups through hydrolysis or hydrogenolysis with an oil-desensitizing solution or dampening water used during printing. In any case, it is possible to avoid various problems, e.g. deterioration of the electrophotographic properties (dark charge retention, photosensitivity, etc,) which are considered to be caused in the case of using resins intrinsically having hydrophilic groups per se, and at the same time, a number of prints with clear image quality and without background stains can be obtained, since the hydrophilic property of non-image areas rendered hydrophilic with an oil-desensitizing solution is further increased by the above described hydrophilic groups formed through decomposition in the binder resin or resin grains to make clear the lipophilic property of image areas and the hydrophilic property of non-image areas and to prevent the non-image areas from adhesion of a printing ink during printing.

In the binder resin or resin grains of such a type as to form a hydrophilic group such as carboxyl group, hydroxyl group, sulfo group, phosphono group, etc. by the above described decomposition reaction, the hydrophilic group previously masked with a protective group is subjected to decomposition reaction with a processing solution to release the protective group, For the binder resin or resin grains of this type, therefore, it is required, as important properties, that during storage, the resin is stably present without being hydrolyzed due to the humidity (moisture) in the air and during processing for rendering hydrophilic, the protective group removing reaction rapidly proceeds to form a hydrophilic group and the hydrophilic property of non-image areas can be improved.

However, it is found that provision of a hydrophilic group-forming functional group (protective group) which is stably present without decomposition even under severer conditions, e.g. during storage at a high temperature and high humidity for a long time, results in difficulty in a rapid decomposition with a processing solution and rapid feasibility of hydrophilic property.

In the scanning exposing system using a semiconductor laser beam, furthermore, higher performances are required for static properties, in particular, dark charge retention and photosensitivity, since the exposing time is longer and the exposing intensity is more restricted than in the overall and simultaneously exposing system of the prior art using visible rays.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an electrophotographic lithographic printing plate precursor, whereby the disadvantages of the prior art, as described above, can be overcome.

It is another object of the present invention to provide a lithographic printing plate precursor excellent in oil-desensitivity as well as static properties, in particular, dark charge retention and photosensitivity, whereby an original is faithfully reproduced without occurrence of overall or spotted stains as an offset master.

It is a further object of the present invention to provide a lithographic printing plate with a clear and good quality image even if the ambient conditions during forming a reproduced image are fluctuated from low temperature and low humidity to high temperature and high humidity.

It is a still further object of the present invention to provide a lithographic printing plate precursor with a high printing durability, in which the hydrophilic property of non-image areas is sufficiently held to prevent occurrence of background stains even if the steps of from etching to printing are speeded up.

It is a still further object of the present invention to provide a CPC photoreceptor with excellent static properties and small dependence on the ambient conditions.

It is a still further object of the present invention to provide a lithographic printing plate precursor which is hardly affected by the kind of sensitizing dyes and which is capable of exhibiting excellent static properties even in the scanning exposing system using a semiconductor laser beam.

It is a still further object of the present invention to provide an electrophotographic lithographic printing plate precursor, in which the effect by the hydrophilic property of non-image areas is further improved, and which is stable during storage even under very severe conditions and capable of readily realizing the hydrophilic property in a short time during processing for rendering hydrophilic and maintaining high static properties even in the scanning exposing system.

These objects can be attained by an electrophotographic lithographic printing plate precursor comprising a conductive support having provided thereon at least one photoconductive layer containing photoconductive zinc oxide and a binder resin, wherein the photoconductive layer contains resin grains containing at least one polymeric component having functional groups represented by the following General Formula (I) and/or General Formula (II) and having an average grain diameter of same as or smaller than the maximum grain diameter of the photoconductive zinc oxide grains:

General Formula (I)

$$-W_1-(CH_2)_{n1}-CH=CH_2$$

General Formula (II)

$$-W_2-(CH_2)_{n2}-CH_2CH_2-X$$

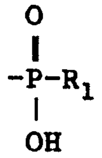
wherein $-W_1-$ and $-W_2-$ represent respectively $-SO_2-$, -CO- or -OOC- and n_1 and n_2 represent respectively 0 or 1 and X represents a halogen atom.

DETAILED DESCRIPTION OF THE INVENTION

In a preferred embodiment of the present invention, the above described binder resin in the photoconductive layer contains at least one of the following Resins [A]:

Resin [A]

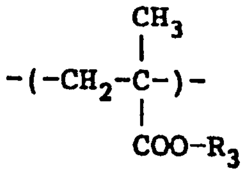
A resin having a weight average molecular weight of 1×10^3 to 2×10^4, containing at least 30% by weight of recurring unit represented by the following General Formula (III) as polymeric components and 0,5 to 15% by weight of polymeric components having at least one polar group selected from the group consisting of $-PO_3H_2$, $-SO_3H$, -COOH, -OH, and



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-R_1$$

wherein R_1 is a hydrocarbon group or $-OR_2$ (R_2 is a hydrocarbon group), and acid anhydride groups:

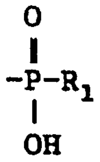
General Formula (III)



$$-(-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COO-R_3}{|}}{C}}-)-$$

wherein R_3 is a hydrocarbon group.

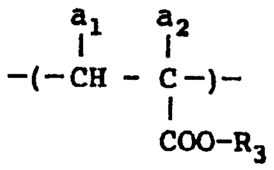
In a further embodiment of the present invention, Resin A is preferably a resin having a weight average molecular weight of 1×10^3 to 2×10^4, containing at least 30% by weight of recurring unit represented by the following General Formula (IV) as polymeric components and at least one polar group is bonded to one end of the polymer main chain, selected from the group consisting of $-PO_3H_2$, SO_3H, -COOH, -OH, and



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-R_1$$

wherein R_1 is a hydrocarbon group or $-OR_2$ (R_2 is a hydrocarbon group), and cyclic acid anhydride-containing groups:

General Formula (IV)



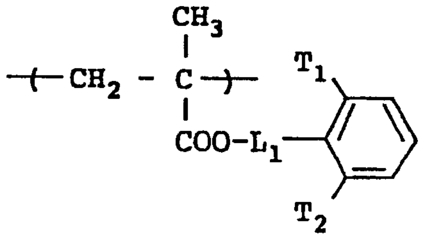
$$-(-\overset{\overset{\displaystyle a_1}{|}}{CH}-\overset{\overset{\displaystyle a_2}{|}}{\underset{\underset{\displaystyle COO-R_3}{|}}{C}}-)-$$

wherein a_1 and a_2 represent, hydrogen atoms, halogen atoms, cyano group or hydrocarbon groups and R_3 represents a hydrocarbon group. This resin will hereinafter be referred to as Resin [A'].

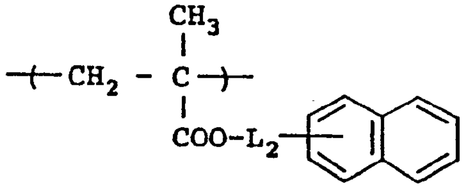
In the above described resin grains of the present invention, the polymeric component having the functional groups represented by General Formula (I) and/or General Formula (II) can have a crosslinked structure and in this case, the resin has water proof property which is preferable, when the hydrophilic property is realized through reaction with a processing solution for rendering hydrophilic.

The above described Resin [A'] of the present invention is preferably one containing, as the copolymeric component represented by General Formula (III), at least one of aryl group-containing methacrylate components represented by the following General Formula (IIIa) and General Formula (IIIb):

General Formula (IIIa);



General Formula (IIIb):



wherein T_1 and T_2 represent independently hydrogen atoms, hydrocarbon groups containing 1 to 10 carbon atoms, chlorine atoms, $-COR_4$ or $-COOR_5$ (R_4 and R_5 are hydrocarbon groups of 1 to 10 carbon atoms) and L_1 and L_2 each represent direct bonds for bonding -COO- and benzene ring or bonding groups containing 1 to 4 bonding atoms.

The feature of the lithographic printing plate precursor of the present invention consists in that the photoconductive layer comprises at least one of the resin grains consisting of a resin (which will hereinafter be referred to as Resin [L]) containing at least one of the functional groups represented by the above described General Formula (I) and/or General Formula (II) and optionally, at least one of the binder resins [A] or [A']. The resin grains are such that when processing with a processing solution containing at least one hydrophilic compound with nucleophilic reactivity, the hydrophilic compound with nucleophilic reactivity can additionally be reacted with the end of the functional group represented by the General Formula (I) or (II), whereby the photoconductive layer can reveal more hydrophilic property, and when the resin grains have a crosslinked structure, they are not or hardly soluble in water and exhibit water-swelling property while maintaining the hydrophilic property.

In the present invention, it is important that the resin grains are dispersed in the photoconductive layer in the form of grains whose average grain diameter is same or smaller than the maximum grain diameter of the photoconductive zinc oxide grains. If there are resin grains having larger grain diameters than zinc oxide grains, the electrophotographic properties are deteriorated and in particular, uniform electrification cannot be obtained, thus resulting in density unevenness in an image, disappearance of letters or fine lines and background staining in a non-image area in a reproduced image.

In the present invention, the crosslinked resin grains do not meet with dissolving-out with dampening water during printing so that good printing properties can be maintained even after a number of prints are obtained.

On the other hand, the binder resin [A'] has a relatively low molecular weight and the specified copolymeric component containing the polar group (including cyclic acid anhydride groups unless otherwise indicated in this specification) at one end thereof, which adsorbs on the stoichiometric defects of the photoconductive zinc oxide, so that the covering property of the surface of the photoconductor is improved to compensate trapping of the photoconductor and the humidity property is remarkably improved, while simultaneously dispersion of the photoconductor is sufficiently carried out to suppress aggregation thereof. Furthermore, the resin grains are uniformly dispersed in the similar manner to suppress an unnecessary interaction between the resin grains and photoconductor.

Thus, the lithographic printing plate precursor of the present invention has various advantages that an image faithful to an original can be reproduced,even when environmental conditions are changed or a laser beam of a low output is used, without occurrence of background stains owing to the high hydrophilic property of non-image areas, the smoothness and electrostatic characteristics of the photoconductive layer are excellent and furthermore, the durability is largely improved.

In addition, the lithographic printing plate precursor of the present invention is not sensitive to environmental influences during plate making, is very excellent in storage property before processing and is capable of undergoing rapidly a processing for rendering hydrophilic.

Such a mechanism that the resin grains contained in the photoconductive layer of the present invention is rendered hydrophilic by a hydrophilic compound with nucleophilic reactivity will be illustrated by the following reaction formula (1) in whichⓟ represents a resin part having a functional group represented by General Formula (I) or (II), for example, as to a case of using sulfite ion as the hydrophilic compound of nucleophilic reactivity:

$$\underbrace{\textcircled{p} \sim W_1-CH_2CH_2Cl}_{\substack{\text{General Formula (II)}\\ X=-Cl\\ \text{lipophilic}}} \xrightarrow[-HCl]{OH^{\ominus}} \underbrace{\textcircled{p} \sim W_1-CH=CH_2}_{\substack{\text{General Formula (I)}\\ \text{lipophilic}}}$$

$$\xrightarrow{SO_3^{2\ominus}} \underset{\text{hydrophilic}}{\textcircled{p} \sim W_1-CH_2CH_2SO_3^{\ominus}} \qquad \cdots\cdots\cdots\cdots (1)$$

That is to say, the resin grains of the present invention has the feature that only when non-image areas as a lithographic printing plate precursor is subjected to oil-desensitization, they are reacted with a nucleophilic compound in a processing solution as described above, whereby the hydrophilic group is added to the end thereof and they are rendered hydrophilic. Since the resin grains are not reactive with moisture in the air, there is no problem to be feared in storage of the lithographic printing plate precursor of the present invention. Since vinylsulfone group, vinylcarbonyl group or acryloxy group, represented by General Formula (I), is a functional group which is very rapidly reactive with a nucleophilic compound, it is possible to rapidly render hydrophilic.

The functional group represented by General Formula (II) can be converted into the corresponding functional group represented by General Formula (I) by an alkali treatment to readily remove the hydrogen halide as shown in Reaction Formula (1) and can thus be used in the similar manner to General Formula (I).

The resin grains of the present invention will now be illustrated in detail. The resin grains of the present invention have an average grain diameter of same as or less than the maximum diameter of the photoconductive zinc oxide grains. Specifically, the resin grains of the present invention have a maximum grain diameter of at most 10 µm, preferably at most 5 µm and an average grain diameter of at most 1.0 µm, preferably at most 0.5 µm. The specific surface areas of the hydrophilic resin grains are increased with the decrease of the grain diameter, resulting in good electrophotographic properties, and the grain size of colloidal grains, i.e., about 0.01 µm or smaller is sufficient. However, very small grains cause the similar troubles to those in the case of molecular dispersion and accordingly a grain size of 0.005 µm or larger is preferable. On the other hand, zinc oxide has generally a grain diameter of 0.05 to 10 µm, preferably 0.1 to 5 µm.

The functional group of the polymeric component or recurring unit contained in Resin [L] is represented by General Formula (I) or (II):

General Formula (I)

$$-W_1-(CH_2)_{n_1}-CH=CH_2$$

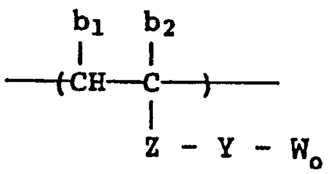
General Formula (II)

$$-W_2-\!\left(CH_2\right)_{n_2}-CH_2CH_2-X$$

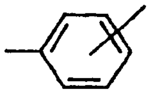
In General Formulae (I) and (II), $-W_1-$ and $-W_2-$ each represent $-SO_2-$, -CO- or -OOC-, n_1 and n_2 each represent 0 or 1 and X represents a halogen atom. In the General Formulae (I) and (II), n_1 and n_2 are preferably 0 and the halogen atom as X includes fluorine, chlorine, bromine and iodine atoms.

Specific, but not limiting, examples of the copolymer constituent containing the functional group represented by General Formula (I) and/or General Formula (II) of Resin [L] include those represented by the following repeating unit of General Formula (V):

General Formula (V)

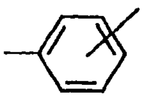


$$-\!\left(\overset{b_1}{\overset{|}{C}H}-\underset{\underset{Z-Y-W_0}{|}}{\overset{b_2}{\overset{|}{C}}}\right)\!-$$

wherein Z represents -COO-, -OCO, -O-, -CO-, $-\overset{r_1}{\overset{|}{CON}}-$, $-SO_2\overset{r_1}{\overset{|}{N}}-$ wherein r_1 represents hydrogen atom or a hydrocarbon group, -CONHCOO-, -CONHCONH-, $-CH_2COO-$, $-CH_2OCO-$ or , Y represents a direct bond or organic radical for connecting -Z- and $-W_0$, $-\!\left(Z-Y\right)\!-$ can directly connect $-\!\left(\overset{b_2}{\overset{|}{C}}\right)\!-$ and $-W_0$, W_0 represents the functional group represented by General Formula (I) or (II) and b_1 and b_2 may be same or different, each being hydrogen atom, a halogen atom, cyano group, an alkyl group or an aryl group.

General Formula (V) will now be illustrated in detail. In this formula, Z represents preferably -COO-, -OCO, -O-, -CO-,

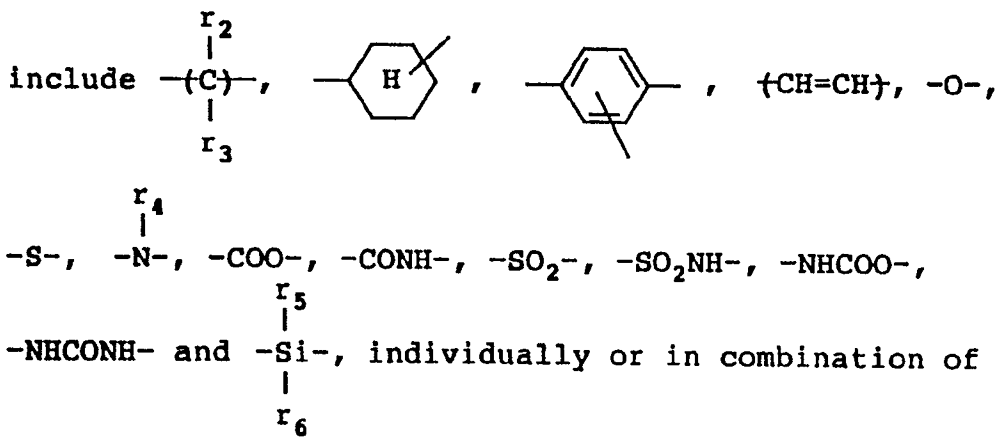
$$-\overset{r_1}{\overset{|}{CON}}-,\quad -SO_2\overset{r_1}{\overset{|}{N}}-\quad \text{or}$$

 ,

wherein r_1 represents hydrogen atom, an optionally substituted alkyl group of 1 to 8 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, 2-chloroethyl, 2-bromoethyl, 2-cyanoethyl, 2-methoxyethyl, 2-

hydroxyethyl, 3-bromopropyl groups etc., an optionally substituted aralkyl group of 7 to 9 carbon atoms, such as benzyl, phenethyl, 3-phenylpropyl, chlorobenzyl, bromobenzyl, methylbenzyl, methoxybenzyl, chloromethylbenzyl, dibromobenzyl groups, etc., an optionally substituted aryl group such as phenyl, tolyl, xylyl, mesityl, methoxyphenyl, chlorophenyl, bromophenyl, chloromethylphenyl groups, etc.

Y represents a direct bond or an organic radical for connecting -Z- and $-W_o$. When Y represents the organic radical, this radical is a carbon-carbon bond, between which hetero atoms (including oxygen, sulfur and nitrogen atom) may be present, which specific examples



include $-(\overset{r_2}{\underset{r_3}{C}})-$, $-CH=CH-$, -O-,

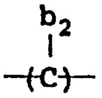
-S-, $-\overset{r_4}{N}-$, -COO-, -CONH-, $-SO_2-$, $-SO_2NH-$, -NHCOO-,

-NHCONH- and $-\overset{r_5}{\underset{r_6}{Si}}-$, individually or in combination of

these groups, wherein r_2, r_3, r_4, r_5 and r_6 have the meaning as the foregoing r_1.

b_1 and b_2 may be the same or different, and have the same meaning as a_1 and a_2 in Formula (IV),each being a hydrogen atom, a halogen atom (e.g., chlorine, bromine), a cyano group, a hydrocarbon residue (an optically substituted alkyl group containing 1 to 12 carbon atoms, such as methyl, ethyl, propyl, butyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, hexyloxycarbonyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, butoxycarbonylmethyl, etc., an aralkyl group such as benzyl, phenetyl, etc., and an aryl group such as phenyl, tolyl, xylyl, chlorophenyl, etc.

In addition, the linkage moiety $(Z-Y)$ in General Formula (V) may directly connect the moiety

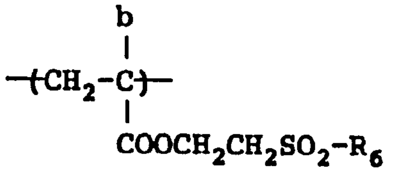


$$-(\overset{b_2}{C})-$$

to the moiety $-W_o$.

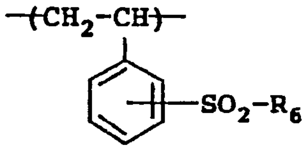
Specific, but not limiting examples of the polymeric constituent containing the functional group represented by General Formula (I) or (II) will be illustrated below. In Examples (a-1) to (a-25), brepresents -H or $-CH_3$, R_6 represents $-CH=CH_2$, $-CH_2CH=CH$ or $-CH_2CH_2X$ and X represents -F, -Cl, -Br or -I.

(a-1)

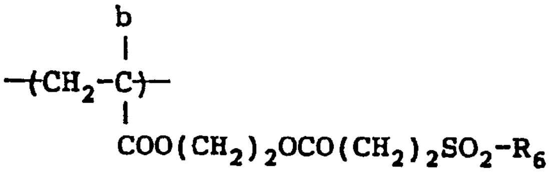


$$-(CH_2-\overset{b}{\underset{COOCH_2CH_2SO_2-R_6}{C}})-$$

(a-2)

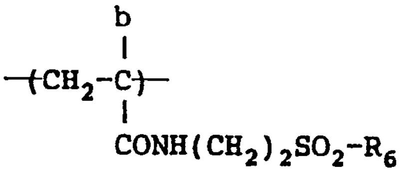


(a-3)



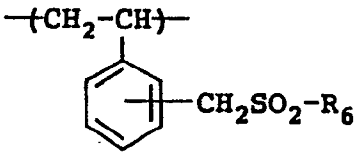
$$-\!\left(CH_2-\underset{COO(CH_2)_2OCO(CH_2)_2SO_2-R_6}{\overset{b}{C}}\right)\!-$$

(a-4)

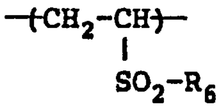


$$-\!\left(CH_2-\underset{CONH(CH_2)_2SO_2-R_6}{\overset{b}{C}}\right)\!-$$

(a-5)

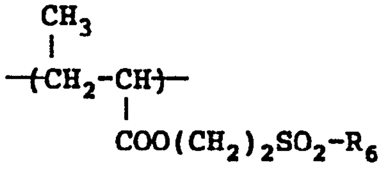


(a-6)



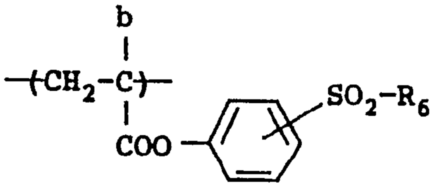
$$-\!\left(CH_2-\underset{SO_2-R_6}{CH}\right)\!-$$

(a-7)

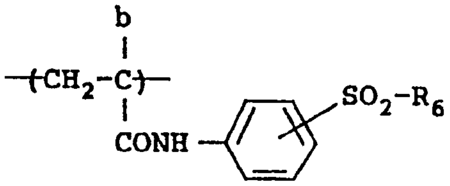


$$-\!\left(\overset{CH_3}{CH_2}-\underset{COO(CH_2)_2SO_2-R_6}{CH}\right)\!-$$

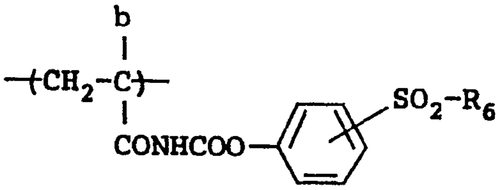
(a-8)



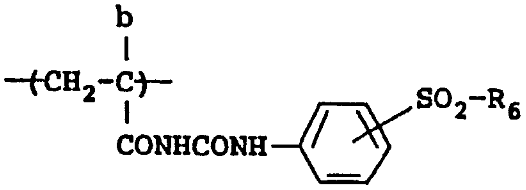
(a-9)



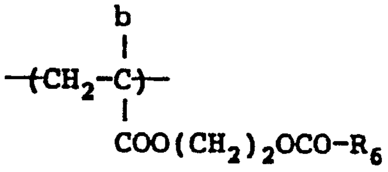
(a-10)



(a-11)

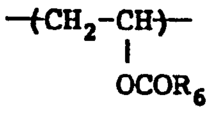


(a-12)



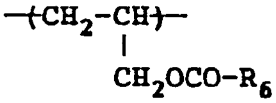
$$-\!\left(\mathrm{CH_2}-\underset{\mathrm{COO(CH_2)_2OCO{-}R_6}}{\overset{b}{\mathrm{C}}}\right)\!-$$

(a-13)



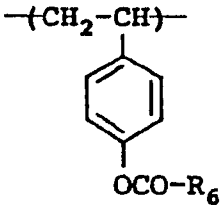
$$-\!\left(\mathrm{CH_2}-\underset{\mathrm{OCOR_6}}{\mathrm{CH}}\right)\!-$$

(a-14)

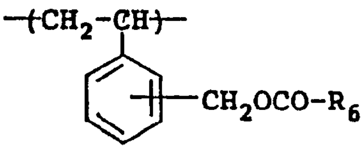


$$-\!\left(CH_2-\underset{\substack{|\\ CH_2OCO-R_6}}{CH}\right)\!-$$

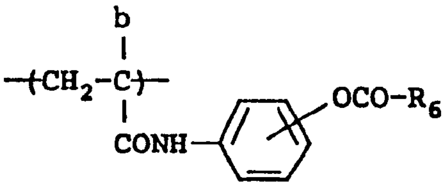
(a-15)



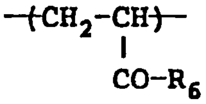
(a-16)



(a-17)

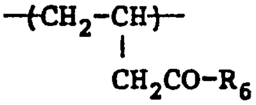


(a-18)



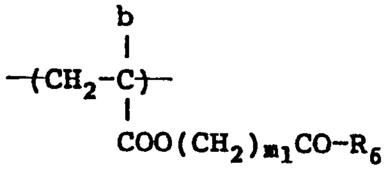
$$-\!\left(CH_2-\underset{\substack{|\\ CO-R_6}}{CH}\right)\!-$$

(a-19)



$$-\!\left(CH_2-\underset{\substack{|\\ CH_2CO-R_6}}{CH}\right)\!-$$

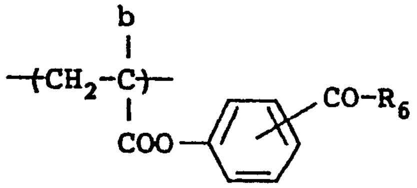
(a-20)



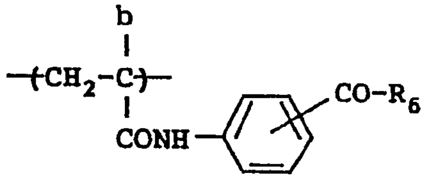
$$-\!\left(CH_2-\overset{\displaystyle b}{\underset{\displaystyle COO(CH_2)_{m_1}CO-R_6}{C}}\right)\!-$$

(m_1: integer of 1~4)

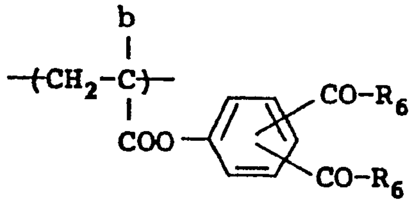
(a-21)



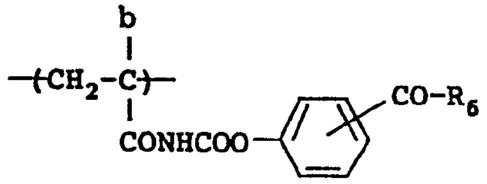
(a-22)



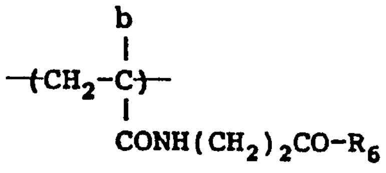
(a-23)



(a-24)



(a-25)



$$-\!\left(CH_2-\overset{\displaystyle b}{\underset{\displaystyle CONH(CH_2)_2CO-R_6}{C}}\right)\!-$$

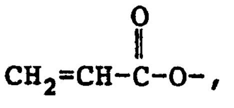
In Resin [L] of the present invention, the polymeric component containing the functional group represented by General Formula (I) and/or General Formula (II) is generally in a proportion of 1 to 95% by weight, preferably 50 to 95% by weight based on the whole copolymer in a case where Resin [L] is of the copolymer. Preferably, this resin has a molecular weight of 10^3 to 10^6, particularly $5x10^3$ to $5x10^5$.

The resin containing the polymeric component containing the functional group represented by General Formula (I) or (II) as described above can be synthesized by any of known methods, for example, by a method comprising subjecting to polymerization reaction a monomer containing the functional group represented by General Formula (I) or (II) and a polymerizable double bond group in the molecule (e.g. monomer corresponding to the recurring unit of General Formula (V)) and a method comprising reacting a low molecular compound containing the functional group represented by General Formula (I) or (II) with a high molecular compound containing a polymeric constituent containing a functional group reactive with the low molecular compound, which is called "polymer reaction".

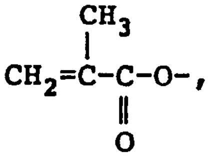
Moreover, the resin containing the functional group represented by General Formula (I) can be synthesized by synthesizing the resin containing the functional group represented by General Formula (II) and then subjecting to an alkali treatment to remove the corresponding hydrogen halide.

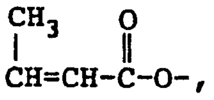
The polymerizable functional group in the above described monomer synthesis includes ordinary polymerizable double bond groups, for example,

$CH_2=CH-CH_2-$,

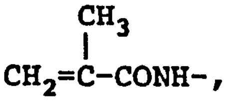

$CH_2=CH-C(=O)-O-$,

$CH_2=CH-$,

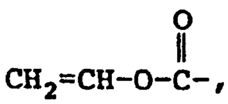

$CH_2=C(CH_3)-C(=O)-O-$,

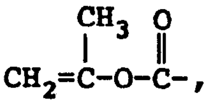

$CH(CH_3)=CH-C(=O)-O-$,

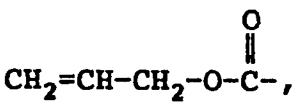
$CH_2=CH-CONH-$,


$CH_2=C(CH_3)-CONH-$,


$CH(CH_3)=CH-CONH-$,


$CH_2=CH-O-C(=O)-$,


$CH_2=C(CH_3)-O-C(=O)-$,


$CH_2=CH-CH_2-O-C(=O)-$,

$CH_2=CH-NHCO-$,

$CH_2=CH-CH_2-NHCO-$, $CH_2=CH-SO_2-$,

$CH_2=CH-CO-$, $CH_2=CH-O-$, $CH_2=CH-S-$.

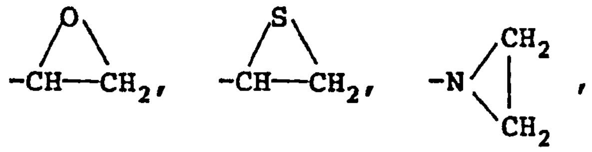
In the above described monomer synthesis or polymer reaction, sulfonylation, carbonylation or carboxylic acid esterification can be carried out by methods, for example, described in Nippon Kagakukai, Shin-Jikken Kagaku Koza, Vol. 14, "Yuki Kagobutsu no Gosei to Hanno (Synthesis and Reaction of Organic Compounds)" page 751, 1000 and 1759 (1978), published by Maruzen KK and S. Patai, Z. Rappoport and C. Stirling "The Chemistry of Sulfones and Sulphoxides" page 165 (1988), published by John Wiley & Sons.

When Resin [L] is of a copolymer, examples of the monomer copolymerizable with the monomer containing the functional group represented by the above described General formula (I) and/or (II) are α-olefins, alkanic acid vinyl or allyl esters, acrylonitrile, methacrylonitrile, vinyl ethers, acrylamides, methacrylamides, styrenes, alicyclic vinyls such as vinylpyrrolidone, vinylpyridine, vinylimidazole, vinylthiophene, vinylpyridineimidazoline, vinylpyrazole, vinyldioxane, vinylquinoline, vinylthiazole, vinyloxazine and the like.

In the present invention, at least a part of the resin grains may be crosslinked. Such a resin that at least a part of the polymer is previously crosslinked (resin having a crosslinked structure in the polymer) is preferably a resin which is hardly soluble or insoluble in acidic or alkaline solutions when the above described functional group contained in the resin gives hydrophilic property through an oil-desensitization treatment. Specifically, the solubility of the resin in distilled water at 20 to 25°C is preferably at most 90% by weight, more preferably at most 70% by weight.

Introduction of a crosslinked structure in a polymer can be carried out by known methods, that is, (I) a method comprising subjecting a monomer containing the functional group of General Formula (I) and/or (II) to polymerization reaction in the presence of a multi-functional monomer (monomer containing two or more polymerizable functional groups) or a multifunctional oligomer and effecting crosslinking among molecules, (2) a method comprising incorporating functional groups for proceeding the crosslinking reaction in the polymer and crosslinking the polymer containing both the functional groups with a crosslinking agent or hardening agent and (3) a method comprising subjecting the crosslinking functional group-containing polymer to polymer reaction with a compound containing the group of General Formula (I) or (II).

The method (3) by the polymer reaction comprises polymerizing specifically the multifunctional monomer or multifunctional oligomer with a monomer containing a polar group such as -OH, -Cl, -Br, -I, $-NH_2$, -COOH, -SH,



-N=C=O, -COCl, $-SO_2Cl$, etc., into which the functional group of General Formula (I) or (II) can be introduced, to prepare a copolymer and then introducing thereinto a low molecular compound containing the functional group of General Formula (I) or (II) by polymer reaction.

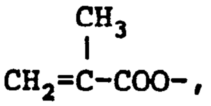
Any of monomers containing two or more same or different ones of these polymerizable functional groups can be used as the multifunctional monomer or oligomer in the above-described method (3).

Of these monomers, as the monomer having two or more same polymerizable functional groups, there can be used styrene derivatives such as divinyl benzene and trivinyl benzene; esters of polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycols Nos. 200, 400 and 600, 1,3-butylene glycol, neopentyl glycol, dipropylene glycol, polypropylene glycol, trimethylolpropane, trimethylolethane, pentaerythritol and the like or polyhydroxyphenols such as hydroquinone, resorcinol, catechol and derivatives thereof with methacrylic acid, acrylic acid or crotonic acid, vinyl ethers and allyl ethers; vinyl esters of dibasic acids such as malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, maleic acid, phthalic acid, itaconic acid and the like, allyl esters, vinylamides and allylamides; and condensates of polyamines such as ethylenediamine, 1,3-propylenediamine, 1,4-butylenediamine and the like with carboxylic acids containing vinyl groups such as methacrylic acid, acrylic acid, crotonic acid, allylacetic acid and the like.

As the multifunctional monomer or oligomer having different polymerizable functional groups, there can be used, for example, ester derivatives or amide derivatives containing vinyl groups of carboxylic acids containing vinyl group, such as methacrylic acid, acrylic acid, methacryloylacetic acid, acryloylacetic acid, methacryloylpropionic acid, acryloylpropionic acid, itaconyloylacetic acid and itaconyloylpropionic acid, reaction products of carboxylic anhydrides with alcohols or amines such as allyloxycarbonylpropionic acid, allyloxycarbonylacetic acid, 2-allyloxycarbonylbenzoic acid, allylaminocarbonylpropionic acid and the like, for example, vinyl methacrylate, vinyl acrylate, vinyl itaconate, allyl methacrylate, allyl acrylate, allyl itaconate, vinyl methacryloylacetate, vinyl methacryloylpropionate, allyl methacryloylpropionate, vinyloxycarbonylmethyl methacrylate, 2-(vinyloxycarbonyl)-ethyl ester of acrylic acid, N-allylacrylamide, N-allylmethacrylamide, N-allylitaconamide, methcaryloylpropionic acid allylamide and the like; and condensates of amino alcohols such as aminoethanol, 1-aminopropanol, 1-aminobutanol, 1-aminohexanol, 2-aminobutanol and the like with carboxylic acids containing vinyl groups.

The monomer or oligomer containing two or more polymerizable functional groups of the present invention is generally used in a proportion of at most 10 mole%, preferably at most 5 mole% to all monomers, which is polymerized to form a resin.

In the case of a polymer containing the functional group represented by General Formula (I), however, it is preferable not to use CH_2=CH-COO-,

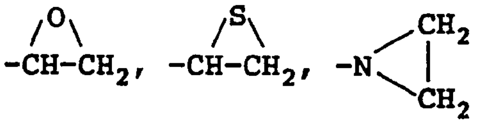
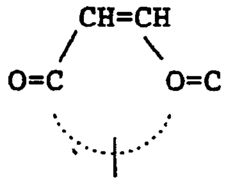
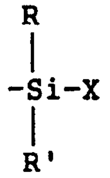


$$CH_2=\overset{CH_3}{\overset{|}{C}}-COO-,$$

CH_2=CH-CONH-, CH_2=CH-SO_2- and CH_2=CH-CO- as the foregoing polymerizable functional group.

As the functional group for effecting the crosslinking reaction by the above described method (2) or (3) according to the present invention, there can be used ordinary polymerizable double bond groups (e.g., above-described as a polymerizable double bond group, or a combination of reactive groups capable of forming chemical bonds by chemical reaction. The crosslinking of polymers by reacting reactive groups among the polymers and forming chemical bonds according to the latter can be carried out in the similar manner to the ordinary reactions of organic low molecular compounds, for example, as disclosed in Yoshio Iwakura and Keisuke Kurita "Reactive Polymers (Hannosei Kobunshi)" published by Kohdansha (1977) and Ryohei Oda "High Molecular Fine Chemical (Kobunshi Fine Chemical)" published by Kohdansha (1976). The chemical bonds by combination of functional groups classified as Group A (functional group having dissociative hydrogen atom) and functional groups classified as Group B in the following Table 1 have well been known.In addition, as the reactive group, there can be used -$CONHCH_2OR_7$ wherein R_7 represents a hydrogen atoms or an alkyl group of 1 to 6 carbon atoms such as methyl, ethyl, propyl, butyl or hexyl group, which has been known as a group for linking by a self-condensation type reaction.

Table 1

Group A	Group B
-COOH, -PO_3H_2	
-OH, -SH -NH_2	-$COCl_2$, -SO_2Cl, cyclic acid anhydride
-SO_2H	-N=C=O, -N=C=S,   $-\overset{R}{\underset{R'}{Si}}-X$ (X=ClBr)

In Table 1, R and R' have the same meaning as the foregoing r_5 and r_6.

Furthermore, there can be used functional groups and compounds described in, for example, Takeshi Endo "Rendering Precise Heat Setting Polymers (Netsu-kokasei Kobunshi no Seimitsuka)" published by C.M.C. KK, 1986, Yuji Harazaki "Latest Binder Technique Handbook (Saishin Binder Gijutsu Binran)" Section II-I, published by Sogogijutsu Center, 1985, Takayuki Otsu "Synthesis and Design of Acrylic Resins and Development of New Uses (Akuriru Jushi no Gosei-Sekkei to Shin-yoto Kaihatsu)" published by Chubu Keiei Kaihatsu Center Shuppanbu, I985, Eizo Omori "Functional Acrylic Resins (Kinosei Akuriru-kei Jushi)" published by Technosystem, 1985, Hideo Inui and Gentaro Nagamatsu "Light-sensitive Polymers (Kankosei Kobunshi)" published by Kodansha, 1977, Takahiro Tsunoda "New Light-sensitive Resins (Shin-Kankosei Jushi)", published by Insatsu Gakkai Shuppanbu, 1981, G.E. Green and B.P. Star "R.J. Macro. Sci. Reas. Macro. Chem.", C 21 (2), 187-273 (1981-82) and C.G. Roffey "Photopolymerization of Surface Coatings" published by A. Wiley Interscience Publ., 1982.

These crosslinking functional groups can be incorporated in one copolymeric constituent with the functional groups represented by General Formula (I) or (II), or can be incorporated in another copolymeric constituent than a copolymeric constituent containing the functional groups represented by General Formula (I) or (II).

Examples of the monomer corresponding to the copolymer constituent containing these crosslinking functional groups include vinyl compounds containing the functional groups copolymerizable with the polymeric constituents of General Formula (V).

These vinyl compounds include those described in, for example, Kobunshi Gakkai "Polymer Data Handbook -Kisohen-", published by Baihukan, 1986, for example, acrylic acid, α and/or β-substituted acrylic acid such as α-acetoxy, α-acetoxymethyl, α-(2-amino)ethyl, α-chloro, α-bromo, α-fluoro, α-tributylsilyl, α-cyano, β-chloro, β-bromo, α-chloro-β-methoxy and α,β-dichloro substituted ones, methacrylic acid, itaconic acid, itaconic acid semi-esters, itaconic acid semiamides, crotonic acid, 2-alkenylcarboxylic acids such as 2- pentenoic acid, 2-methyl-2-hexenoic acid, 2-octenoic acid, 4-methyl-2-hexenoic acid and 4-ethyl-2-octenoic acid, maleic acid, maleic acid semi-esters, maleic acid semi-amides, vinylbenzenecarboxylic acid, vinylbenzenesulfonic acid, vinylsulfonic acid, vinylphosphonic acid, semi-ester derivatives of vinyl groups or allyl groups of dicarboxylic acids and ester derivatives and amide derivatives of these carboxylic acids or sulfonic acids containing crosslinking functional groups in the substituents.

To Resin [L] of the present invention can optionally be added a reaction promoter so as to promote the crosslinking reaction, for example, acids such as acetic acid, propionic acid, butyric acid, benzenesulfonic acid, p-toluenesulfonic acid, etc., peroxides, azobis compounds, crosslinking agents, sensitizers, photopolymerizable monomers and the like.

As the crosslinking agent in the present invention, there can be used compounds commonly used as crosslinking agents, for example, described in Shinzo Yamashita and Tosuke Kaneko "Handbook of Crosslinking Agents (Kakyozai Handbook)" published by Taiseisha (1981) and Kobunshi Gakkai Edition "High Molecular Data Handbook -Basis- (Kobunshi Data Handbook -Kisohen-)" published by Baihunkan (1986).

Examples of the crosslinking agent are organosilane compounds such as vinyltrimethoxysilane, vinyltributoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-mercaptopropyltriethoxysilane, γ-aminopropyltriethoxysilane and other silane coupling agents; polyisocyanate compounds such as tolylene diisocyanate, o-tolylene diisocyanate, diphenylmethane diisocyanate, triphenylmethane diisocyanate, triphenylmethane triisocyanate, polymethylenepolyphenyl isocyanate, hexamethylene diisocyanate, isophorone diisocyanate, high molecular polyisocyanates; polyol compounds such as 1,4- butanediol, polyoxypropylene glycol, polyoxyalkylene glycol, 1,1,1,-trimethylolpropane and the like; polyamine compounds such as ethylenediamine, γ-hydroxypropylated ethylenediamine, phenylenediamine, hexamethylenediamine, N-aminoethylpiperazine, modified aliphatic polyamines and the like; polyepoxy group-containing compounds and epoxy resins, for example, as described in Hiroshi Kakiuchi "New Epoxy Resins (Shin Epoxy Jushi)" published by Shokodo (1985), and Kuniyuki Hashimoto "Epoxy Resins (Epoxy Jushi)" published by Nikkan Kogyo Shinbunsha (1969); melamine resins such as described in Ichiro Miwa and Hideo Matsunaga "Urea and Melamine Resins (Urea-Melamine Jushi)" published by Nikkan Kogyo Shinbunsha (1969); and poly(meth)acrylate compounds as described in Shin Ogawara, Takeo Saegusa and Toshinobu Higashimura "Oligomers" published by Kodansha (1976) and Eizo Omori "Functional Acrylic Resins" published by Technosystem (1985), for example, polyethylene glycol diacrylate, neopentyl glycol diacrylate, 1,6-hexanediol diacrylate, trimethylol-propane triacrylate, pentaerythritol polyacrylate, bisphenol A-diglycidyl ether diacrylate, oligoester acrylate and methacrylates thereof and the like.

In the present invention, Resin [L] containing at least one of functional groups capable of forming at least one hydrophilic group by processing with a processing solution containing a compound with nucleophilic reactivity is in the form of grains with a maximum grin diameter of at most 10 µm and an average grain diameter of at most 1.0 µm.

The resin grains of the present invention, with fine grain diameter, are produced by dispersing the resin powder as it is, when preparing the composition for forming a photoconductive layer, to thus give a desired grain size. Alternately, it is possible to use a dry or wet pulverizing method well known in the art or a method of obtaining high molecular gel latexes.

That is to say, it is possible to use a known method of directly pulverizing a resin powder to give fine grains by a known grinder or dispersing machine, e.g., ball mill, point shaker, sand mill, hammer mill, jet mill, keddy mill, etc., and a known method of producing latex grains of paings or liquid developers for electrophotography.

The latter method of obtaining high molecular latex grains is a method comprising dispersing the resin powder by the joint use of a dispersing polymer, more specifically previously mixing the resin powder and dispersion aid polymer followed by pulverizing, and then dispersing the pulverized mixture in the presence of the dispersing polymer.

For example, these methods are described in "Flowing and Pigment Dispersion of Paints" translated by Kenji Ueki and published by Kyoritsu Shuppan (1971), Solomon "Chemistry of Paints", "Paint and Surface Coating Theory and Practice", Yuji Harasaki "Coating Engineering (Coating Kogaku)" published by Asakura Shoten (1971), Yuji Harasaki "Fundamental Science of Coating (Kiso Kagaku of Coating)" by Maki Shoten (1977) and Japanese Patent Laid-Open Publication Nos. 96954/1987, 115171/1987 and 75651/1987.

Furthermore, the prior art method of obtaining readily latex grains or particles by suspension polymerization or dispersion polymerization can also be used in the present invention, for example, as described in Soichi Muroi "Chemistry of High Molecular Latex (Kobunshi Latex no Kagaku)" published by Kobunshi Kankokai (1970), Taira Okuda and Hiroshi Inagaki "Synthetic Resin Emulsions (Gosei Jushi Emulsion)" published by Kobunshi Kankokai (1978), Soichi Muroi "Introduction to High Molecular Latexes (Kobunshi Latex Nyumon)" published by Kobunsha (1983).

In the present invention, it is preferable to use a method of obtaining high molecular latex grains, whereby resin grains with an average grain diameter of at most 1.0 μm can readily be obtained.

In the electrophotographic lithographic printing plate precursor of the present invention, formation of a photoconductive layer can be carried out by any of methods of dispersing photoconductive zinc oxide in an aqueous system, for example, described in Japanese Patent Publication Nos. 450/1976, 18599/1972 and 41350/1971 and methods of dispersing in a non-aqueous solvent system, for example, described in Japanese Patent Publication No. 31011/1975 and Japanese Patent Laid-Open Publication Nos. 54027/1978, 20735/1979, 202544/1982 and 68046/1983. If water remains in the photoconductive layer, however, the electrophotographic property is deteriorated, and accordingly, the latter methods using a non-aqueous solvent system is preferable. Therefore, in order to adequately disperse the resin latex grains of the present invention in the photoconductive layer dispersed in a non-aqueous system, the latex grains are preferably non-aqueous system latex grains.

As the non-aqueous solvent for the non-aqueous system latex, there can be used any of organic solvents having a boiling point of at most 200°C, individually or in combination. Useful examples of the organic solvent are alcohols such as methanol, ethanol, propanol, butanol, fluorinated alcohols and benzyl alcohol, ketones such as acetone, methyl ethyl ketone, cyclohexanone and diethyl ketone, ethers such as diethyl ether, tetrahydrofuran and dioxane, carboxylic acid esters such as methyl acetate, ethyl acetate, butyl acetate and methyl propionate, aliphatic hydrocarbons containing 6 to 14 carbon atoms such as hexane, octane, decane, dodecane, tridecane, cyclohexane and cyclooctane, aromatic hydrocarbons such as benzene, toluene, xylene and chlorobenzene and halogenated hydrocarbons such as methylene chloride, dichloroethane, tetrachloroethane, chloroform, methylchloroform, dichloropropane and trichloroethane.

When a high molecular latex is synthesized by the dispersion polymerization method in a non-aqueous solvent system, the average grain diameter of the latex grains can readily be adjusted to at most 1 μm while simultaneously obtaining grains of monodisperse system with a very narrow distribution of grain diameters. Such a method is described in, for example, K.E.J. Barrett "Dispersion Polymerization in Organic Media" John Wiley & Sons (1975), Koichiro Murata "Polymer Processings (Kobunshi Kako)" 23, 20 (1974), Tsunetaka Matsumoto and Toyokichi Tange "Journal of Japan Adhesive Association (Nippon Setchaku Kyokaishi)" 9, 183 (1973), Toyokichi Tange "Journal of Japan Adhesive Association" 23, 26 (1987), D.J. Walbridge "NATO. Adv. Study Inst. Ser. E." No. 67, 40 (1983), British Patent No.s 893,429 and 934,038 and U.S. Patent Nos. 1,122,397, 3,900,412 and 4,606,989, and Japanese Patent Laid-Open Publication Nos. 179751/1985 and 185963/1985.

The resin grains of the present invention form hydrophilic groups by the reaction with a hydrophilic compound with nucleophilic property through processing with an oil-desensitizing solution or dampening water used during printing. Therefore, in the lithographic printing plate precursor having a photoconductive layer containing the resin grains, the hydrophilic property of non-image areas rendered hydrophilic with an oil-desensitizing solution is further increased by the above-described hydrophilic groups formed in the resin grains to make clear the lipophilic property of image areas and the hydrophilic property of non-image areas and to prevent the non-image areas from adhesion of a printing ink during printing. Consequently, a number of prints with clear image quality and without background stains can be obtained.

Furthermore, in the case of the above-described resin grains a part of which is crosslinked, the solubility in water is remarkably lowered, while maintaining the hydrophilic property, to be hardly or not soluble.

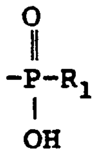
Therefore, such an effect is improved that the hydrophilic property on non-image areas is more enhanced by the hydrophilic groups formed by the resin grains, and the durability is improved.

More specifically, even if the quantity of the above-described functional groups in the resin grains is decreased, the effect of improving the hydrophilic property can unchangeably be maintained, or even if printing conditions are severer, e.g., enlargement of a printing machine and fluctuation of printing pressure taking place, a number of prints with clear image quality and without background stains can be obtained.

As the binder resin of the present invention, there can be used all of known resins, typical of which are vinyl chloride-vinyl acetate copolymers, styrenebutadiene copolymers, styrene-methacrylate copolymers, methacrylate copolymers, acrylate copolymers, vinyl acetate copolymers, polyvinyl butyral, alkyd resins, silicone resins, epoxy resins, epoxyester resins, polyester resins and the like, as described in Takaharu Kurita and Jiro Ishiwataru "High Molecular Materials (Kobunshi)" 17, 278 (1968), Harumi Miyamoto and Hidehiko Takei "Imaging" No. 8, page 9 (1973), Koichi Nakamura "Practical Technique of Binders for Recording Materials (Kiroku Zairyoyo Binder no Jissai Gijutsu)" Section 10, published by C.M.C. Shuppan (1985), D.D. Tatt, S.C. Heidecker "Tappi" 49, No. 10, 439 (1966), E.S. Baltazzi, R.G. Blanckette et al. "Photo Sci. Eng," 16, No. 5, 354 (1972), Nguyen Chank Khe, Isamu Shimizu and Eiichi Inoue "Journal of Electrophotographic Association (Denshi Shashin Gakkaishi)" 18 No. 2, 28 (1980), Japanese Patent Publication No. 31011/1975, Japanese Patent Laid-OpenPublication Nos. 54027/1978, 20735/1979, 202544/1982 and 68046/1983.

The binder resin of the present invention is preferably Resin A containing at least 30% by weight of the specified recurring unit represented by the foregoing General Formula (III) as polymeric components and 0.5 to 15% by weight of polymeric components having the specified polar groups and/or cyclic acid arihydride groups (in this specification, the polar group is defined to include cyclic acid anhydride polar groups unless otherwise indicated.), and having a relatively low molecular weight, i.e. a weight average molecular weight of $1x10^3$ to $2x10^4$ and a glass transition point of -20 to 110°C, preferably -10 to 90°C.

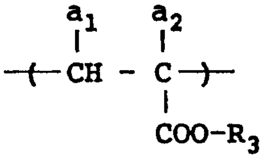
In another preferred embodiment of the present invention, the binder resin is Resin A′ having a weight average molecular weight of $1x10^3$ to $2x10^4$, containing at least 30% by weight of recurring unit represented by the following general formula (IV) as polymeric components and at least one polar group is bonded to one end of the polymer main chain, selected from the group consisting of $-PO_3H_2$, $-SO_3H$, -COOH, -OH, and



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-R_1$$

wherein R_1 is a hydrocarbon group or $-OR_2$ (R_2: hydrocarbon group) and cyclic acid anhydride-containing groups:

General Formula (IV)



$$-\!\!\left(\overset{\overset{\displaystyle a_1}{|}}{CH} - \underset{\underset{\displaystyle COO-R_3}{|}}{\overset{\overset{\displaystyle a_2}{|}}{C}}\right)\!\!-$$

in which a_1 and a_2 represent, hydrogen atoms, halogen atoms, cyano groups and hydrocarbon groups, $-COO-R_8$ or $-COO-R_8$ via a hydrocarbon group, wherein R_8 represents a hydrocarbon group, and R_3 represents a hydrocarbon group.

In Resin A′, the weight average molecular weight is $1x10^3$ to $2x10^4$, preferably $3x10^3 1x10^4$ and a glasstransition point of -20°C to 110°C, preferably -10°C to 90°C.

If the molecular weight of Resin [A] or [A′] is less than 10^3, the film-forming property is too lowered to maintain a sufficient film strength, while if more than $2x10^4$, in a photoreceptor using a near infrared to infrared spectral sensitizing dye, fluctuation of the dark decay retention ratio and photosensitivity under severe conditions such as high temperature and high humidity or low temperature and low humidity is somewhat increased and consequently, the benefit of the present invention cannot sufficiently be obtained that a stable reproduced image can be obtained.

In Resin [A] or [A′], the polymeric components corresponding to the recurring unit of General Formula (III) or (IV) are generally in a proportion of at least 30% by weight, preferably 50 to 97% by weight and the copolymeric components containing the polar groups bonded to the end of the main chain are generally in a proportion of 0.5 to 15% by weight, preferably 1 to 10% by weight.

If the polar group in Resin [A] or Resin [A′] is less than 0.5% by weight, the initial potential is too low to obtain a sufficient image density, while if more than 15% by weight, the dispersibility is lowered in spite of its lower molecular weight, and background staining is increased when used as an offset master.

In the recurring unit represented by General Formula (IV), contained in Resin [A'] in a proportion of at least of 30% by weight, R_3 represents hydrocarbon groups, for example, alkyl groups, aralkyl groups and aromatic groups, preferably aralkyl groups and aromatic groups as hydrocarbon groups containing benzene ring or naphthalene rain. Specifically R_3 represents optionally substituted alkyl groups containing 1 to 18 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tridecyl, tetradecyl, 2-chloroethyl, 2-bromoethyl, 2-cyanoethyl, 2-hydroxyethyl, 2-methoxyethyl, 2-ethoxyethyl, and 3-hydroxypropyl groups, optionally substituted alkenyl groups containing 2 to 18 carbon atoms such as vinyl, allyl, isopropenyl, butenyl, hexenyl, heptenyl and octenyl groups, optionally substituted aralkyl groups containing 7 to 12 carbon atoms such as benzyl, phenethyl, naphthylmethyl, 2-naphthylethyl, methoxybenzyl, ethoxybenzyl and methylbenzyl groups, optionally substituted cycloalkyl groups containing 5 to 8 carbon atoms such as cyclopentyl, cyclohexyl and cycloheptyl groups and optionally substituted aryl groups such as phenyl, tolyl, xylyl, mesityl, naphthyl, methoxyphenyl, ethoxyphenyl, fluorophenyl, difluorophenyl, bromophenyl, chlorophenyl, dichlorophenyl, iodophenyl, methoxycarbonylphenyl, ethoxycarbonylphenyl and cyanophenyl groups.

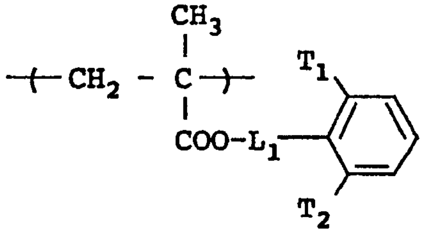
In the recurring unit of General Formula (III) as the methacrylate component having such substituents R_3, there is more preferably recurring units represented by the following General Formula (IIIa) and/or General Formula (IIIb).

Furthermore, as the low molecular weight Resin [A'], there is preferably used a Resin [A'] having the polar group bonded to the end and containing the methacrylate component having the specified substituent containing a benzene ring having the specified substituent on 2- and/or 6-position or non-substituted naphthalene ring, represented by General Formula (IIIa) and/or (IIIb), which low molecular weight polymer will hereinafter be referred to as Resin [A''].

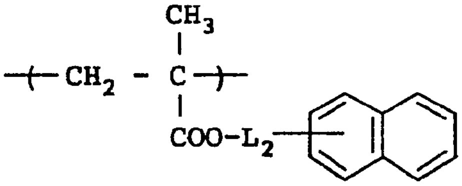
In Resin [A''], the methacrylate components corresponding to the recurring units of General Formula (IIIa) and/or (IIIb) are generally in a proportion of at least 30% by weight, preferably 50 to 90% by weight and the polar groups contained at the end of the polymer main chain are generally in a proportion of 0.5 to 15% by weight, preferably 1 to 10% by weight based on 100% by weight of Resin [A''].

In the recurring unit represented by General Formula (IV), a_1 and a_2 preferably represent hydrogen atoms, cyano groups, alkyl groups containing 1 to 18 carbon atoms, such as methyl, ethyl, propyl and butyl groups, -COO-R_8 or -COO-R_8 via a hydrocarbon group, wherein R_8 represents a hydrocarbon group preferably an alkyl group containing 1 to 18 carbon atoms, alkenyl group, aralkyl group, alicyclic group or aryl group, which can be substituted, specifically the same meanings as R_3. As the hydrocarbon group in the above-described -CO-OR_8 group via a hydrocarbon group, for example, there is methylene, ethylene, propylene group, etc.

Furthermore, preferable copolymeric components of Resin [A] or [A'] are copolymeric components of methacrylates containing substituted benzene rings or naphthalene ring, represented by the following General Formula (IIIa) and/or (IIIb). Resin [A''] contains this copolymeric component and the copolymeric component containing the polar group bonded to one end of the polymer chain.



(IIIa)



(IIIb)

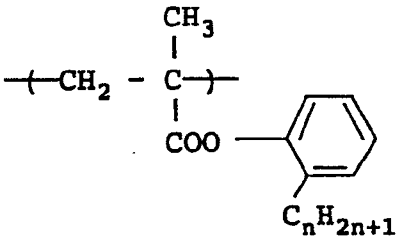
In General Formulae (IIIa) and (IIIb), T_1 and T_2 each represent independently hydrogen atom, hydrocarbon groups containing 1 to 10 carbon atoms, chlorine atom, bromine atom, -COR_9 or -$COOR_9$ wherein R_9 represents a hydrocarbon group containing 1 to 10 carbon atoms, and L_1 and L_2 each represents direct bonds for bonding -COO-and benzene ring or bonding groups containing 1 to 4 bonding atoms.

In Formula (IIIa), preferably, T_1 and T_2 each represents, same or different, hydrogen atom, chlorine atom, bromine atom, hydrocarbon groups containing 1 to 10 carbon atoms, more preferably alkyl groups containing 1 to 4 carbon atoms such as methyl, ethyl, propyl and butyl groups, aralkyl groups containing 7 to 9 carbon atoms such as benzyl, phenethyl, 3-phenylpropyl, chlorobenzyl, dichlorobenzyl, bromobenzyl, methylbenzyl, methoxybenzyl and chloromethylbenzyl groups and aryl groups such as phenyl, tolyl, xylyl, bromophenyl, methoxyphenyl, chlorophenyl and dichlorophenyl groups, and $-COR_9$ and $-COOR_9$ wherein R_9 is preferably that described for the foregoing preferable hydrocarbon groups containing 1 to 10 carbon atoms.

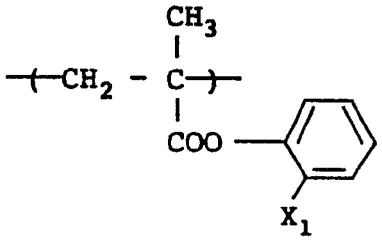
In General Formulae (IIIa) and (IIIb), L_1 and L_2 each represent a direct bond for bonding -COO- and benzene ring or bonding groups containing 1 to 4 bondingatoms such as $\left(CH_2\right)_{n3}$ wherein n_3 is an integer of 1 to 3, $-CH_2OCO-$, $-CH_2CH_2OCO-$, $\left(CH_2\right)_{m2}$ wherein m_2 is an integer of 1 or 2 and $-CH_2CH_2O-$, preferably a direct bond or bonding groups containing 1 or 2 bonding atoms.

Examples of the recurring unit represented by Formula (IIIa) or (IIIb), used in Resin [A] to [A″] of the present invention, will be given below without limiting the same. In the following (b-1) to (b-20), n is an integer of 1 to 4, m is 0 or an integer of 1 to 4, p is an integer of 1 to 3, R_{10} to R_{13} each represent $-C_nH_{2n+l}$ or $\left(CH_2\right)_mC_6H_5$ wherein n and m have the same meaning as described above, and X_1 and X_2 each represent any of -Cl, -Br and -I.

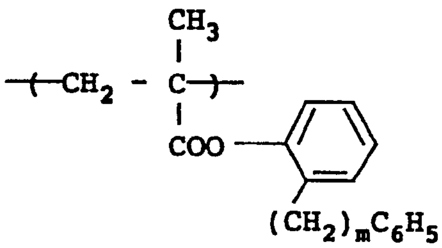
(b-1)



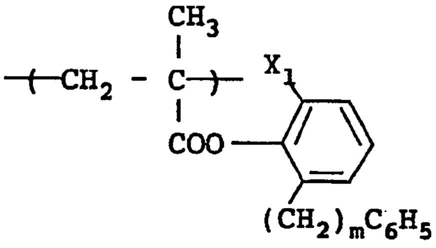
(b-2)



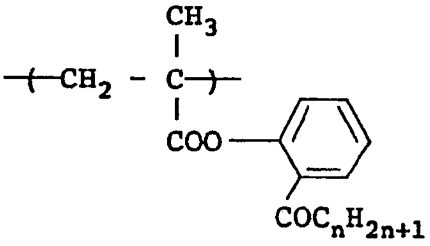
(b-3)



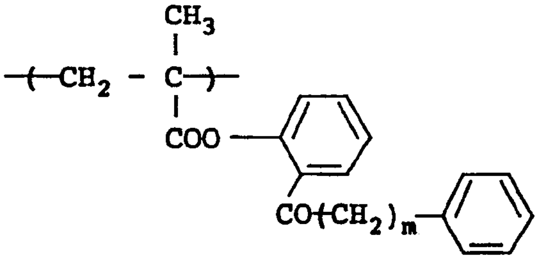
(b-4)


CH3
CH2
C
X1
COO
(CH2)mC6H5

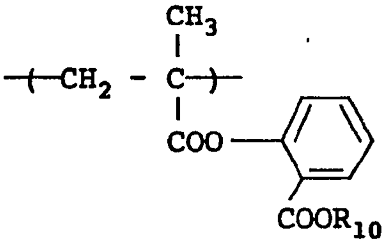
(b-5)


CH3
CH2
C
COO
COCnH2n+1

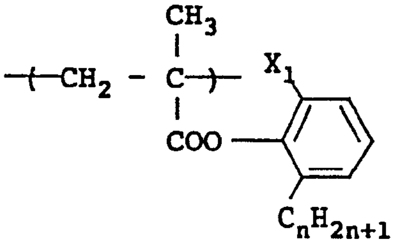
(b-6)


CH3
CH2
C
COO
CO(CH2)m

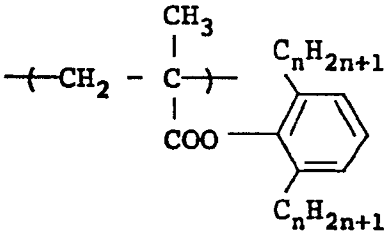
(b-7)


CH3
CH2
C
COO
COOR10

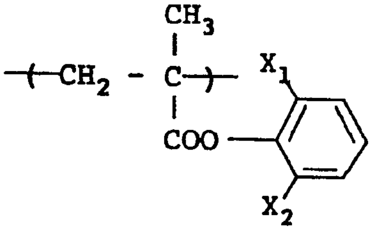
(b-8)


CH3
CH2
C
COO
X1
CnH2n+1

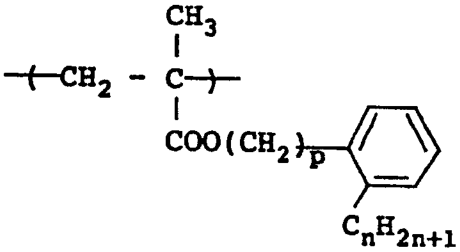
(b-9)


CH3
CH2
C
COO
CnH2n+1
CnH2n+1

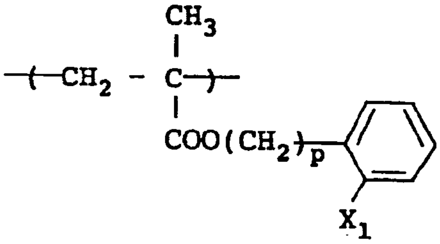
(b-10)


CH3
CH2
C
COO
X1
X2

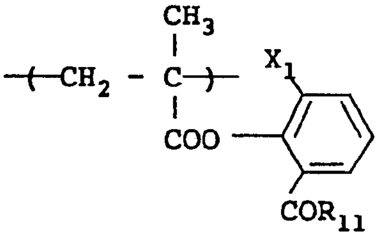
(b-11)


CH3
CH2
C
COO(CH2)p
CnH2n+1

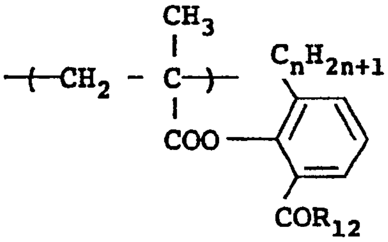
(b-12)



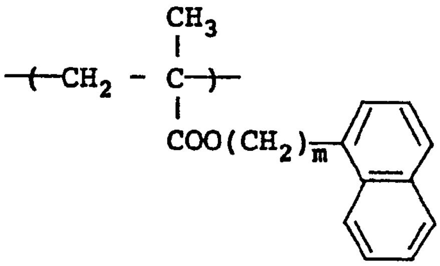
(b-13)



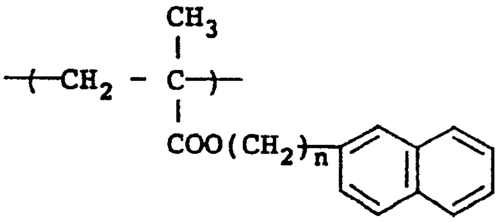
(b-14)



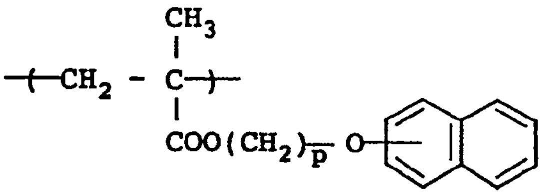
(b-15)



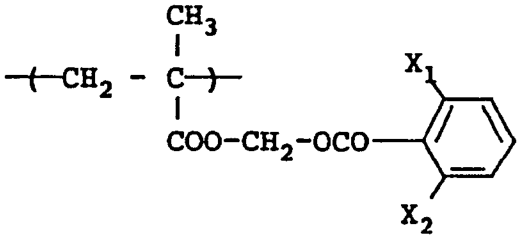
(b-16)



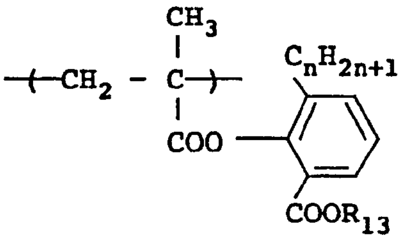
(b-17)



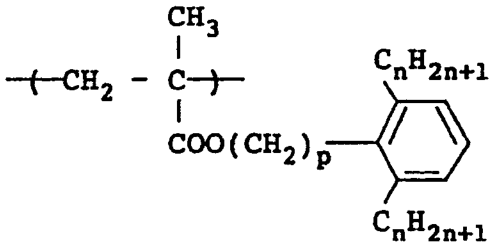
(b-18)



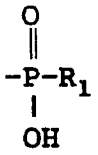
(b-19)



(b-20)



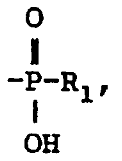
The polar group optionally bonded to one end of the polymer main chain of Resin [A] to [A'] will now be illustrated. The polar group is at least one member selected from the group consisting of $-PO_3H_2$, $-SO_3H$, $-COOH$,



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-R_1$$

and cyclic acid anhydride-containing groups.

In



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-R_1,$$

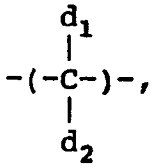
R_1 represents a hydrocarbon group or -OR_2 group wherein R_2 is a hydrocarbon group. Specifically, R_1 represents optionally substituted hydrocarbon groups containing 1 to 22 carbon atoms such as methyl, ethyl, propyl, butyl, hexyl, octyl, decyl, dodecyl, octadecyl, 2-chloroethyl, 2-methoxyethyl, 3-ethoxypropyl, allyl, crotonyl, butenyl, cyclohexyl, benzyl, phenethyl, 3-phenylpropyl, methylbenzyl, chlorobenzyl, fluorobenzyl, methoxybenzyl groups, etc. or optionally substituted aryl groups such as phenyl, tolyl, ethylphenyl, propylphenyl, chlorophenyl, fluorophenyl, bromophenyl, choromethylphenyl, dichlorophenyl, methoxyphenyl, cyanophenyl, acetoamidophenyl, acetylphenyl, butoxyphenyl groups, etc. R_2 has the same meaning as R_1.

The cyclic acid anhydride-containing group means a group containing at least one cyclic acid anhydride, illustrative of which are aliphatic dicarboxylic acid anhydrides and aromatic dicarboxylic acid anhydrides.

Examples of the aliphatic dicarboxylic acid anhydride include rings of succinic anhydride, glutaconic anhydride, maleic anhydride, cyclopentane-1,2-dicarboxylic anhydride, cyclohexane-1,2-dicarboxylic anhydride, cyclohexene-1,2-dicarboxylic anhydride and 2,3-bicyclo[2,2,2]octadicarboxylic anhydride. These rings can be substituted, for example, by halogen atoms such as chlorine and bromine atoms and/or alkyl groups such as methyl, ethyl, butyl and hexyl groups.

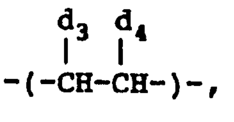
Examples of the aromatic dicarboxylic acid anhydride include rings of phthalic anhydride, naphthalene dicarboxylic anhydride, pyridine dicarboxylic anhydride and thiophene dicarboxylic anhydride. These rings can be substituted by, for example, halogen atoms such as chlorine and bromine atoms, alkyl groups such as methyl, ethyl, propyl and butyl groups, hydroxyl group, cyano group, nitro group, alkoxycarbonyl groups wherein alkoxy groups are methoxy and ethoxy groups, and the like.

These polar groups can be bonded directly or through a bonding group. As the bonding group, any bonding group can be used, for example, selected from the group consisting of:



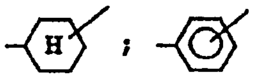
$$-(-\overset{\overset{\displaystyle d_1}{|}}{\underset{\underset{\displaystyle d_2}{|}}{C}}-)-,$$

wherein d_1 and d_2 each represent, same or different, hydrogen atoms, halogen atoms such as chlorine and bromine atoms, OH groups, cyano groups, alkyl groups such as methyl, ethyl, 2-chloroethyl, 2-hydroxyethyl, propyl, butyl, hexyl groups, etc., aralkyl groups such as benzyl, phenethyl groups, etc., phenyl group and the like;



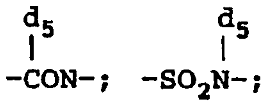
$$-(-\overset{\overset{\displaystyle d_3}{|}}{CH}-\overset{\overset{\displaystyle d_4}{|}}{CH}-)-,$$

wherein d_3 and d_4 have the same meanings as $d_1$and d_2;



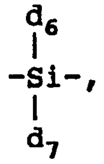
$$; \quad -O-; \quad -S-; \quad -\overset{\overset{\displaystyle d_5}{|}}{N}-,$$

wherein d_5 represents a hydrogen atom or hydrocarbon group, illustrative of which are hydrocarbon groups containing 1 to 12 carbon atoms, such a methyl, ethyl, propyl, butyl hexyl, octyl, decyl, dodecyl, 2-methoxyethyl, 2-chloroethyl, 2-cyanoethyl, benzyl, methylbenzyl, phenethyl, tolyl, chlorophenyl, methoxyphenyl, butylphenyl, etc.; -CO-; -COO-; -OCO-;



$$-\overset{d_5}{\underset{|}{CON}}-;\quad -SO_2\overset{d_5}{\underset{|}{N}}-;$$

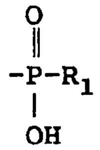
$-SO_2-$; -NHCONH-; -NHCOO-; $-NHSO_2-$; -CONHCOO-; -CONHCONH-; heterocyclic rings illustrative of which are 5 to 6 membered rings containing at least one of O, S and N as a hetero atom or condensed rings thereof, such as thiophene ring, pyridine ring, furan ring, imidazole ring, piperidine ring, morpholine ring and the like; and



$$-\overset{d_6}{\underset{d_7}{Si}}-,$$

wherein d_6 and d_7 each represent, same or different, hydrocarbon groups or $-Od_8$ wherein d_8 represent a hydrocarbon group, these hydrocarbon groups including the same materials as d_5. These bonding groups can be used individually or in combination.

Preferably, the binder resins [A] to [A″] can contain, in addition to the copolymeric component represented by the foregoing General Formulae (III) and (IV) including ones represented by General Formulae (IIIa) and (IIIb), 0,5 to 10% by weight of a copolymeric component, as a polymeric component to be copolymerized therewith, containing at least one polar group selected from the group consisting of $-PO_3H_2$, $-SO_3H$, -COOH,



$$-\overset{O}{\underset{OH}{\overset{\|}{P}}}-R_1$$

and cyclic acid anhydride-containing groups, whereby the electrostatic properties are improved.

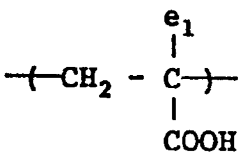
These specified polar groups have the same contents as the polar groups bonded to one end of the polymer main chain.

In Resin [A′], the presence ratio of the polar groups contained as the copolymeric component and those bonded to one end of the polymer main chain depends on the kinds and amounts of other binder resins, spectral sensitizing dyes, chemical sensitizers and other additives and it is preferable to control the ratio in suitable manner. Furthermore, it is important that the total amounts of both the polar groups are in the range of 0.5 to 15% by weight.

The copolymeric component containing the polar groups according to the present invention can be vinyl compounds containing the polar group copolymerizable with a monomer corresponding to the recurring unit represented by General Formula (III) including General Formulae (IIIa) and (IIIb), for example, described in, for example, Kobunshi Gakkai "Polymer Data Handbook - Kisohen-", published by Baihukan, 1986, for example, acrylic acid, α and/or β-substituted acrylic acid such as α-acetoxy, α-acetoxymethyl, α-(2-amino)ethyl, α-chloro, α-bromo, α-fluoro, α-tributylsilyl, α-cyano, β-chloro, β-bromo, α-chloro-β-methoxy and α,β-dichloro substituted ones, methacrylic acid, itaconic acid, itaconic acid semi-esters, itaconic acid semi-amides, crotonic acid, 2-alkenylcarboxylic acids such as 2-pentenoic acid, 2-methyl-2-hexenoic acid, 2-octenoic acid, 4-methyl-2-hexenoic acid and 4-ethyl-2-octenoic acid, maleic acid, maleic acid semi-esters, maleic acid semi-amides, vinylbenzenecarboxylic acid, vinylbenzenesulfonic acid, vinylsulfonic acid, vinylphosphonic acid, semi-ester derivatives of vinyl groups or allyl groups of dicarboxylic acids and ester derivatives and amide derivatives of these carboxylic acids or sulfonic acids containing crosslinking functional groups in the substituents.

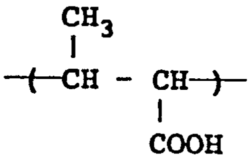
Examples of the copolymeric component containing the polar group are shown in the following, in which e_1 is H or CH_3, e_2 is H, CH_3 or CH_2COOCH_3, R_{14} is an alkyl group of 1 to 4 carbon atoms, R_{15} is an alkyl group of l to 6 carbon atoms, benzyl group or phenyl group, c is an integer of 1 to 3, d is an integer of 2 to 11, e is an integer of 1 to 11, f is an integer of 2 to 4 and g is an integer of 2 to 10.

(C-1)



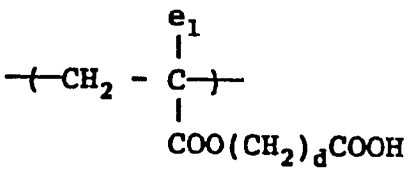
$$-\!\left(CH_2-\overset{e_1}{\underset{COOH}{C}}\right)\!-$$

(C-2)



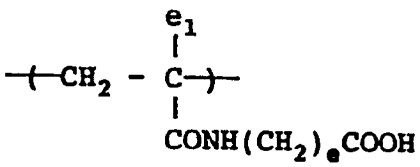
$$-\!\left(\overset{CH_3}{CH}-\underset{COOH}{CH}\right)\!-$$

(C-3)



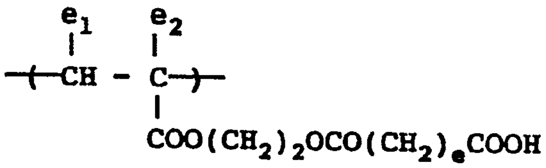
$$-\!\left(CH_2-\overset{e_1}{\underset{COO(CH_2)_dCOOH}{C}}\right)\!-$$

(C-4)



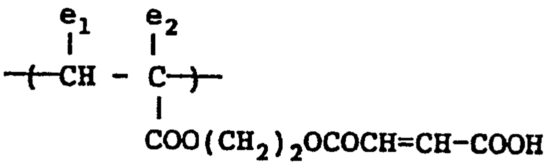
$$-\!\left(CH_2-\overset{e_1}{\underset{CONH(CH_2)_eCOOH}{C}}\right)\!-$$

(C-5)



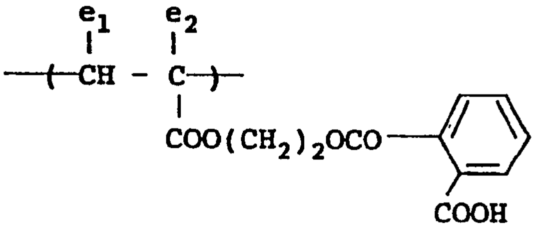
$$-\!\left(\overset{e_1}{CH}-\overset{e_2}{\underset{COO(CH_2)_2OCO(CH_2)_eCOOH}{C}}\right)\!-$$

(C-6)

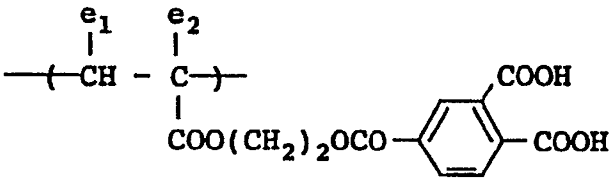


$$-\!\!\left(\overset{e_1}{\underset{}{CH}}-\overset{e_2}{\underset{COO(CH_2)_2OCOCH=CH-COOH}{C}}\right)\!\!-$$

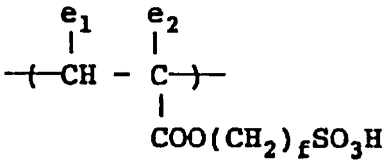
(C-7)



(C-8)

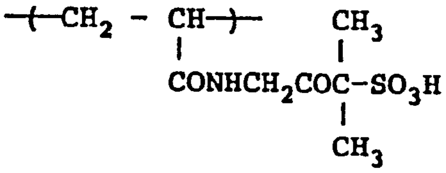


(C-9)

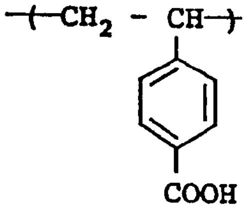


$$-\!\!\left(\overset{e_1}{\underset{}{CH}}-\overset{e_2}{\underset{COO(CH_2)_fSO_3H}{C}}\right)\!\!-$$

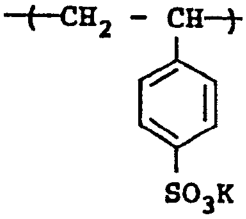
(C-10)



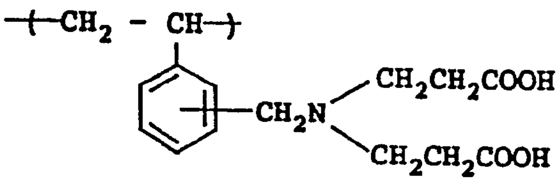
(C-11)



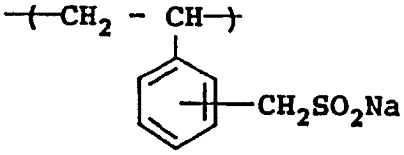
(C-12)



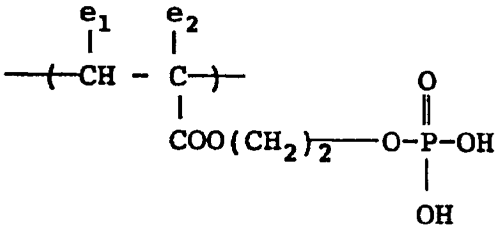
(C-13)



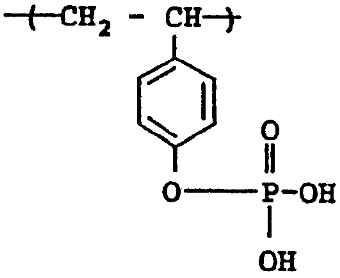
(C-14)



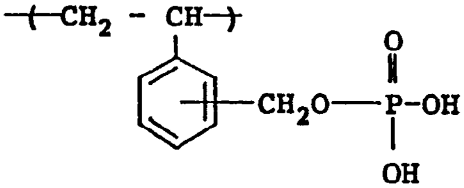
(C-15)



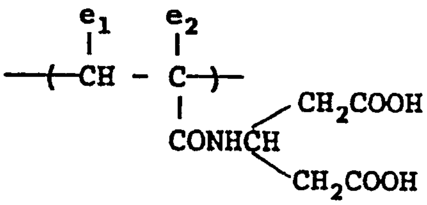
(C-16)



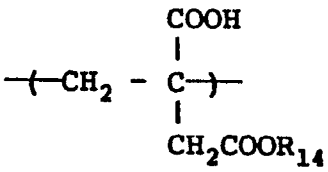
(C-17)



(C-18)

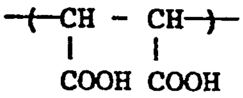


(C-19)



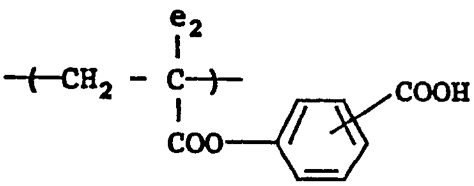
$$-\!\left(\mathrm{CH_2} - \underset{\mathrm{CH_2COOR_{14}}}{\overset{\mathrm{COOH}}{\mathrm{C}}}\right)\!-$$

(C-20)

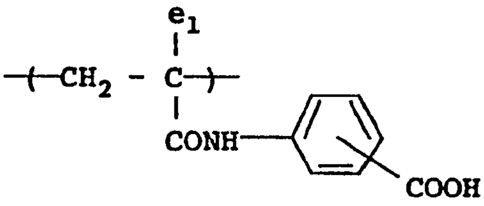


$$-\!\left(\underset{\mathrm{COOH}}{\mathrm{CH}} - \underset{\mathrm{COOH}}{\mathrm{CH}}\right)\!-$$

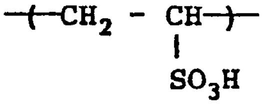
(C-21)



(C-22)

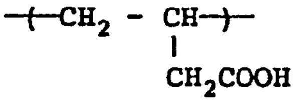


(C-23)



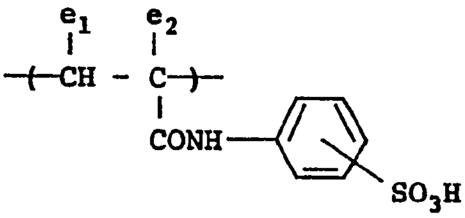
$$-\!\!\left(\!-CH_2 - \underset{\substack{|\\ SO_3H}}{CH}-\right)\!\!-$$

(C-24)

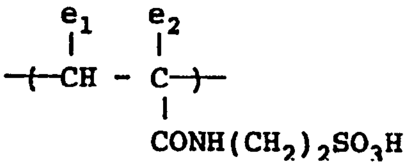


$$-\!\!\left(\!-CH_2 - \underset{\substack{|\\ CH_2COOH}}{CH}-\right)\!\!-$$

(C-25)

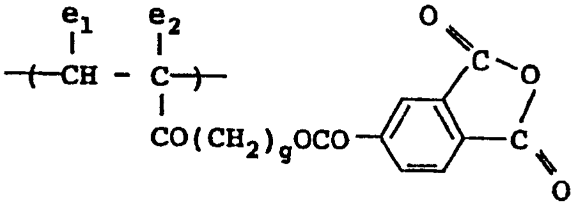


(C-26)

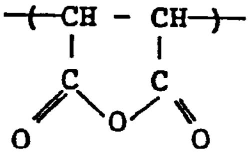


$$-\!\!\left(\!-\overset{\substack{e_1\\ |}}{CH} - \underset{\substack{|\\ CONH(CH_2)_2SO_3H}}{\overset{\substack{e_2\\ |}}{C}}-\right)\!\!-$$

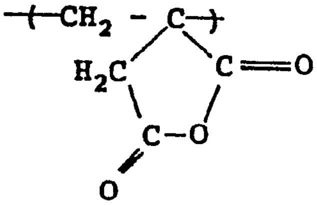
(C-27)



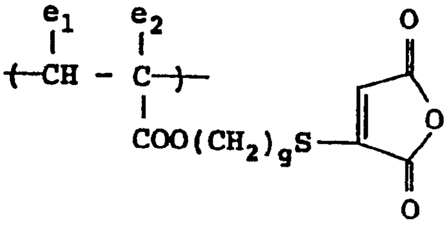
(C-28)



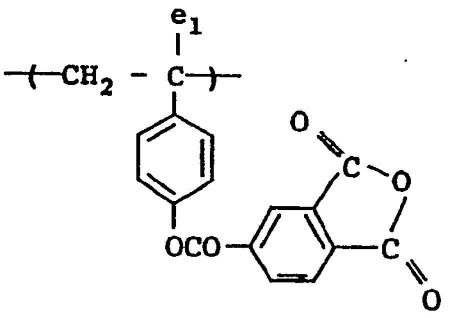
(C-29)



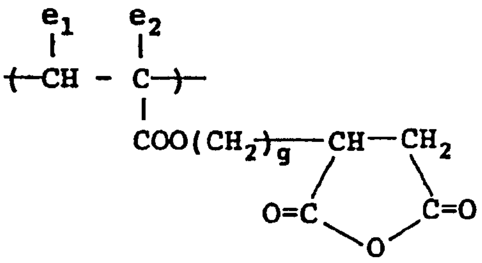
(C-30)



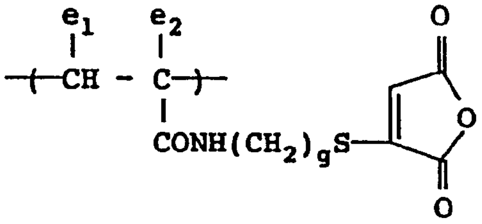
(C-31)



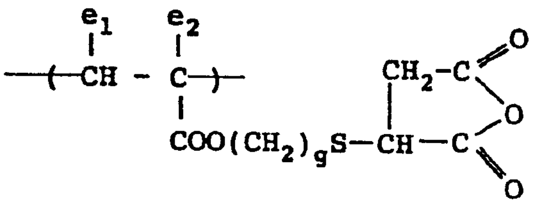
(C-32)



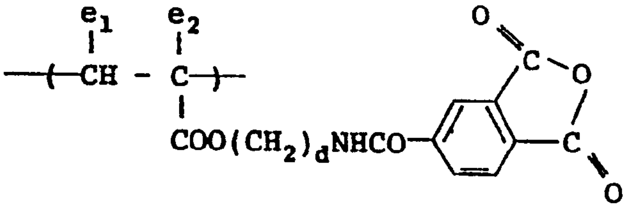
(C-33)



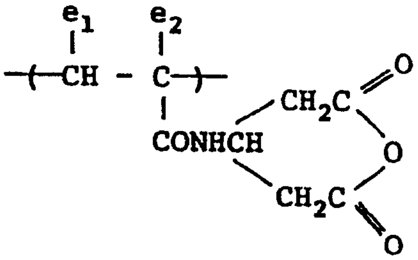
(C-34)



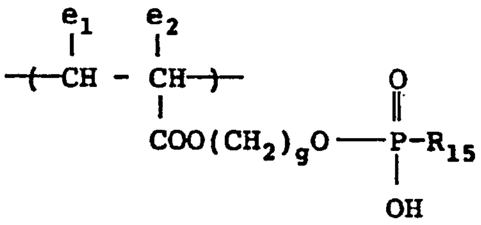
(C-35)



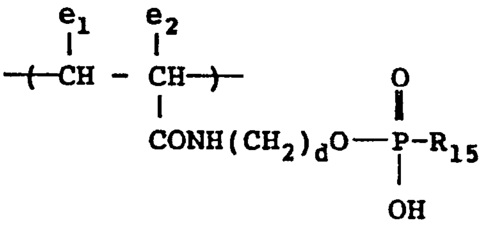
(C-36)



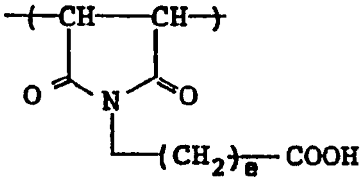
(C-37)



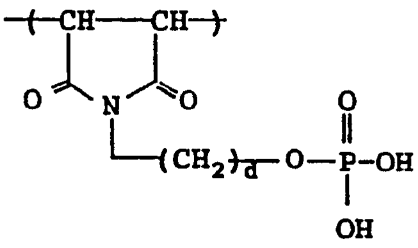
(C-38)



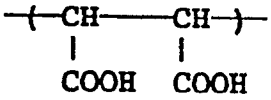
(C-39)



(C-40)

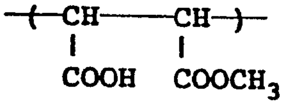


(C-41)



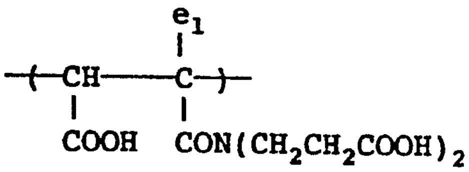
$$-\!\!\left(\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}\right)\!\!-$$

(C-42)



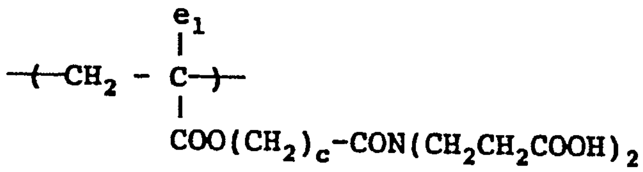
$$-\!\!\left(\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{COOCH_3}}{\underset{|}{\mathrm{CH}}}\right)\!\!-$$

(C-43)



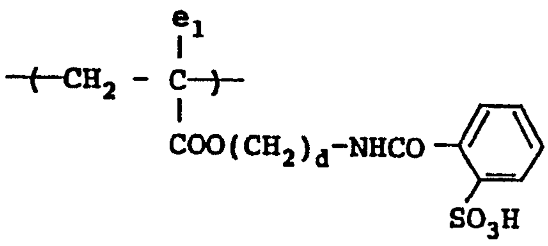
$$-\!\!\left(\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}-\overset{e_1}{\overset{|}{\underset{\mathrm{CON(CH_2CH_2COOH)_2}}{\underset{|}{\mathrm{C}}}}}\right)\!\!-$$

(C-44)

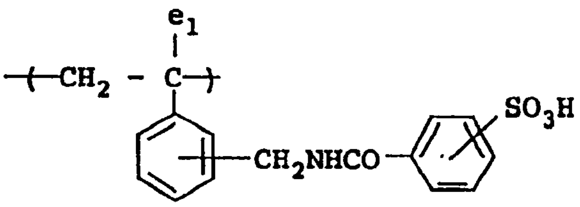


$$-\!\!\left(\mathrm{CH_2}-\overset{e_1}{\overset{|}{\underset{\mathrm{COO(CH_2)_c-CON(CH_2CH_2COOH)_2}}{\underset{|}{\mathrm{C}}}}}\right)\!\!-$$

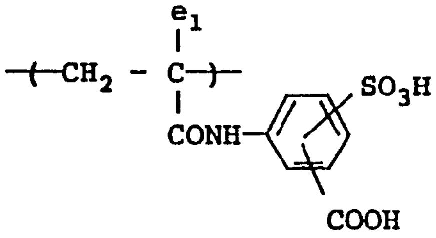
(C-45)



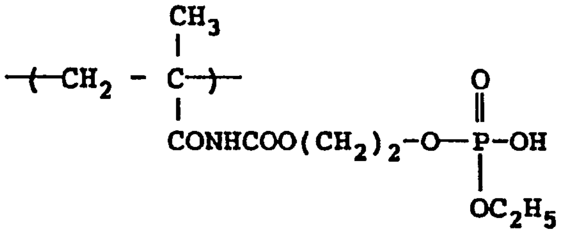
(C-46)



(C-47)

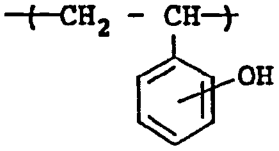


(C-48)

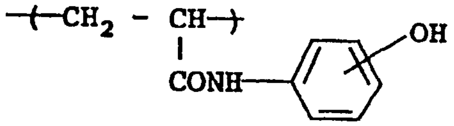


$$-\!\!\left(\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{CONHCOO(CH_2)_2{-}O{-}\underset{\substack{|\\ \mathrm{OC_2H_5}}}{\overset{\substack{\mathrm{O}\\ \|}}{P}}{-}OH}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{C}}}\right)\!\!-$$

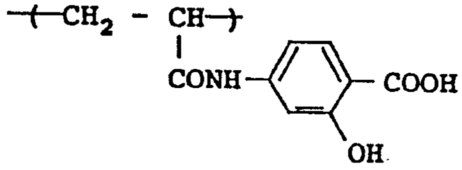
(C-49)



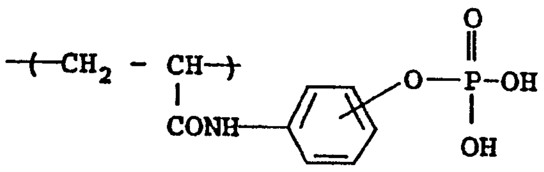
(C-50)



(C-51)



(C-52)



Resin [A] to Resin [A'] of the present invention can contain, in addition to the monomers of General Formulae (III), (IIIa) and/or (IIIb) and the monomers containing the polar groups, other monomers as copolymeric components.

As the other copolymeric components, for example, there are given methacrylic acid esters containing other substituents than those represented by General Formula (III), acrylic acid esters, crotonic acid esters, α-olefins, vinyl or allyl esters of carboxylic acids such as acetic acid, propionic acid, butyric acid, valeic acid, benzoic acid, naphthalene carboxylic acid and the like, acrylonitrile, methacrylonitrile, vinyl esters, itaconic acid esters such as dimethyl ester, diethyl ester and the like, acrylamide, methacrylamide, styrenes such as styrene, vinyltoluene, chlorostyrene, hydroxystyrene, N,N-dimethylaminomethylstyrene, methoxycarbonylstyrene, methanesulfonyloxystyrene, vinylnaphthalene and the like, vinylsulfone- containing compounds, vinyl ketone-containing compounds, heterocyclic vinyl compounds such as vinylpyrrolidone, vinylpyridine, vinylimidazole, vinylthiophene, vinylimidazoline, vinylpyrazole, vinyldioxane, vinylquinoline, vinyltetrazole, vinyloxazine and the like.

Preferably, these other monomers are respectively in a proportion of less than 30% by weight in Resin [A], [A'] or [A"].

In Resins [A'] and [A"], bonding the polar group to one end of the polymer main chain is generally carried out by a method comprising reacting the end of a living polymer obtained by the prior art anionic polymerization or cationic polymerization with various reagents (method by ionic polymerization), method comprising radical polymerization using a chain transfer agent and/or polymerization initiator containing a specific acid group in the molecule, method comprising subjecting a polymer containing a reactive group such as amino group, halogen atoms, epoxy group, acid halides group or the like at the end thereof, obtained by the ionic polymerization or radical polymerization as described above, to polymer reaction convert it into the specified polar group according to the present invention, for example, as described in introductions and literatures cited therein of P. Dreyfuss and R.P. Quirk, "Encycl. Polym. Sci. Eng." 7, 551 (1987); Yoshiki Nakajo and Yuya Yamashita, "Senryo to Yakuhin (Dyes and Chemicals)" 30, 232 (1985), Akira Ueda and Susumu Nagai "Kagaku to Kogyo (Science and Industry)" 60, 57 (1986), etc.

As the chain transfer agent, for example, there can be used mercapto compounds having the above-described polar group or reactive group capable of being converted into the polar group, such as thioglycolic acid, thiomalic acid, thiosalicylic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 3-mercaptobutyric acid, N-(2-mercaptopropionyl)glycine, 2-mercaptonicotinic acid, 3-[N-(2-mercaptoethyl)carbamoyl]propionic acid, 3-[N-(2-mercaptoethyl)amino]propionic acid, N-(3-mercaptopropionyl)alanine, 2-mercaptoethanesulfonic acid, 3-mercaptopropanesulfonic acid, 4-mercaptobutanesulfonic acid, 2-mercaptoethanol, 3-mercapto-1,2-propane diol, 1-mercapto-2-propanol, 3-mercapto-2-butanol, mercaptophenol, 2-mercaptoethylamine, 2-mercaptoimidazole, 2-mercapto-3-pyridinol, 4-(2-mercaptoethyloxycarbonyl)phthalic anhydride, 2-mercaptoethylphosphono acid anhydride, 2-mercaptoethylphosphono acid anhydride monomethyl ester and the like, and iodoalkyl compounds having the above described polar group or substituent, such as iodoacetic acid, iodopropionic acid, 2-iodoethanol, 2-iodoethanesulfonic acid, 3-iodopropanesulfonic acid and the like.

As the polymerization initiator containing the polar group or the specified reactive group capable of being converted into the polar group, for example, 4,4′- azobis(4-cyanovaleic acid), 4,4′-azobis(4-cyanovaleic acid chloride), 2,2′-azobis(2-cyanopropanol), 2,2′azobis(2-cyanopentanol), 2,2′-azobis[2-methyl-N-(2-hydroxyethyl)-propionamide], 2,2′-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}, 2,2′-azobis{2-[1-(2-hydroxyethyl)-2-imidazoline-2-il]propane}, 2,2′-azobis[2-(2-imidazoline-2-il)propane] and 2,2′-azobis[2-(4,5,6,7-tetrahydro-1H-1,3-diazepine-2-il)propane].

These chain transfer agents or polymerization initiators are generally used in a proportion of 0.5 to 15 parts by weight, preferably 2 to 10 parts by weight to 100 parts by weight of all the monomers.

The low molecular weight resins [A] to [A″] as described above are preferably used jointly with the prior art resins for photoconductive zinc, in particular, in a proportion of 5 to 50 of the former to 95 to 50 of the latter by weight.

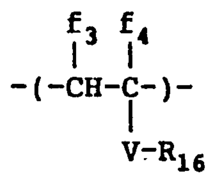
As the other resin, there can be used medium to high molecular weight resins with a molecular weight of $3x10^4$ to $1x10^6$, preferably $5x10^4$ to $5x10^5$ and a glass transition point of -10°C to 120°C, preferably 0°C to 90°C.

Examples of the other resin are described in Takaharu Kurata and Jiro Ishiwataru "High Molecular Materials (Kobunshi)" 17, 278 (1968), Harumi Miyamoto and Hidehiko Takei "Imaging" No. 8, page 9 (1973), Koichi Nakamura "Practical Technique of Binders for Recording Materials (Kiroku Zairyoyo Binder no Jissai Gijutsu)" Section 10, published by C.M.C. Shuppan (1985), D.D. Tatt, S.C. Heidecker "Tappi" 49, No. 10, 439 (1966), E.S. Baltazzi, R.G. Blanckette et al. "Photo Sci. Eng" 16, No. 5, 354 (1972), Nguyen Chank Keh, Isamu Shimizu and Eiichi Inoue "Journal of Electrophotographic Association (Denshi Shashin Gakkaishi)" 18, No. 2, 28 (1980), Japanese Patent Publication No. 31011/1975, Japanese Patent Laid-Open Publication Nos. 54027/1978, 20735/1979, 202544/1982 and 68046/1983.

Specifically, there are given olefin polymers and copolymers, vinyl chloride copolymers, vinylidene chloride copolymers, vinyl alkanate polymers and copolymers, allyl alkanate polymers and copolymers, styrene and its derivative polymers and copolymers, butadienestyrene copolymers, isoprene-styrene copolymers, butadiene-unsaturated carboxylic acid ester copolymers, acrylonitrile copolymers, metharylonitrile copolymers, alkyl vinyl ether copolymers, acrylic acid ester polymers and copolymers, methacrylic acid ester polymers and copolymers, styrene-acrylic acid, styrene-methacrylic acid ester copolymers, itaconic acid diester polymers and copolymers, maleic anhydride copolymers, acrylamide copolymers, methacrylamide copolymers, hydroxyl group-modified silicone resins, polycarbonate resins, ketone resins, amide resins, hydroxyl group and carboxyl group-modified polyester resins, butyral resins, polyvinyl acetal resins, cyclic rubber-methacrylic acid ester copolymers, cyclic rubber-acrylic acid ester copolymers, nitrogen atom-free heterocyclic ring containing copolymers (examples of heterocyclic ring: furan, tetrahydrofuran, thiophene, dioxane, dioxofuran, lactone, benzofuran, benzothiophene, 1,3-dioxetane rings, etc.) and epoxy resins.

Furthermore, as the medium to high molecular weight resins to be jointly used, there are preferably used polymers containing at least 30% by weight of a polymeric component of a recurring unit represented by the following General Formula (V) and satisfying the foregoing properties:

General Formula (V)



$$-(-\overset{f_3}{\overset{|}{CH}}-\underset{\underset{V-R_{16}}{|}}{\overset{f_4}{\overset{|}{C}}}-)-$$

wherein V represents -COO-, -OCO-, $-(-CH_2-)_h-OCO-$, -(-CH2-)h-COO-, -O- or $-SO_2-$, h represents an integer of 1 to 4, f_3 and f_4 have the same meaning as a_1 and a_2 in General Formula (IV) and R_{16} has the same meaning as R_3 in General Formula (IV).

Examples of the medium to high molecular weight binder resin containing the polymeric component represented by General Formula (V), which will hereinafter be referred to as Resin [B], are random copolymer resins containing the polymeric component represented by General Formula (V), as described in Japanese Patent Laid-Open Publication Nos. 49817/1988, 220149/1988 and 220148/1988, jointly used resins of the random copolymers with crosslinking resins, as described in Japanese Patent Laid-Open Publication Nos. 211766/1989 and 102573/1989, copolymers containing the polymeric component represented by General Formula (V) and previously partially crosslinked as described in Japanese Patent Laid-Open Publication Nos. 34860/1990 and 40660/1990, block copolymers of graft type obtained by polymerization of monofunctional macromonomer comprising the specified recurring unit and a monomer corresponding to the constituent represented by General Formula (V), as described in Japanese Patent Application Nos. 203933/1988, 207317/1988, 163796/1989, 212994/1989, 229379/1989 and 189245/1989.

In the present invention, Resins [A], [A′] and [A″] are copolymers containing at least methacrylate copolymeric components having the specified substituents and copolymeric components containing the polar groups which adsorb on the stoichiometric defects of the photoconductive zinc oxide, so that the covering property of the surface of the photoconductive zinc oxide is improved, because of the low molecular weight materials, to compensate trapping of the photoconductive zinc oxide and the humidity property is remarkably improved, while simultaneously dispersion of the photoconductive zinc oxide is sufficiently carried out to suppress aggregation thereof. Furthermore, the resin grains capable of exhibiting hydrophilic property by processing with a processing solution containing a compound having nucleophilic reactivity are uniformly dispersed without unfavorably affecting the photoconductive zinc oxide.

It is found that when jointly using resin [B] of medium to high molecular weight, the mechanical strength of a photoconductive layer can be more improved than when using only Resin [A], [A′] or [A″] without deteriorating the electrophotographic property obtained by the use of Resin [A], [A′] or [A″]. That is, the interaction of adsorption and covering can suitably be carried out in an inorganic photoconductor and a binder resin and the film strength of the eletroconductive coating layer can be maintained.

This is probably due to the following actions of the binder resin according to the present invention. In the present invention, Resin [A], [A′] or [A″] and Resin [B] are jointly used as the binder resin and the weight average molecular weight Mw of each of these resins and the contents of the polar groups in the resins are specified to thus change the intensity of the interaction between the inorganic photoconductor and resins. Thus, Resin [A], [A′] or [A″] having a stronger interaction adsorbs on a photoconductor selectively and suitably, while Resin [B] having a weaker interaction than Resin [A], [A′] or [A″] interacts moderately with an inorganic photoconductor to such an extent that the polar group bonded to the specified position to the polymer chain in the resin does not deteriorate the electrophotographic property and Resins [B] each having long molecular length and graft chain length interact with each other, whereby both the electrophotographic property and mechanical film strength are markedly improved.

As the photoconductive zinc oxide of the present invention, there can be used ordinary ones well known in the art, i.e. not only the so-called zinc oxide, but also zinc oxide subjected to processing with an acid.

In the lithographic printing plate precursor of the present invention, the quantity of the binder resin used for photoconductive zinc oxide is generally in a proportion of 10 to 100 parts by weight of the binder resin, preferably 15 to 50 parts by weight to 100 parts by weight of the photoconductive zinc oxide.

In the present invention, if necessary, various coloring matters or dyes can be used as a spectro sensitizer, depending on the variety of light sources such as exposure to visible rays and semiconductor laser beam, illustrative of which are carbonium dyes, diphenylmethane dyes, triphenylmethane dyes, xanthene dyes, phthalein dyes, polymethine dyes such as oxonol dyes, merocyanine dyes, cyanine dyes, rhodacyanine dyes, styryl dyes, etc. and phthalocyanine dyes which can contain metals, as described in Harumi Miyamoto and Hidehiko Takei "Imaging" No. 8, page 12 (1973), C.Y. Young et al. "RCA Review" 15, 469 (1954), Kohei Kiyota et al. "Denki Tsushin Gakkai Ronbunshi" J63-C (No. 2), 97 (1980), Yuji Harasaki et al. "Kogyo Kagaku Zasshi" 66, 78 and 188 (1963) and Tadaaki Tani "Nippon Shashin Gakkaishi" 35, 208 (1972).

For example, those using carbonium dyes, triphenylmetahe dyes, xanthene dyes or phthalein dyes are described in Japanese Patent Publication No. 452/1976, Japanese Patent Laid-Open Publication Nos. 90334/1975, 114227/1975, 39130/1978, 82353/1978 and 16456/1982 and U.S. Patent Nos. 3,052,540 and 4,054,450.

As the polymethine dyes such as oxonol dyes, merocyanine dyes, cyanine dyes and rhodacyanine dyes, there can be used dyes described in F.M. Harmmer "The Cyanine Dyes and Related Compounds" and specifically dyes described in U.S. Patent Nos. 3,047,384, 3,110,591, 3,121,008, 3,125,447, 3,128,179, 3,132,942 and 3,622,317; British Patent Nos. 1,226,892, 1,309,274 and 1,405,898; and Japanese Patent Publication Nos.

7814/1973 and 18892/1980.

The polymethine dyes capable of spectrally sensitizing near infrared radiations to infrared radiations with longer wavelengths of at least 700 nm are described in Japanese Patent Publication No. 41061/1976; Japanese Patent Laid-Open Publication Nos. 840/1972, 44180/1972, 5034/1974, 45122/1974, 46245/1982, 35141/1981, 157254/1982, 26044/1986 and 27551/l986; U.S. Patent Nos. 3,619,154 and 4,175,956; and "Research Disclosure" 2416, pages 117-118 (1982).

The photoreceptor of the present invention is excellent in that its performance is hardly fluctuated even if it is used jointly with various sensitizing dyes. Furthermore, various additives for electrophotographic light-sensitive layers, such as chemical sensitizers, well known in the art can jointly be used as occasion demands, for example, electron accepting compounds such as benzoquinone, chloranil, acid anhydrides, organic carboxylic acids and the like, described in the foregoing "Imaging" No. 8, page 12 (1973) and polyarylalkane compounds, hindered phenol compounds, p-phenylenediamine compounds and the like, described in Hiroshi Komon et al. "Latest Development and Practical Use of Photoconductive Materials and Light-Sensitive Materials (Saikin no Kododenzairyo to Kankotai no Kaihatsu to Jitsuyoka)" Sections 4 to 6, published by Nippon Kagaku Joho Shuppanbu (1986).

The amounts of these additives are not particularly limited, but are generally 0.0001 to 2.0 parts by weight based on 100 parts by weight of the photoconductive zinc oxide.

The thickness of the photoconductive layer is generally 1 to 100 µm, preferably 10 to 50 µm.

When in a photoreceptor of laminate type consisting of a charge generating layer and charge transporting layer, a photoconductive layer is used as the charge producing layer, the thickness of the charge producing layer is generally 0.01 to 1 µm, preferably 0.05 to 0.5 µm.

As the charge transporting material of the laminate type photoreceptor, there are preferably used polyvinylcarbazole, oxazole, dyes, pyrazoline dyes, triphenylmethane dyes and the like. The charge transporting layer has generally a thickness of 5 to 40 µm, preferably 10 to 30 µm.

Typical examples of the resin used for forming the charge transporting layer are thermoplastic resins and thermosetting resins such as polystyrene resins, polyester resins, cellulose resins, polyether resins, vinyl chloride resins, vinyl acetate resins, vinyl chloride-vinyl acetate copolymer resins, polyacrylic resins, polyolefin resins, urethane resins, epoxy resins, melamine resins and silicone resins.

The photoconductive layer of the present invention can be provided on a support as well known in the art. Generally, a support for an electrophotographic light-sensitive layer is preferably electroconductive and as the electroconductive support, there can be used, as known in the art, substrates such as metals, papers, plastic sheets, etc. which are made electroconductive by impregnating low resistance materials therein, substrates whose back surface, opposite to the surface to be provided with a light-sensitive layer, is made electroconductive, which is further coated with at least one layer for the purpose of preventing it from curling; the above described support provided with, on the surface thereof, a water proof adhesive layer; the above described support optionally provided with, on the surface layer, one or more pre-coat layer; and papers laminated with plastics which are made electroconductive, for example, by vapor deposition of Al or the like thereon, Examples of the substrates or materials which are electroconductive or made electroconductive are described in Yukio Sakamoto "Electrophotography (Denshi Shashin)" 14 (No. 1), pages 2 to 11 (1975), Hiroyuki Moriga "Introduction to Chemistry of Special Papers (Nyumon Tokushushi no Kagaku)" Kobunshi Kankokai (1975), M.F. Hoover "J. Macromol. Sci. Chem." A-4 (6), pp. 1327-1417 (1970), etc.

Production of a print using the electrophotographic lithographic printing plate precursor of the present invention can be carried out in known manner by forming a copied image and subjecting the non-image area to an oil-desensitizing treatment.

The oil-desensitization of the resin of the present invention, containing the functional groups represented by General Formula (I), can be accomplished by processing with a solution containing a compound having hydrophilic groups capable of readily undergoing nucleophilic reaction with the double bonds in water or a water-soluble organic solvent.

The hydrophilic compound causing a nucleophilic substitution reaction with the double bond of the functional group represented by General Formula (I) includes a hydrophilic compound containing a substituent having a nucleophilic constant n of at least 5.5 (Cf. R.G. Pearson, H. Sobel and J. Songstad "J. Amer. Chem. Soc." 90, 319 (1968)) and being dissolved in distilled water in a proportion of at least 1 part by weight to 100 parts by weight of distilled water, illustrative of which are hydrazines, hydroxylamine, sulfites such as ammonium, sodium, potassium and zinc sulfites, thiosulfates, mercapto compounds each containing at least one polar group selected from the group consisting of hydroxyl, carboxyl, sulfo, phosphono and amino groups in the molecules, hydrazide compounds, sulfinic acid compounds, primary amine compounds and secondary amine compounds.

Examples of the mercapto compound are 2-mercaptoethanol, 2-mercaptoethylamine, N-methyl-2-mercaptoethylamine, N-(2-hydroxyethyl)-2-mercaptoethylamine, thioglycolic acid, thiomalic acid, thiosalicylic acid, mercaptobenzenedicarboxylic acid, 2-mercaptoethanesulfonic acid, 2-mercaptoethylphosphonic acid, mercaptobenzenesulfonic acid, 2-mercaptopropionylaminoacetic acid, 2-mercapto-1-aminoacetic acid, 1-mercaptopropionylaminoacetic acid, 1,2-dimercaptopropionylaminoacetic acid, 2,3-dihydroxypropylmercaptan, 2-methyl-2-mercapto-1-aminoacetic acid and the like.

Examples of the sulfinic acid are 2-hydroxy-ethylsulfinic acid, 3-hydroxypropanesulfinic acid, 4-hydroxybutanesulfinic acid, carboxybenzenesulfinic acid, dicarboxybenzenesulfinic acid and the like.

Examples of the hydrazide compound are 2-hydrazinoethanesulfonic acid, 4-hydrazinobutanesulfonic acid, hydrazinobenzenesulfonic acid, hydrazinobenzenedisulfonic acid, hydrazinobenzoic acid, hydrazinobenzenedicarboxylic acid and the like.

Examples of the primary or secondary amine compound are N-(2-hydroxyethyl)amine, N,N-di(2-hydroxyethyl)amine, N,N-di(2-hydroxyethyl)ethylenediamine, tri-(2-hydroxyethyl)ethylenediamine, N-(2,3-dihydroxypropyl)amine, N,N-di(2,3-dihydroxypropyl)amine, 2-aminopropionic acid, aminobenzoic acid, aminopyridine, aminobenzenedicarboxylic acid, 2-hydroxyethylmorpholine, 2-carboxyethylmorpholine, 3-carboxypiperidine and the like.

The nucleophilic compounds are used in such a manner that each of them is contained in the foregoing oil-desensitization processing solution of the photoconductor or in the foregoing processing solution of the binder resin.

The quantity of the nucleophilic compound in such a processing solution is generally 0.1 to 10 mol/ℓ, preferably 0.5 to 5 mol/ℓ. The processing solution has preferably a pH of at least 4. The processing conditions are a temperature of 15 to 60°C and a period of time of 10 seconds to 5 minutes.

In addition to the above described nucleophilic compound and pH regulating agent, the processing solution may contain other compounds, for example, water-soluble organic solvents, individually or in combination, in a proportion of 1 to 50 parts by weight to 100 parts by weight of water, examples of which are alcohols such as methanol, ethanol, propanol, propargyl alcohol, benzyl alcohol, phenethyl alcohol, etc., ketones such as acetone, methyl ethyl ketone, acetophenone etc., ethers such as dioxane, trioxane, tetrahydrofuran, ethylene glycol, propylene glycol, ethylene glycol monomethyl ether, propylene glycol monomethyl ether, tetrahydropyran, etc., amides such as dimethylformamide, dimethylacetamide, etc., esters such as methyl acetate, ethyl acetate, ethyl formate, etc.

Furthermore, a surfactant can be incorporated in the processing solution in a proportion of 0.1 to 20 parts by weight to 100 parts by weight of water, illustrative of which are anionic, cationic and nonionic surfactants well known in the art, for example, described in Hiroshi Horiguchi "New Surfactants (Shin-Kaimen Kasseizai)" published by Sankyo Shuppan KK, 1975, Ryohei Oda and Kazuhiro Teramura "Synthesize of Surfactants and Applications Thereof (Kaimen Kasseizai no Gosei to sono Oyo)" published by Maki Shoten, 1980.

The scope of the present invention should not be construed to be limited to the above described and specified compounds.

The oil-desensitization of the resin of the present invention, containing the functional group represented by General Formula (II), is characterized in that it is rendered hydrophilic by carrying ou the hydrogen halide removing reaction as shown in the foregoing Reaction Formula (I) and then subjecting the resulting double bond to nucleophilic reaction with a nucleophilic reagent.

Since the hydrogen halide removing reaction readily proceeds in a processing solution with a pH of at least 6, removing the hydrogen halide and rendering hydrophilic though the nucleophilic reaction are accomplished by adjusting the pH of the oil-desensitization processing solution containing at least the above described nucleophilic compound to 6 or more.

More preferably, the processing solution has a pH of at least 8. In addition, after the hydrogen halide removing reaction is allowed to proceed in a solution with a pH of at least 6, the oil-desensitization can be carried out with the processing solution containing the nucleophilic compound.

The present invention will now be illustrated in greater detail by way of examples, but it should be understood that the present invention is not limited thereto.

Examples

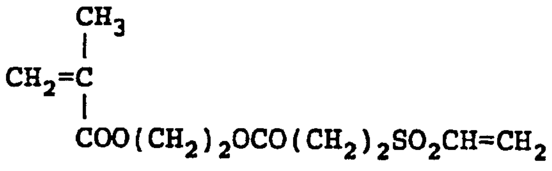
Preparation Example 1 of Resin Grains; [L-1]

A mixed solution of 95 g of dodecyl methacrylate, 5 g of acrylic acid and 200 g of toluene was heated to 70°C while stirring under a nitrogen stream, and 1.5 g of 2,2-azobis(isobutyronitrile) (referred to as A.I.B.N.) was added thereto and reacted for 8 hours. To this reaction mixture were added 12 g of glycidyl methacrylate, 1 g of t-butylhydroquinone and 0.8 g of N,N-dimethyldodecylamine, followed by allowing the mixture to react at 100°C for 15 hours (Dispersed Resin [P-1]).

A mixture of 7,5 g (as solid content) of the above described Dispersed Resin [P-1], 50 g of a monomer [M-1] having the following structure and 200 g of methyl ethyl ketone was heated to 65°C while stirring under a nitrogen stream, and 0.7 g of 2,2-azobis(isovaleronitrile) (referred to as A. I. V. N.) was then added thereto and reacted for 6 hours.

After passage of 20 minutes from the addition of the initiator (A. I. V. N.), the homogeneous solution became slightly opaque, the reaction temperature being raised to 90°C. After cooling, the reaction product was passed through a nylon cloth of 200 mesh to obtain a white dispersion having an average grain diameter of 0.45 µm as a white latex [L-1].

Monomer [M-1]

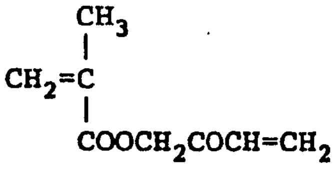


$CH_2=C(CH_3)COO(CH_2)_2OCO(CH_2)_2SO_2CH=CH_2$

Preparation Example 2 of Resin Grains: [L-2]

A mixture of 20 g of a monomer [M-2] having the following structure, 8 g of Dispersed Resin [P] (as solid content), 150 g of ethyl acetate and 150 g of n-hexane was heated to 55°C while stirring under a nitrogen stream, and 0.5 g of A. I. V. N. was added thereto and reacted for 4 hours, thus obtaining a white dispersion. After cooling, the reaction product was passed through a nylon cloth of 200 mesh. The resulting dispersion was a latex [L-2] with an average grain diameter of 0.30 µm.

Monomer [M-2]

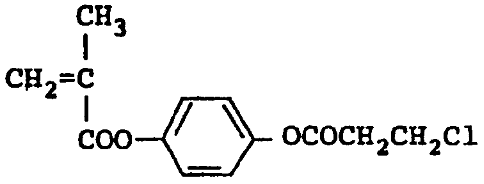


$CH_2=C(CH_3)COOCH_2COCH=CH_2$

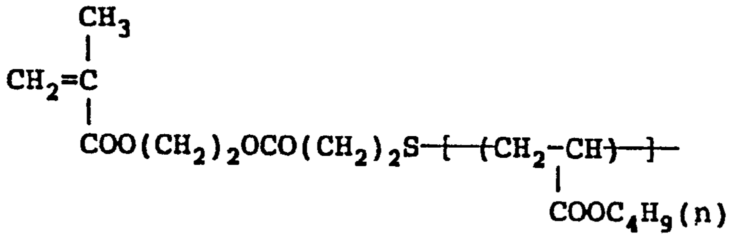
Preparation Example 3 of Resin Grains: [L-3]

Preparation Example 1 was repeated except using a mixed solution of 20 g of a monomer [M-3] having the following structure, 5 g of a macromonomer [P-2] having the following structure and 150 g of methyl ethyl ketone, thus obtaining a white latex [L-3] having a mean grain diameter of 0.30 µm.

Monomer [M-3]



Macromonomer [P-2]



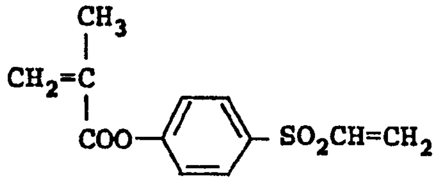
$$CH_2=C(CH_3)-COO(CH_2)_2OCO(CH_2)_2S-[-(CH_2-CH(COOC_4H_9(n)))-]-$$

$\overline{M}w$ 6.5×10^3

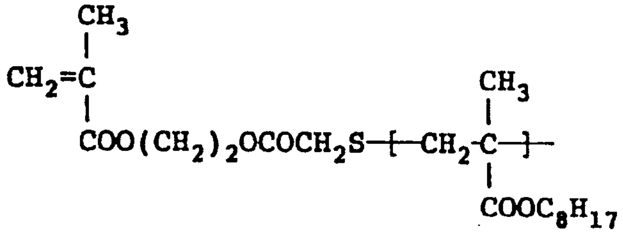
Preparation Example 4 of Resin Grains: [L-4]

Preparation Example 1 was repeated except using a mixed solution of 20 g of a monomer [M-4] having the following structure, 2.0 g of divinylbenzene, 6 g of a macromonomer [P-2] having the following structure and 150 g of methyl isobutyl ketone, thus obtaining a white latex [L-4] having a mean grain diameter of 0.25 μm.

Monomer [M-4]



Macromonomer [P-3]



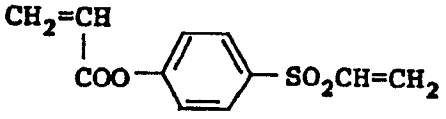
$$CH_2=C(CH_3)-COO(CH_2)_2OCOCH_2S-[-CH_2-C(CH_3)(COOC_8H_{17})-]-$$

$\overline{M}w$ 7×10^3

Preparation Example 5 of Resin Grains: [L-5]

Preparation Example 1 was repeated except using a mixed solution of 20 g of a monomer [M-5] having the following structure, 2.5 g of ethylene glycol diacrylate, 5 g of acrylic acid, 6 g of a macromonomer [P-2] having the following structure and 200 g of methyl ethyl ketone, thus obtaining a white latex [L-5] having a mean grain diameter of 0.20 μm.

Monomer [M-5]



Preparation Examples 6 to 13 of Resin Grains: [L-6] to [L-13]

Preparation Example 4 was repeated except using monomers described in the following Table 2 instead of Monomer [M-4], thus obtaining resin grains [L-6] to [L-13].

Table-2

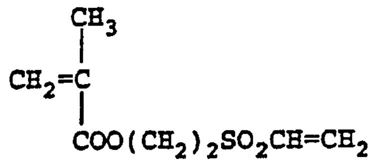
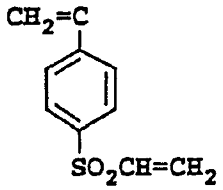
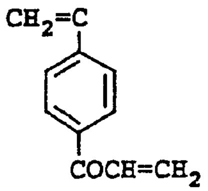
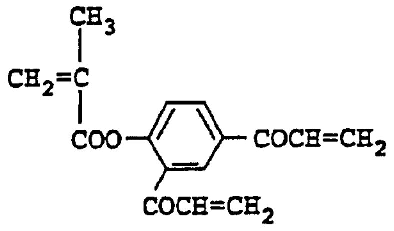
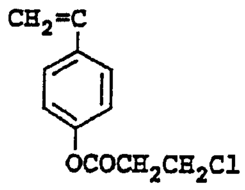
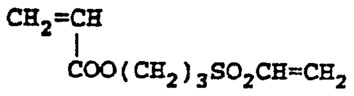
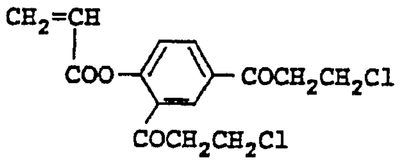
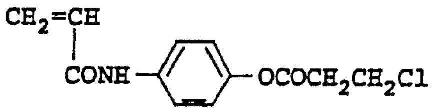
Preparation Example	Resin Grain	Monomer [M]		Mean grain diameter of Grains
6	[L-6]	[M-6]	 $CH_2=C(CH_3)COO(CH_2)_2SO_2CH=CH_2$	0.30 μm
7	[L-7]	[M-7]		0.25
8	[L-8]	[M-8]		0.35
9	[L-9]	[M-9]		0.40

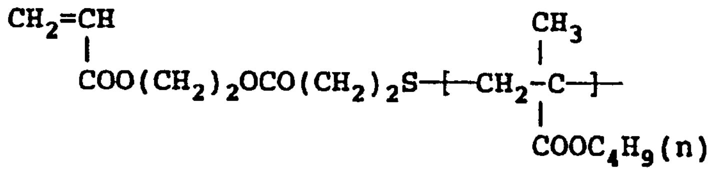
Table-2 (continued)

Preparation Example	Resin Grain	Monomer [M]		Mean grain diameter of Grains
10	[L-10]	[M-10]		0.40 µm
11	[L-11]	[M-11]	 $CH_2=CH-COO(CH_2)_3SO_2CH=CH_2$	0.20
12	[L-12]	[M-12]		0.25
13	[L-13]	[M-13]		0.50

Preparation Examples 14 to 20 of Resin Grains: [L-14] to [L-20]

Preparation Example 1 was repeated except using a mixed solution of 20 g of a monomer [M] of the following Table 3, predetermined amounts of monomers for bridging, 5 g of a macromonomer [P-4] having the following structure and 200 g of methyl ethyl ketone, thus obtaining latexes [L-14] to [L-20].

Macromonomer [P-4]



$$\underset{\displaystyle COO(CH_2)_2OCO(CH_2)_2S\!-\!\!\left[-CH_2-\underset{\displaystyle COOC_4H_9(n)}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\right]\!\!-}{\overset{\displaystyle CH_2=CH}{|}}$$

Table-3

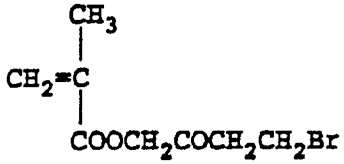
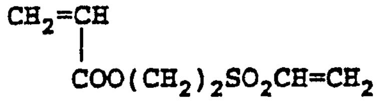
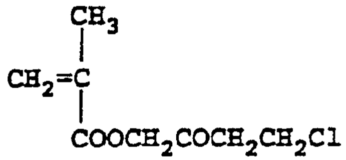
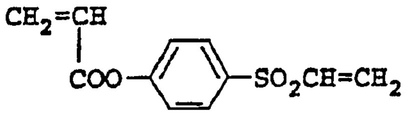
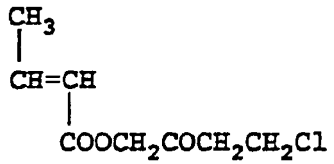
Preparation Example	Resin Grain	Monomer [M]		Monomer for Bridging	Mean grain diameter of Grains
14	[L-14]	[M-14]	 $CH_2=C(CH_3)COOCH_2COCH_2CH_2Br$	divinylbenzene 2 g	0.30 µm
15	[L-15]	[M-15]	 $CH_2=CHCOO(CH_2)_2SO_2CH=CH_2$	trivinylbenzene 1.6 g	0.40
16	[L-16]	[M-16]	 $CH_2=C(CH_3)COOCH_2COCH_2CH_2Cl$	ethylene glycol dimethacryalate 2.5 g	0.20
17	[L-17]	[M-17]		ethylene glycol dimethacryalate 2.5 g	0.35

Table-3 (continued)

Preparation Example	Resin Grain	Monomer [M]	Monomer for Bridging	Mean grain diameter of Grains
18	[L-18]	[M-1]	divinylbenzene 1.8 g	0.30
19	[L-19]	[M-1]	Propylene glycol dimethacrylate 2.2 g	0.40
20	[L-20]	[M-18]  $CH_3-CH=CH-COOCH_2COCH_2CH_2Cl$	divinylbenzene 1.9 g	0.60

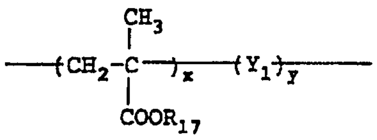
Synthetic Example 1 of Binder Resin [A] [A-1]

A mixed solution of 95 g of benzyl methacrylate, 5 g of acrylic acid and 200 g of toluene was heated at a temperature of 90°C under a nitrogen stream, to which 6.0 g of A.I.B.N. was then added, followed by reacting for 4 hours. 2 g of A.I.B.N. was further added thereto and reacted for 2 hours to obtain a copolymer [A-1] with a molecular weight Mw of 8500.

Synthetic Examples 2 to 28 of Binder Resins [A]: [A-2] to [A-28]

Synthetic Example 1 was repeated to obtain resins [A-2] to [A-28] shown in Table 4.

Table 4



$$-\!\left(CH_2-\underset{\displaystyle COOR_{17}}{\overset{\displaystyle CH_3}{C}}\right)_x\!-\!\left(Y_1\right)_y\!-$$

Mw of Resins [A]: $5.0\times10^3\sim9.0\times10^3$

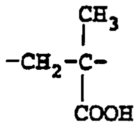
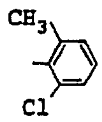
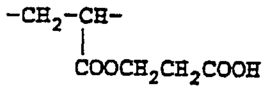
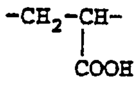
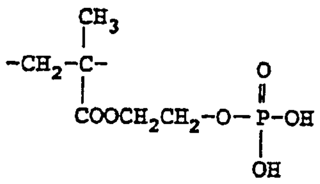
Synthetic Example of Resin [A]	Resin [A]	R_{17}	$-Y_1-$	x/y (weight ratio)
2	[A-2]	$-CH_2C_6H_5$	 $-CH_2-\underset{\displaystyle COOH}{\overset{\displaystyle CH_3}{C}}-$	94/6
3	[A-3]		 $-CH_2-\underset{\displaystyle COOCH_2CH_2COOH}{CH}-$	95/5
4	[A-4]	$-C_6H_5$	 $-CH_2-\underset{\displaystyle COOH}{CH}-$	95/5
5	[A-5]	$-CH_2C_6H_5$	 $-CH_2-\underset{\displaystyle COOCH_2CH_2-O-\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{P}}}-OH}{\overset{\displaystyle CH_3}{C}}-$	97/3

Table 4 (continued)

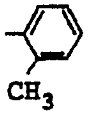
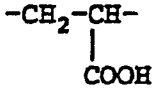
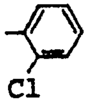
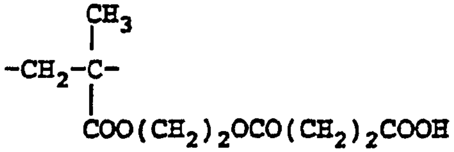
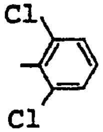
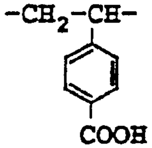
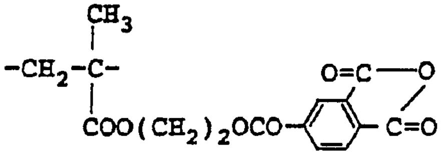
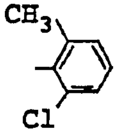
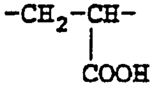
6	[A-6]		 $-CH_2-\underset{\displaystyle COOH}{CH}-$	95/5
7	[A-7]		 $-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COO(CH_2)_2OCO(CH_2)_2COOH}{C}}-$	94/6
8	[A-8]			95/5
9	[A-9]	$-CH_2C_6H_5$		93/7
10	[A-10]		 $-CH_2-\underset{\displaystyle COOH}{CH}-$	95/5

Table 4 (continued)

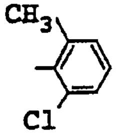
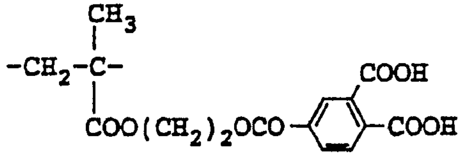
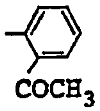
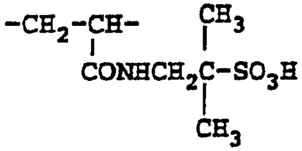
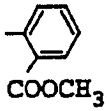
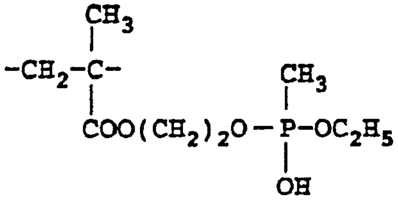
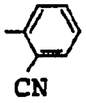
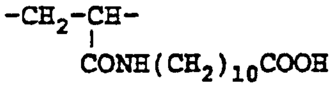
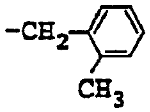
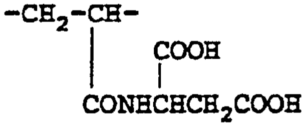
11	[A-11]			96/4
12	[A-12]		 $-CH_2-CH(CONHCH_2C(CH_3)_2-SO_3H)-$	97/3
13	[A-13]		 $-CH_2-C(CH_3)(COO(CH_2)_2O-P(CH_3)(OH)-OC_2H_5)-$	97/3
14	[A-14]		 $-CH_2-CH(CONH(CH_2)_{10}COOH)-$	94/6
15	[A-15]		 $-CH_2-CH(CONHCH(COOH)CH_2COOH)-$	97/3

Table 4 (continued)

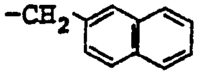
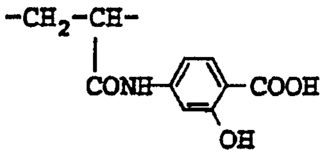
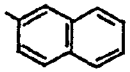
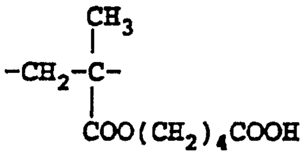
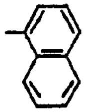
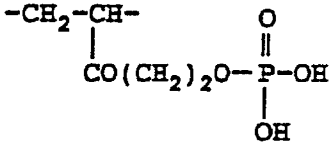
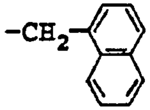
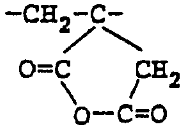
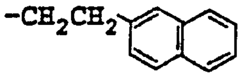
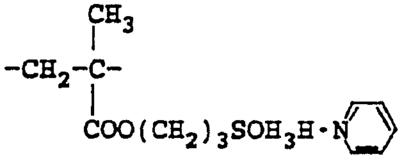
16	[A-16]			95/5
17	[A-17]			93/7
18	[A-18]			97/3
19	[A-19]			95/5
20	[A-20]			98/2

Table 4 (continued)

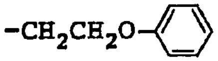
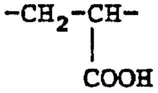
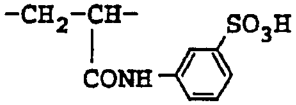
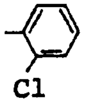
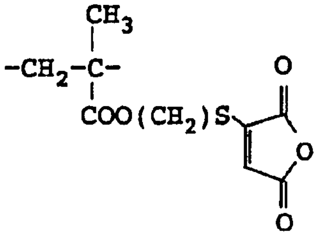
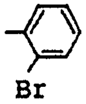
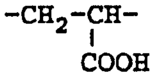
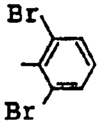
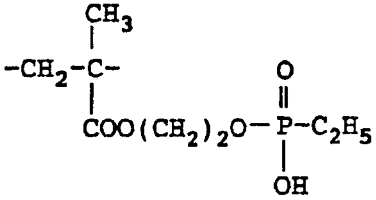
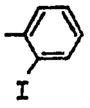
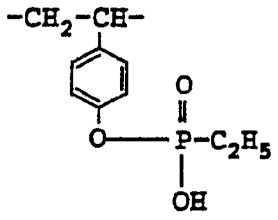
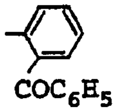
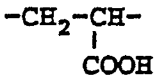
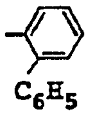
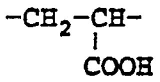
21	[A-21]		 $-CH_2-\underset{\mid}{CH}-$ COOH	96/4
22	[A-22]	$-CH_2C_6H_5$		97/3
23	[A-23]			94/4
24	[A-24]		 $-CH_2-\underset{\mid}{CH}-$ COOH	95/5
25	[A-25]			92/8

Table 4 (continued)

26	[A-26]			97/3
27	[A-21]		 $-CH_2-\underset{\large COOH}{CH}-$	95/5
28	[A-22]		 $-CH_2-\underset{\large COOH}{CH}-$	95/5

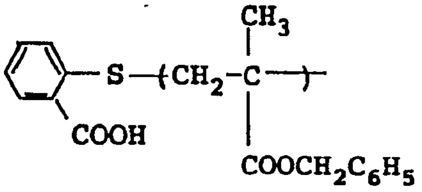
Synthetic Example 29 of Binder Resin [A]: [A-29]

A mixed solution of 95 g of 2,6-dichlorophenyl methacrylate, 5 g of acrylic acid, 2 g of n-dodecylmercaptan and 200 g of toluene was heated at a temperature of 90°C under a nitrogen stream, to which 2 g of A.I.B.N. was then added, followed by reacting for 4 hours, 0.5 g of A.I.B.N. was then added thereto and reacted for 2 hours and 0.5 g of A.I.B.N. was further added and reacted for 3 hours. After cooling, the reaction mixture was subjected to reprecipitation in 2000 ml of a mixed solution of methanol/water (9/l) and the precipitate was collected by decantation and dried under reduced pressure to obtain 78 g of a waxlike copolymer with a molecular weight Mw of 6.3xl0^3.

Synthetic Example 30 of Resin A: Resin A-30

A mixed solution 96 g of benzyl methacrylate, 4 g of thiosalicylic acid and 200 g of toluene was heated at a temperature of 75°C under a nitrogen stream. 1.0 g of A. I. B. N. was added thereto and reacted for 4 hours, 0.4 g of A. I. B. N. was further added and stirred for 2 hours and 0.2 g of A. I. B. N. was then added and stirred for 3 hours. The resulting copolymer (A-1) has the following structure and a weight average molecular weight $\overline{M}w$ of 6.8x10^3:

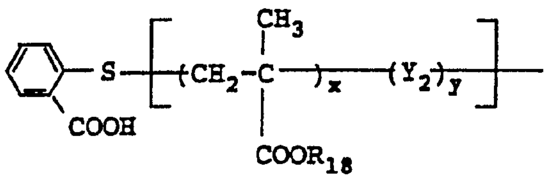
A-30



Synthetic Examples 31 to 42 of Resin A: Resins A-31 to A-42

Synthetic Example 30 was repeated except using monomers shown in the following Table 5 instead of 96 g of benzyl methacrylate, thus obtaining Resins A-31 to A-42. Each of these resins had $\overline{M}w$ of 6.0x10^3 to 8x10^3.

Table 5



x and y: weight ratio

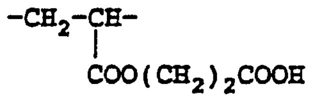
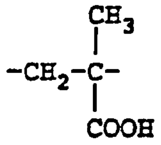
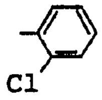
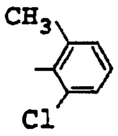
Synthetic Example of Resin A	Resin [A]	R_{18}	$-Y_2-$	x/y
31	[A-31]	$-C_2H_5$	 $-CH_2-\underset{\textstyle COO(CH_2)_2COOH}{\underset{\mid}{CH}}-$	94/2
32	[A-32]	$-C_6H_5$	 $-CH_2-\overset{\textstyle CH_3}{\overset{\mid}{\underset{\textstyle COOH}{\underset{\mid}{C}}}}-$	94/2
33	[A-33]		-	96/0
34	[A-34]		-	96/0

Table 5 (continued)

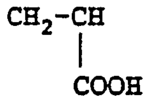
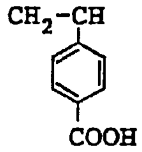
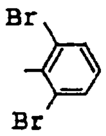
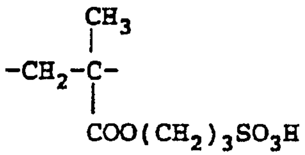
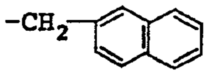
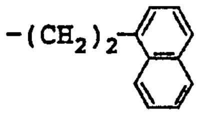
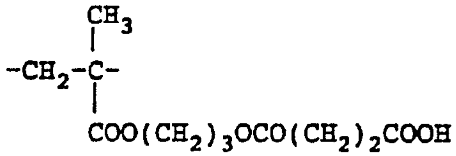
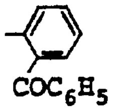
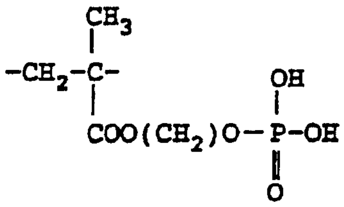
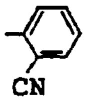
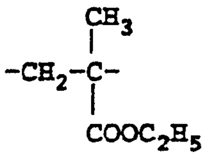
Synthetic Example of Resin A	Resin [A]	R_{18}	$-Y_2-$	x/y
35	[A-35]	$-CH_2C_6H_5$	 $\underset{\displaystyle COOH}{CH_2-CH}$	93.5/2.5
36	[A-36]	$-C_2H_5$		93/3
37	[A-37]		 $-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COO(CH_2)_3SO_3H}{C}}-$	95/1
38	[A-38]		-	96/0
39	[A-39]		 $-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COO(CH_2)_3OCO(CH_2)_2COOH}{C}}-$	92/4

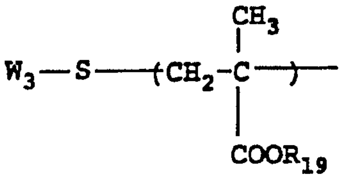
Table 5 (continued)

Synthetic Example of Resin A	Resin [A]	R_{18}	$-Y_2-$	x/y
40	[A-40]		 $-CH_2-C(CH_3)(COO(CH_2)O-P(=O)(OH)-OH)-$	94.5/1.5
41	[A-41]		 $-CH_2-C(CH_3)(COOC_2H_5)-$	76/20
42	[A-42]	$\leftarrow CH_2)_2-O-C_6H_5$	-	96/0

Synthetic Examples 43 to 53 of Resin A: Resins A-43 to A-53

Synthetic Example 30 was repeated except using methacrylates and mercapto compounds as shown in Table 6 instead of 96 g of benzyl methacrylate and 4 g of thiosalicylic acid and using 150 g of toluene and 50 g of isopropanol instead of 200 g of toluene, thus obtaining Resins A-43 to A-53.

Table 6



$$W_3\text{—}S\text{—}\left(CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOR_{19}}{|}}{C}}\right)\text{—}$$

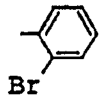
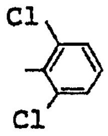
Synthetic Example of Resin A	Resin A	W_3-	(amount)	$-R_{19}$-	(amount)	Mw
43	[A-43]	$HOOCCH_2CH_2CH_2$-	4 g	$-C_2H_5$	96 g	7.3×10^3
44	[A-44]	$HOOCCH_2$-	5 g	$-C_3H_7$	95 g	5.8×10^3
45	[A-45]	$\begin{array}{l}HOOC\text{-}CH\text{-}\\ \qquad\ \ | \\ HOOC\text{-}CH_2\end{array}$	5 g	$-CH_2C_6H_5$	95 g	7.5×10^3
46	[A-46]	$HOOCCH_2CH_2$-	5.5 g	$-C_6H_5$	94.5 g	6.5×10^3
47	[A-47]	$HOOCCH_2$-	4 g		96 g	5.3×10^3
48	[A-48]	$HO\text{-}\underset{\underset{\displaystyle OH}{\vert}}{\overset{\overset{\displaystyle O}{\|}}{P}}\text{-}OCH_2CH_2\text{-}$	3 g		97 g	6.6×10^3

Table 6 (continued)

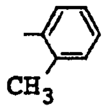
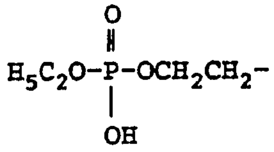
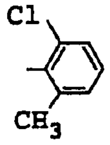
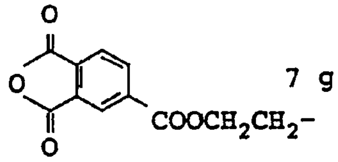
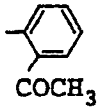
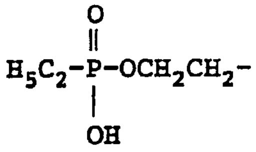
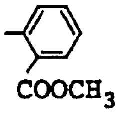
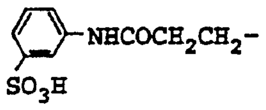
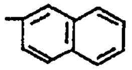
Synthetic Example of Resin A	Resin A	W_3-	(amount)	$-R_{19}-$	(amount)	Mw
49	[A-49]	$HO_3SCH_2CH_2-$	3 g		97 g	8.8×10^3
50	[A-50]	 $H_5C_2O-\underset{OH}{\underset{\mid}{\overset{\overset{O}{\Vert}}{P}}}-OCH_2CH_2-$	4 g		96 g	7.5×10^3
51	[A-51]		7 g		93 g	5.5×10^3
52	[A-52]	 $H_5C_2-\underset{OH}{\underset{\mid}{\overset{\overset{O}{\Vert}}{P}}}-OCH_2CH_2-$	6 g		94 g	4.5×10^3

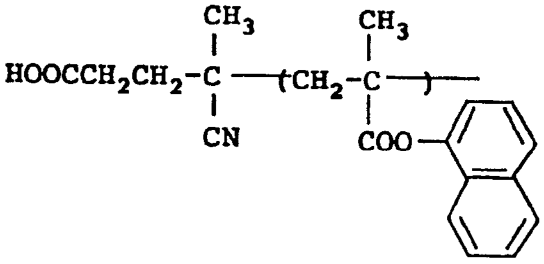
Table 6 (continued)

Synthetic Example of Resin A	Resin A	W_3- (amount)		$-R_{19}-$ (amount)		Mw
53	[A-53]		4 g		96 g	5.6×10^3

Synthetic Example 54 of Resin A: Resin A-54

A mixed solution of 100 g of 1-naphthyl methacrylate, 150 g of toluene and 50 g of isopropanol was heated at 80°C under a nitrogen stream. 5.0 g of 4,4'-azobis(4-cyano)valeic acid (hereinafter referred to as A. C. V.) was then added thereto and stirred for 5 hours, 1 g of A. C. V. was further added and stirred for 2 hours and then 1 g of A. C. V. was further added and stirred for 3 hours. The thus resulting polymer has a weight average molecular weight $\overline{M}w$ of 7.5×10^3.

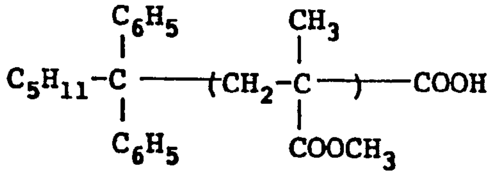
A-54



Synthetic Example 55 of Resin A. Resin A-55

A mixed solution of 50 g of methyl methacrylate and 150 g of methylene chloride was cooled at -20°C under a nitrogen stream, to which 1.0 g of a 10% hexane solution of 1,1-diphenylhexyllithium, prepared just before it, was added, followed by stirring for 5 hours. Carbon dioxide was introduced thereinto at a flow rate of 10 ml/cc while stirring for 10 minutes, cooling was then stopped and the reaction mixture was stirred and allowed to stand until the temperature became room temperature. The reaction mixture was reprecipitated in a solution of 1000 ml of methanol in which 50 ml of 1N hydrochloric acid had been dissolved and a white powder was collected by filtering. The thus resulting white powder was washed with water and dried under reduced pressure, thus obtaining 18 g of a polymer with $\overline{M}$ of 6.5×10^3.

A-55

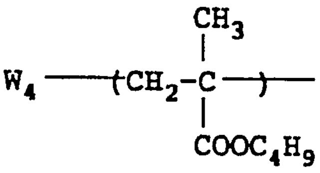


$$C_5H_{11}-\underset{C_6H_5}{\overset{C_6H_5}{C}}-\!\!(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}})\!\!-COOH$$

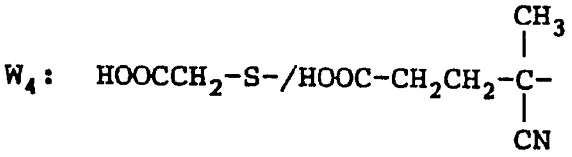
Synthetic Example 56 of Resin A: Resin A-56

A mixed solution of 95 g of benzyl methacrylate, 4 g of thioglycolic acid and 200 g of toluene was heated at a temperature of 75°C. 1.0 g of A. C. V. was added thereto and reacted for 6 hours and then 0.4 g of A. I. B. N. was further added and reacted for 3 hours. The thus resulting copolymer had $\overline{M}w$ of 7.8×10^3.

A-56



$$W_4 - \!\!\left(CH_2 - \overset{\displaystyle CH_3}{\underset{\displaystyle COOC_4H_9}{C}} \right)\!\! -$$



$$W_4: \quad HOOCCH_2-S-/HOOC-CH_2CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}-$$

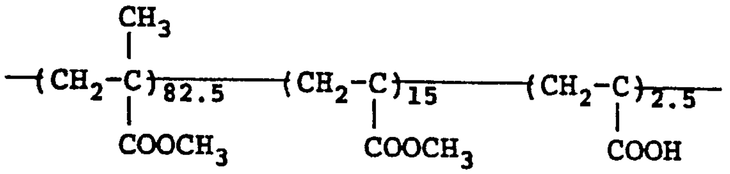
=4/1 (weight ratio)

Example 1 and Comparative Example A

Example 1

A mixture 6 g (as solid content) of Resin [A-7], 30 g (as solid content) of Resin [B-1], 4 g (as solid content) of Resin Grains [L-1], 0.018 g of Methine Dye [I], 0,15 g of salicylic acid and 30 g of toluene was ball milled for 3 hours to prepare a light-sensitive layer-forming composition, which was then applid to a paper rendered electrically conductive to give a dry coverage of 25 g/m² by a wire bar coater, followed by drying at 110°C for 30 seconds. The thus coated paper was allowed to stand in a dark place at a temperature of 20°C and a relative humidity of 65% for 24 hours to prepare an electrophotographic light-sensitive material.

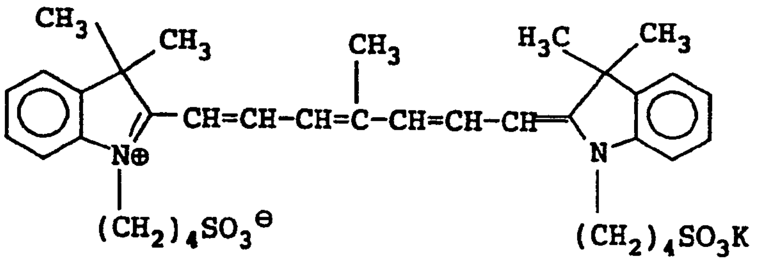
Resin [B-1]



$$-\!\!\left(CH_2 - \overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}} \right)_{82.5}\!\! - \!\!\left(CH_2 - \underset{\displaystyle COOCH_3}{C} \right)_{15}\!\! - \!\!\left(CH_2 - \underset{\displaystyle COOH}{C} \right)_{2.5}\!\! -$$

$\overline{M}w$ 5.5×10^4 (weight ratio)

Methine Dye [I]



Comparative Example A

Example 1 was repeated except omitting 4.0 g of Resin Grains [L-1] and using 34 g of Resin [B-1] to prepare an electrophotographic light-sensitive material for comparison.

Table 7

	Example 1	Comparative Example A
Smoothness of Photoconductive Layer 1)	135	140
Electrostatic Characteristics 2) $V_{10}/(-V)$		
I (20°C, 65%RH)	680	685
II (30°C, 80%RH)	670	670
D. R. R. (%)		
I	89	88
II	85	85
$E_{1/10}$ (erg/m^2)		
I	25	20
II	28	22
Image Quality 3)		
I	good	good
II	good	good
Water Retention 4)	very good	remarkable background staining from printing start
Printing Durability 5)	no stain even after 5000 prints	background staining from printing start

The characteristic items described in Table 7 are evaluated as follows:

1) Smoothness of Photoconductive Layer

The resulting light-sensitive material was subjected to measurement of its smoothness (sec/cc) under an air volume of 1 cc using a Beck smoothness tester (manufactured by Kumagaya Riko KK).

2) Electrostatic Characteristics

Each of the light-sensitive materials was subjected to corona discharge at a voltage of -6 kV for 20 seconds in a dark room at a temperature of 20°C and relative humidity of 65% using a paper analyzer (Paper Analyzer Sp-428 -commercial name- manufactured by Kawaguchi Denki KK) and after allowed to stand for 10 seconds, the surface potential V_{10} was measured. Then, the sample was further allowed to stand in the dark room as it was for 120 seconds to measure the surface potential V_{130}, thus obtaining the retention of potential after the dark decay for 120 seconds, i.e., dark decay retention ratio (DRR (%)) represented by $(V_{130}/V_{10})\times100$ (%). Moreover, the surface of the photoconductive layer was negatively charged to -500 V, by corona discharge, then irradiated with monochromatic light of a wavelength of 780 nm and the time required for dark decay of the surface potential (V_{10}) to 1/100 was measured to evaluate and exposure quantity $E_{1/100}$ (erg/cm^2).

The ambient conditions for the measurement of the electrostatic characteristics were:

I ..... 20°C, 65% RH

II .....30°C, 85% RH

3) Image quality

Each of the light-sensitive materials was allowed to stand for a whole day and night under the following ambient conditions, charged at -5 kV, imagewise exposed rapidly at a pitch of 25 μm and a scanning speed of 330 m/sec under irradiation of 50 erg/cm^2 on the surface of the light-sensitive material using a gallium-aluminum-arsenic semiconductor laser (oscillation wavelength: 780 nm) with an output of 2,8 mW as a light source, developed with a liquid developer, ELP-T (-commercial name- manufactured by Fuji Photo Film Co., Ltd.) and fixed to obtain a reproduced image which was then subjected to visual evaluation of the fog and image quality:

I ..... 20°C, 65% RH
II .....30°C, 80% RH

4) Water Retention

Each of the light-sensitive materials was passed once through an etching processor using an oil-desensitizing solution ELP-EX (-commercial name- made by Fuji Photo Film Co., Ltd,) 10 times diluted with distilled water, immersed in an oil-desensitizing processing solution [E-I] having the following recipe for 30 seconds, washed with water and subjected to an offset printing machine (Oliver 52 type -commercial name- manufactured by Sakurai Seisakujo KK) and to printing using ELP-EX 100 times diluted with distilled water as dampening water. Visual estimation of a 20th print from the start of printing was carried out as to the background staining.

Oil-desensitizing Processing Solution [E-1]

Disodium Thiomalate	60 g
Benzyl Alcohol	100 g
Distilled Water to 1000 ml	

5) Printing Durability

Each of the light-sensitive materials was subjected to printing plate making under the same conditions as the above described item 3) to form a toner image and then to oil-desensitization under the same conditions as in the above-described item 4). The resulting printing plate was mounted, as an offset master, on an offset printing machine (Oliver 52 type -commercial name- manufactured by Sakurai Seisakujo KK) to obtain the printing durability which was defined by the number of prints which could be obtained without forming background stains on the non-image areas of the print and meeting with any problem on the image quality of the image areas by printing. The more the prints, the better the printing durability.

As can be seen from Table 7, the light-sensitive materials of the present invention and Comparative Example A showed excellent smoothness and electrostatic characteristics of the photoconductive layer and gave a reproduced image free from background stains and excellent in image quality. This tells that the photoconductive material and binder resin are sufficiently adsorbed and coated on the grain surfaces.

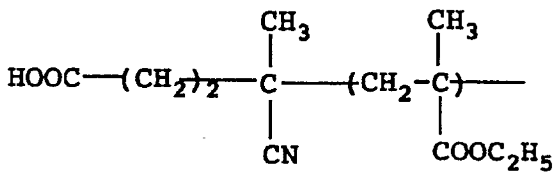
When the light-sensitive material of the present invention was used as a master plate for offset printing and the light-sensitive material before plate making was subjected to oil-desensitizing processing and to real printing to examine the water retention, that of the present invention gave 5000 clear prints without background staining from the start of printing even under severer conditions examined. On the other hand, in Comparative Example A wherein no resin grains for rendering hydrophilic were added, the water retention was insufficient so that background staining occurred from the start of printing and this could not be eliminated after considerable printing.

It will clearly be understood from these facts that according to only the present invention, there can be obtained an electrophotographic photoreceptor capable of satisfying electrophotographic properties as well as printing adaptability.

Example 2

Example 1 was repeated except using 5.5 g (as solid content) of Resin [A-1], 30 g of Resin [B-2] having the following structure and 4.5 g (as solid content) of Resin Grains [I-3], thus preparing an electrophotographic light-sensitive material.

Resin [B-2]



$$\mathrm{HOOC{-}(CH_2)_2{-}\overset{CH_3}{\underset{CN}{C}}{-}(CH_2{-}\overset{CH_3}{\underset{COOC_2H_5}{C}}){-}}$$

$\bar{M}w$: 8×10^4

The resulting light-sensitive was subjected to evaluation of the electrophotographic characteristics and printing performances in an analogous manner to Example 1 except using the following processing solution [E-2] for rendering hydrophilic instead of the processing solution [E-1] for rendering hydrophilic:

Processing solution for Rendering Hydrophilic [E-2]:

Cysteine	50 g
Newcol B4SN (Commercial name, made by Nippon Nyukazai KK)	5 g
Methyl Ethyl Ketone	1.00g
Distilled Water to 100 ml	
pH 11.5 adjusted with KOH	

The light-sensitive material of the present invention was then subjected to measurement of the properties to obtain the following results:

Electrostatic Characteristics (30°C, 80% RH)

V_{10}: -560 V

DRR: 85 %

$E_{1/10}$ 28 erg/cm^2

Image Quality I (20°C, 65% RH); good

II (30°C, 80% RH); good

Water Retention; good

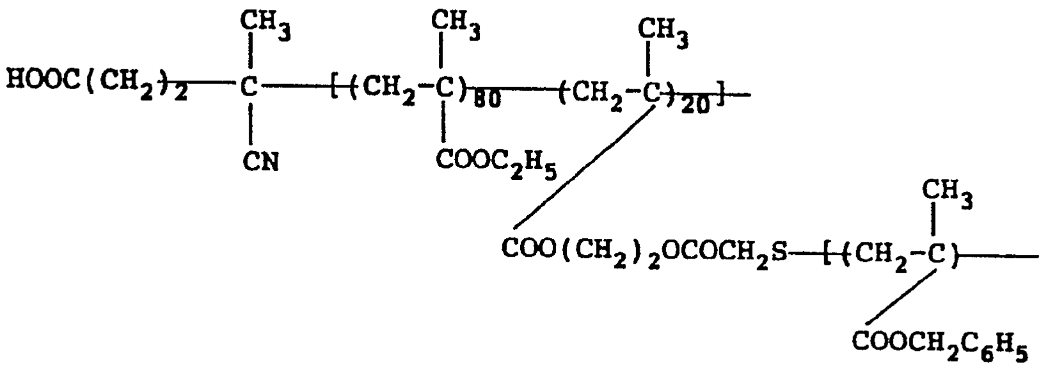
Printing Durability; 5000 prints

As described above, the light-sensitive material of the present invention exhibited excellent electrostatic characteristics and printing property.

Example 3

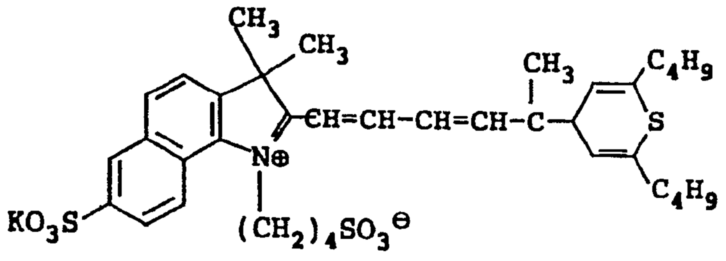
Example 1 was repeated except using 6 g (as solid content) of Resin [A-10], 30 g of Resin [B-3] having the following structure and 4 g (as solid content) of Resin Grains [I-6] and 0.02 g of methine dye [II] having the following structure, thus preparing an electrophotographic light-sensitive material.

Resin [B-3]



$\overline{M}w$: 9.0×10^4 (weight ratio)

[Methine Dye II]



The resulting light-sensitive was subjected to evaluation of the electrophotographic characteristics and printing performances in an analogous manner to Example 1,thus obtaining the following results:

Electrostatic Characteristics (30°C, 80% RH)

V_{10}:	-630 V
DRR:	88 %
$E_{1/10}$	18 erg/cm^2

Image Quality I (20°C, 65% RH); good

II (30°C, 80% RH); good

Water Retention; good

Printing Durability; 5000 prints

As described above, the light-sensitive material of the present invention exhibited excellent electrostatic characteristics and printing property.

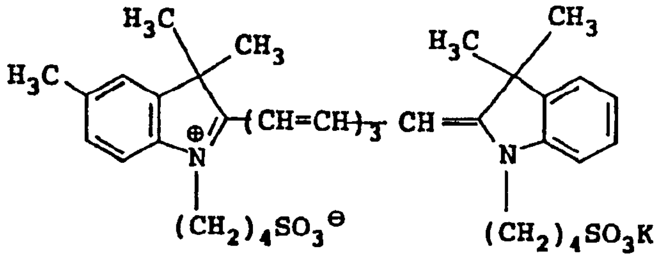
Example 4 to 19

Example 1 was repeated except using 6.0 g (as solid content) of each of Resins [A], 4 g (as solid content) of each of Resin Grains [L], shown in Table 8, 30 g of the following Resin [B-4] (partially crosslinked) and 0.018 g of Methine Dye [III] to prepare a light-sensitive material.

Synthesis of Resin [B-4]

A mixed solution of 98 g of ethyl methacrylate, 2 g of ethylene glycol dimethacrylate, 1 g of thioglycolic acid and 200 g of toluene was heated at 70°C with agitation in a nitrogen stream. Then, 1.0 g of A.I.B.N. was added thereto and reacted for 4 hours to obtain a polymer [B-4] with a weight average molecular weight Mw of $8x10^4$.

Methine Dye [III]



Each of these light-sensitive materials was subjected to measurement of the electrostatic characteristics and printing performances in an analogous manner to Example 3 to obtain results shown in Table 8:

Table 8

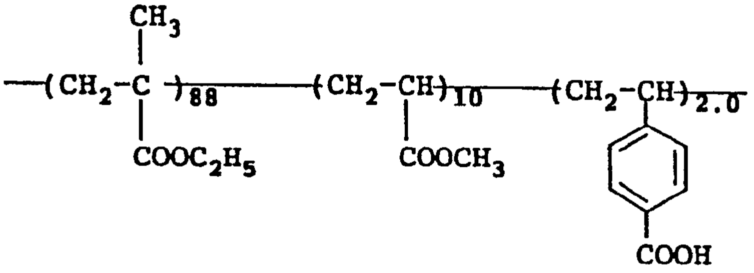
Example No.	Resin [A]	Resin [B]	Electrostatic Characteristics (30°C, 80% RH) V_{10} (-V)	DRR	$E_{1/10}$ (erg/cm^2)
4	[A-2]	[L-1]	550	84	30
5	[A-3]	[L-2]	600	86	22
6	[A-4]	[L-3]	550	86	25
7	[A-5]	[L-4]	550	83	33
8	[A-6]	[L-5]	555	82	28
9	[A-8]	[L-6]	580	85	20
10	[A-9]	[L-7]	540	80	32
11	[A-11]	[L-8]	585	86	20
12	[A-12]	[L-9]	550	83	24
13	[A-13]	[L-10]	540	80	33
14	[A-14]	[L-11]	540	82	26
15	[A-16]	[L-12]	570	86	20
16	[A-18]	[L-13]	580	86	19
17	[A-19]	[L-14]	585	87	19
18	[A-24]	[L-16]	560	85	22
19	[A-29]	[L-20]	600	86	21

As shown in Table 8, the light-sensitive materials exhibited very good results even under severer conditions of a temperature of 30°C and a humidity of 80% RH, i.e. gave good image quality in practice, excellent water retention as an offset master plate and such a high printing durability as to resist to 5000 prints.

Example 20 and 21

A mixture of 5.5 g of Resin [A-1] and 30 g of Resin [B-5] having the following structure (Example 20), or 35.5 g of Resin [B-5] (Example 21) and 4.5 g of Resin Grains [L-2], 200 g of zinc oxide, 0.02 g of uranine, 0.04 g of Rose Bengal, 0.03 g of bromophenol blue, 0.20 g of phthalic anhydride and 300 g of toluene was ball milled for 3 hours to prepare a light-sensitive layer-forming composition, which was then applied to a paper a light-sensitive layer-forming composition, which was then applied to a paper rendered electrically conductive to give a dry coverage of 20 g/m^2 by a wire bar coater, followed by drying at 110°C for 1 minutes. The thus coated paper was allowed to stand in a dark place at a temperature of 20°C and a relative humidity of 65% for 24 hours to prepare an electrophotographic light-sensitive material, as shown in Table 9.

Resin [B-5]



$\overline{M}w$: 5.8×10^4 (weight ratio)

Table 9

		Example 20	Example 21
Binder Resin		[A-1]/[B-5]	[B-5]
Resin Grains		[L-2]	[L-2]
Smoothness of Photoconductive Layer (sec/cc)		135	135
Electrostatic Characteristics$^{(6)}$			
V^{10}(-V)	I(20°C, 65% RH)	555	550
	II(30°C, 80% RH)	550	540
D.R.R.(%)	I(20°C, 65% RH)	95	90
	II(30°C, 65% RH)	93	88
$E_{1/10}$(lux/sec)	I(20°C, 65% RH)	9.8	12.5
	II(30°C, 80% RH)	10.0	13.0
Image Quality$^{7)}$	I(20°C, 65% RH)	very good	good
	II(30°C, 80% RH)	very good	good
Water Retention		good	good
Printing Durability		5000 prints	4500 prints

The characteristic items described in Table 9 were evaluated in an analogous manner to Example 1 except that the electrostatic characteristics and image quality were measured by the following procedures (Notes 6) and 7)):

6) Measurement of electrostatic characteristics E_1/10 and $E_1/_{100}$

The surface of the photoconductive layer was statistically charged to -400 V by corona discharge and irradiated by a visible ray of at an illumination of 2.0 lux and the time required for dark decay of the surface potential (V_{10}) to 1/10 or 1/100 was measured to evaluate an exposure quantity $E_{1/10}$ or $E_{1/100}$ (lux·sec).

7) Image quality

Each of the light-sensitive materials was allowed to stand for a whole day and night under the following ambient conditions and a reproduced image was formed thereon using an automatic printing plate making machine ELP-404 V (commercial name-, manufactured by Fuji Photo Film Co., Ltd.) to visually evaluate the fog and image quality: (I) 20°C, 65% RH and (II) 30°C, 80% RH.

As shown in Table 9, each of the light-sensitive materials exhibited good electrostatic characteristics and image quality, but that of Example 20 in which Resin [A-1] had been jointly used gave better photosensitivity and a reproduced image with a clearer image quality.

When using as an offset master plate, the light-sensitive material of the present invention exhibited good water retention and such a printing durability that there occurred little bad reproduction of fine lines and fine letters on a print when printing 5000 prints in the case of Example 20 and 4500 prints in the case of Example 21. This is probably due to the reproducibility of a reproduced image on an offset master plate.

In comparison of Examples 21 and 3, in which the random copolymers of medium molecular weight, known in the art, were used as a binder resin and spectral sensitizing dyes were different in variety, it will be apparent that a good light-sensitive material can be prepared independently of the variety of spectral sensitizing dyes by the joint use of Resin [A] in view of the results of Example 1.

Examples 22 to 29

Example 20 was repeated except using 6.0 g (as solid content) of Resins [A] and 5 g (as solid content) of Resin Grains [L], shown in Table 10, thus preparing light-sensitive materials.

Table 10

Example	Resin [A]	Resin Grains [L]
22	[A-2]	[L-1]
23	[A-3]	[L-3]
24	[A-4]	[L-9]
25	[A-5]	[L-11]
26	[A-9]	[L-12]
27	[A-11]	[L-15]
28	[A-16]	[L-17]
29	[A-22]	[L-18]

Each of the light-sensitive materials of the present invention exhibited excellent electrostatic characteristics, dark decay retention and photosensitivity and gave a clear reproduced image that was free from occurrence of background stains and disappearance of fine lines even under severer conditions, e.g. high temperature and high humidity (30°C, 80% RH).

When printing was carried out using as an offset master plate, 5000 prints were obtained with a clear image without occurrence of background stains.

Examples 30 to 41

Using each of the light-sensitive materials prepared in Examples 2, 3, 5, 6, 8, 9, 11, 12, 16, 18, 20 and 21, master plates for offset printing were prepared by carrying out the etching treatment as in the following.

0.5 mole of each of nucleophilic compounds shown in Table 11, 100 g of each of organic solvents shown in Table 11 and 10 g of Newcol B 4 SN (-commercial name-, manufactured by Nippon Nyukazai KK) were added to distilled water to 1000 ml, the pH being adjusted to 10.0 to prepare a processing solution. Each of the light-sensitive materials was immersed in a solution prepared by diluting by 2 times ELP-E with distilled water at 25°C for 1 minute.

The thus resulting plate was subjected to printing under the same printing conditions as in Example 1. 5000 prints were obtained with a good water retention as well as good image quality.

Table 11

Example	Light-sensitive Material	Nucleophilic Compound	Organic Solvent
30	Example 2	sodium sulfite	benzyl alcohol
31	Example 3	monoethanolamine	-do-
32	Example 5	diethanolamine	methyl ethyl ketone
33	Example 6	thiomalic acid	ethylene glycol
34	Example 8	thiosalicylic acid	benzyl alcohol
35	Example 9	taurine	isopropyl alcohol
36	Example 11	4-sulfobenzene-sulfinic acid	benzyl alcohol
37	Example 12	thioglycolic acid	ethanol
38	Example 16	2-mercaptoethyl-phosphonic acid	dioxane
39	Example 18	2-mercapto-1-aminoacetic acid	-
40	Example 20	sodium thiosulfate	methyl ethyl ketone
41	Example 21	ammonium sulfite	benzyl alcohol

Example 42

The light-sensitive material obtained in Example I was processed by the following oil-desensitizing processing to prepare an offset printing master plate. The light-sensitive material of Example 1 was immersed in a processing solution [E-2] for rendering hydrophilic for 30 seconds, washed with water and passed once through an etching processor using ELP-EX diluted by 10 times with distilled water. When this master plate was subjected to visual estimation of a 20th print from the start of printing in an analogous manner to the estimation of water retention of Example 1, there was found no fog.

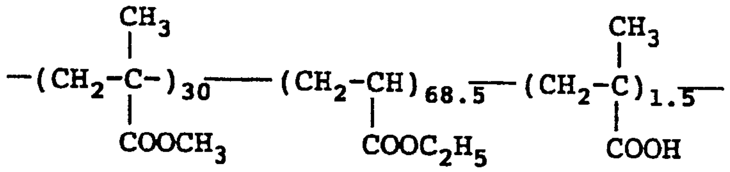
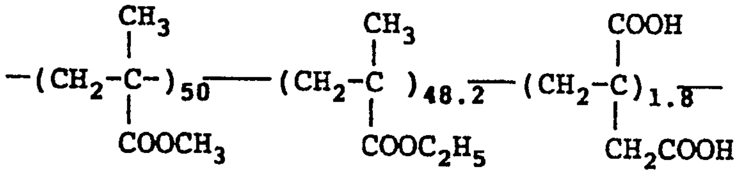
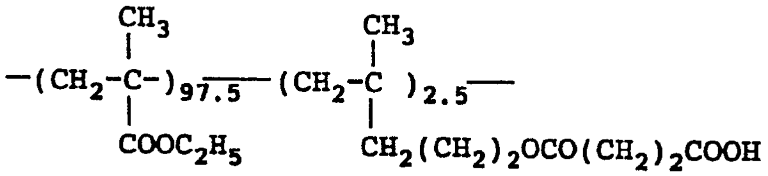
The light-sensitive material of Example 1 was subjected to plate making, to oil-desensitization in the same manner as described above and then to estimation of the printing durability in an analogous manner to Example 1. 5000 prints were obtained with a clear image without forming background stains.

As described above, the light-sensitive material of the present invention has an improved hydrophilic property independently of the order of the processings.

Examples 43 to 46

Example 20 was repeated except using 35.5 g of binder resins shown in Table 12 instead of 5.5 g of Resin [A-1] in Example 20 to prepare electrophotographic materials.

Table 12

Example No.	Binder Resin (weight ratio)
43	[B-5]
44	[B-6]  $-(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-)_{30}-(CH_2-\underset{COOC_2H_5}{CH})_{68.5}-(CH_2-\underset{COOH}{\overset{CH_3}{C}})_{1.5}-$ $\overline{M}w$ 6.2×10^4
45	[B-7]  $-(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-)_{50}-(CH_2-\underset{COOC_2H_5}{\overset{CH_3}{C}})_{48.2}-(CH_2-\underset{CH_2COOH}{\overset{COOH}{C}})_{1.8}-$ $\overline{M}w$ 5.5×10^4
46	[B-8]  $-(CH_2-\underset{COOC_2H_5}{\overset{CH_3}{C}}-)_{97.5}-(CH_2-\underset{CH_2(CH_2)_2OCO(CH_2)_2COOH}{\overset{CH_3}{C}})_{2.5}-$ $\overline{M}w$ 3.8×10^4

Each of the light-sensitive materials of the present invention exhibited excellent electrostatic characteristics, dark decay retention and photosensitivity and gave a clear reproduced image that was free from occurrence of background stains and disappearance of fine lines even under severer conditions, e.g. high temperature and high humidity (30°C, 80% RH).

When printing was carried out using as an offset master plate, 5000 prints were obtained with a clear image without occurrence of background stains.

Example 47 and Comparative Examples B and C

Example 47

A mixture of 6 g (as solid content) of Resin [A-33], 30 g (as solid content) of Resin [B-1], 4 g (as solid content) of Resin Grains [L-1], 0.018 g of Methine Dye [I], 0.15 g of salicylic acid and 30 g of toluene was ball milled for 3 hours to prepare a light-sensitive layer-forming composition, which was then applied to a paper rendered electrically conductive to give a dry coverage of 25 g/m^2 by a wire bar coater, followed by drying at 110°C for 30 seconds. The thus coated paper was allowed to stand in a dark place at a temperature of 20°C and a relative humidity of 65% for 24 hours to prepare an electrophotographic light-sensitive material.

Comparative Example B

Example 47 was repeated except omitting 4.0 g of Resin Grains [L-1] and using 34 g of Resin [B-1] to prepare an electrophotographic light-sensitive material for comparison.

Comparative Example C

Example 47 was repeated except using 36 g of Resin [B-1] instead of 6 g of Resin [A-1] and 30 g of Resin [B-1] to prepare an electrophotographic light-sensitive material.

These light-sensitive materials were subjected to evaluation of the film property (smoothness of surface), electrostatic characteristics and image quality (ambient conditions: 20°C, 65% RH and 30°C, 80% RH). Furthermore, when these light-sensitive materials was used as an offset master plate, the water retention and printing durability of the photoconductive layer were examined.

The results are shown in Table 13.

Table 13

	Example 47	Comparative Example B	Comparative Example C
Smoothness of Photoconductive Layer 1)	135	140	140
Electrostatic Characteristics$^{2)}$			
V^{10}(-V)			
I	630	685	550
II	620	670	490
D.R.R.(%)			
I	89	88	65
II	85	85	50
$E_{1/10}$(lux/sec)			
I	18	15	885
II	19	16	100
Image Quality$^{3)}$			
I	good	good	background stains, disappearance of fine lines and letter, D.M. lowered
II	good	good	much background stains
Water Retention$^{4)}$	good	marked background stains	good
Printing Durability$^{5)}$	5000 prints	background staining from printing start	background staining from printing start

The characteristic items of Notes 1) to 5) described above were evaluated in an analogous manner to Table 7.

As can be seen from Table 13, the light-sensitive materials of the present invention and Comparative Example B showed excellent smoothness and electrostatic characteristics of the photoconductive layer and gave a reproduced image free from background stains and excellent in image quality. This tells that the photoconductive material and binder resin are sufficiently adsorbed and coated on the grain surfaces.

When the light-sensitive material of the present invention was used as a master plate for offset printing and the light-sensitive material before plate making was subjected to oil-desensitizing processing and to real printing to examine the water retention, that of the present invention gave a good water retention without background stains even under severer conditions examined and even using the master plate after plate making, it gave 5000 clear prints without background staining from the start of printing. On the other hand, in Comparative Example B wherein no resin grains for rendering hydrophilic were added, the water retention was insufficient so that background staining occurred from the start of printing and this could not be eliminated after considerable printing.

In Comparative Example C, the electrostatic characteristics were markedly deteriorated and a reproduced image with a satisfactory image quality could not be obtained. On the other hand, the water retention as an offset master plate was good by the effect of the resin grains, but the master plate after plate making could not give a satisfactory reproduced image from the start of printing.

It will clearly be understood from these facts that according to only the present invention, there can be obtained an electrophotographic photoreceptor capable of satisfying electrophotographic properties as well as printing adaptability.

Example 48

Example 47 was repeated except using 5.5 g (as solid content) of Resin [A-30], 30 g of Resin [B-2] having the following structure and 4.5 g (as solid content) of Resin Grains [I-3], thus preparing an electrophotographic light-sensitive material.

The resulting light-sensitive was subjected to evaluation of the electrophotographic characteristics and printing performances in an analogous manner to Example 1 except using the following processing solution [E-2] for rendering hydrophilic instead of the processing solution [E-1] for rendering hydrophilic, respectively used in Examples 1 and 2.

The light-sensitive material of the present invention was then subjected to measurement of the properties to obtain the following results:

Electrostatic Characteristics (30°C, 80% RH)

V_{10}:	-560 V
DRR:	88 %
$E_{1/10}$	23 erg/cm^2

Image Quality I (20°C, 65% RH); good
II (30°C, 80% RH); good

Water Retention; good
Printing Durability; 5000 prints

As described above, the light-sensitive material of the present invention exhibited excellent electrostatic characteristics and printing property.

Example 49

Example 47 was repeated except using 6 g (as solid content) of Resin [A-39], 30 g of Resin [B-3] having the following structure, 4 g (as solid content) of Resin Grains [I-6] and 0.02 g of a methine dye [II] having the following structure, thus preparing an electrophotographic light-sensitive material.

The resulting light-sensitive was subjected to evaluation of the electrophotographic characteristics and printing performances in an analogous manner to Example 47, thus obtaining the following results:

Electrostatic Characteristics (30°C, 80% RH)

V_{10}:	-630 V
DRR:	88 %
$E_{1/10}$	15 erg/cm^2

Image Quality I (20°C, 65% RH); good
II (30°C, 80% RH); good

Water Retention; good
Printing Durability; 5000 prints

As described above, the light-sensitive material of the present invention exhibited excellent electrostatic characteristics and printing property.

Examples 50 to 65

Example 47 was repeated except using 6.0 g (as solid content) of Resins [A], shown in Table 14, 4 g (as solid content) of each of Resin Grains [L], shown in Table 14, 30 g of Resin [B-4] (partially crosslinked) and 0.018 g of a Methine Dye [III] to prepare a light-sensitive material.

Each of these light-sensitive materials was subjected to measurement of the electrostatic characteristics and printing performances in an analogous manner to Example 49 to obtain results shown in Table 14:

Table 14

Example No.	Resin [A]	Resin [B]	Electrostatic Characteristics (30°C, 80% RH)		
			V_{10} (-V)	DRR	$E_{1/10}$ (erg/cm^2)
4	[A-2]	[L-1]	510	80	33
5	[A-3]	[L-2]	550	86	26
6	[A-4]	[L-3]	630	88	15
7	[A-5]	[L-4]	650	89	16
8	[A-6]	[L-5]	555	84	26
9	[A-8]	[L-6]	565	85	20
10	[A-9]	[L-7]	590	84	21
11	[A-11]	[L-8]	550	84	23
12	[A-12]	[L-9]	540	80	28
13	[A-13]	[L-10]	540	79	28
14	[A-16]	[L-11]	540	80	28
15	[A-17]	[L-12]	550	82	25
16	[A-18]	[L-13]	580	86	19
17	[A-19]	[L-14]	570	88	19
18	[A-26]	[L-16]	530	80	35
19	[A-27]	[L-20]	550	84	27

As shown in Table 14, the light-sensitive materials exhibited very good results even under severer conditions of a temperature of 30°C and a humidity of 80% RH, i.e. gave good image quality in practice, excellent water retention as an offset master plate and such a high printing durability as to resist to 5000 prints.

Example 66 and 67

A mixture of 5.5 g of Resin [A-30] and 30 g of Resin [B-5] (Example 66), or 35.5 g of Resin [B-5](Example 67) and 4.5 g of Resin Grains [L-2], 200 g of zinc oxide, 0.02 g of uranine, 0.04 g of Rose Bengal, 0.03 g of bromophenol blue, 0.20 g of phthalic anhydride and 300 g of toluene was ball milled for 3 hours to prepare a light-sensitive layer-forming composition, which was then applied to a paper a light-sensitive layer-forming composition, which was then applied to a paper rendered electrically conductive to give a dry coverage of 20 g/m^2 by a wire bar coater, followed by drying at 110°C for 1 minutes. The thus coated paper was allowed to stand in a dark place at a temperature of 20°C and a relative humidity of 65% for 24 hours to prepare an electrophotographic light-sensitive material, as shown in Table 15:

Table 15

	Example 66	Example 67
Binder Resin	[A-30]/[B-5]	[B-5]
Resin Grains	[L-2]	[L-2]
Smoothness of Photoconductive Layer (sec/cc)	135	135
Electrostatic Characteristics$^{(6)}$		
V^{10}(-V) I(20°C, 65% RH)	555	550
II(30°C, 80% RH)	550	540
D.R.R.(%) I(20°C, 65% RH)	97	90
II(30°C, 65% RH)	95	88
$E_{1/10}$(lux/sec) I(20°C, 65% RH)	8.3	12.5
II(30°C, 80% RH)	9.5	13.0
Image Quality$^{7)}$ I(20°C, 65% RH)	very good	good
II(30°C, 80% RH)	very good	good
Water Retention	good	good
Printing Durability	5000 prints	4500 prints

The characteristic items described in Table 15 were evaluated in an analogous manner to Example 1 and Examples 20 and 21.

As shown in Table 15, each of the light-sensitive materials exhibited good electrostatic characteristics and image quality, but that of Example 66 in which Resin [A-30] had been jointly used gave better photosensitivity and a reproduced image with a clearer image quality.

When using as an offset master plate, the light-sensitive material of the present invention exhibited good water retention and such a printing durability that there occurred little bad reproduction of fine lines and fine letters on a print when printing 5000 prints in the case of Example 66 and 4500 prints in the case of Example 67. This is probably due to the reproducibility of a reproduced image on an offset master plate.

In comparison of Examples 67 and Comparative Example C, in which the random copolymers of medium molecular weight, known in the art, were used as a binder resin and spectral sensitizing dyes were different in variety, it will be apparent that a good light-sensitive material can be prepared independently of the variety of spectral sensitizing dyes by the joint use of Resin [A] in view of the results of Example 47.

Examples 68 to 75

Example 66 was repeated except using 6.0 g (as solid content) of Resins [A] and 5 g (as solid content) of Resin Grains [L], shown in Table 16, thus preparing light-sensitive materials.

Table 16

Example	Resin [A]	Resin Grains [L]
68	[A-36]	[L-1]
69	[A-37]	[L-3]
70	[A-39]	[L-9]
71	[A-49]	[L-11]
72	[A-50]	[L-12]
73	[A-51]	[L-15]
74	[A-52]	[L-17]
75	[A-53]	[L-18]

Each of the light-sensitive materials of the present invention exhibited excellent electrostatic characteristics, dark decay retention and photosensitivity and gave a clear reproduced image that was free from occurrence of background stains and disappearance of fine lines even under severer conditions, e.g. high temperature and high humidity (30°C, 80% RH).

When printing was carried out using as an offset master plate, 5000 prints were obtained with a clear image without occurrence of background stains.

Examples 76 to 87

Using each of the light-sensitive materials prepared in Examples 48, 49, 51, 52, 54, 55, 57, 58, 62, 64 and 67, master plates for offset printing were prepared by carrying out the etching treatment as in the following.

0.5 mole of each of nucleophilic compounds shown in Table 17, 100 g of each of organic solvents shown in Table 17 and 10 g of Newcol B 4 SN were added to distilled water to 1000 ml, the pH being adjusted to 10.0 to prepare a processing solution. Each of the light-sensitive materials was immersed in a solution prepared by diluting by 2 times ELP-E with distilled water at 25°C for l minute.

The thus resulting plate was subjected to printing under the same printing conditions as in Example 47. thus, 5000 prints were obtained with a good water retention as well as good image quality.

Table 17

Example	Light-sensitive Material	Nucleophilic Compound	Organic Solvent
76	Example 48	sodium sulfite	benzyl alcohol
77	Example 49	monoethanolamine	-do-
78	Example 51	diethanolamine	methyl ethyl ketone
79	Example 52	thiomalic acid	ethylene glycol
80	Example 54	thiosalicylic acid	benzyl alcohol
81	Example 55	taurine	isopropyl alcohol
82	Example 57	4-sulfobenzene-sulfinic acid	benzyl alcohol
83	Example 58	thioglycolic acid	ethanol
84	Example 62	2-mercaptoethyl-phosphonic acid	dioxane
85	Example 64	serine	-
86	Example 66	sodium thio-sulfate	methylethyl ketone
87	Example 67	ammonium sulfite	benzyl alcohol

Example 88

The light-sensitive material obtained in Example 47 was processed by the following oil-desensitizing processing to prepare an offset printing master plate. The light-sensitive material of Example 47 was immersed in a processing solution [E-2] for rendering hydrophilic for 30 seconds, washed with water and passed once through an etching processor using ELP-EX diluted by 10 times with distilled water. When this master plate was subjected to visual estimation of a 20th print from the start of printing in an analogous manner to the estimation of water retention of Example 47, there was found no fog.

The light-sensitive material of Example 47 was subjected to plate making, to oil-desensitization in the same manner as described above and then to estimation of the printing durability in an analogous manner toExample 47. 5000 prints were obtained with a clear image without forming background stains.

As described above, the light-sensitive material of the present invention has an improved hydrophilic property independently of the order of the processings.

According to the present invention, there can be provided an electrophotographic lithographic printing plate precursor having an excellent image and high printing durability even under severer conditions. Furthermore, the lithographic printing plate of the present invention is useful for the scanning exposure system using a semiconductor laser beam.

Claims

(1) An electrophotographic lithographic printing plate precursor comprising a conductive support having provided thereon at least one photoconductive layer containing photoconductive zinc oxide and a binder resin, wherein the photoconductive layer contains resin grains containing at least one polymer component having at least one of functional groups represented by the following General Formula (I) and General Formula (II) and having an average grain diameter of same as or smaller than the maximum grain diameter of the photoconductive zinc oxide grains:

General Formula (I)

$$-W_1-(CH_2)_{n1}-CH=CH_2$$

General Formula (II)

$$-W_2-(CH_2)_{n2}-CH_2CH_2-X$$

wherein $-W_1-$ and $-W_1-$ represent respectively $-SO_2-$, $-CO-$ or $-OOC-$ and n_1 and n_2 represent respectively 0 or 1 and X represents a halogen atom.

(2) An electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the resin grains have a crosslinked structure.

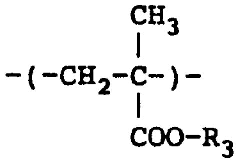
(3) The electrophotographic lithographic print ing plate precursor as claimed in Claim 1, wherein the binder resin contains the following Resin [A]:

Resin [A]

A resin having a weight average molecular weight of 1×10^3 to 2×10^4, containing at least 30% by weight of recurring units represented by the following General Formula (III) as polymeric components and 0.5 to 15% by weight of polymeric components having at least one polar group selected from the group consisting of $-PO_3H_2$,

$-SO_3H$, $-COOH$, $-OH$, and $-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-R_1$ wherein R_1 is a hydrocarbon group or $-OR_2$ (R_2: hydrocarbon group), and a cyclic acid anhydride groups:

General Formula (III)

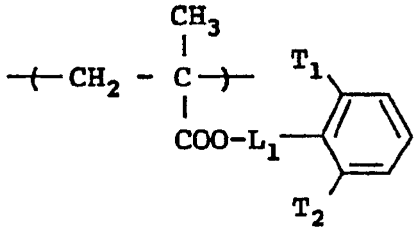


$$-(-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{COO-R_3}{|}}{C}}-)-$$

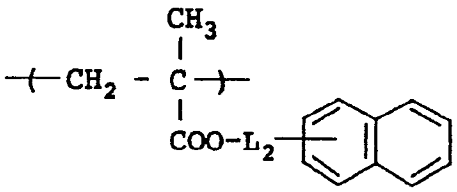
wherein R_3 is a hydrocarbon group.

(4) The electrophotographic lithographic printing plate precursor as claimed in Claim 3, wherein the polymeric component represented by General Formula (III) is at least one of aryl group-containing methacrylate components represented by the following General Formula (IIIa) and General Formula (IIIb)

General Formula (IIIa):



General Formula (IIIb):

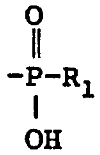


wherein T_1 and T_2 each represents independently a hydrogen atom, a hydrocarbon group containing 1 to 10 carbon atoms, a chlorine atom, $-COR_4$ or $-COOR_5$ (R_4 and R_5 are hydrocarbon groups of 1 to 10 carbon atoms) and L_1 and L_2 each represents direct bonds for bonding -COO- and benzene ring or bonding groups containing 1 to 4 bonding atoms.

(5) The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the binder resin contains the following Resin [A'];

Resin [A']

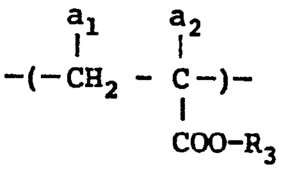
A resin having a weight average molecular weight of 1×10^3 to 2×10^4, containing at least 30% by weight of recurring unit represented by the following General Formula (IV) as polymeric components and having at least one polar group bonded to one end of the polymer main chain, selected from the group consisting of $-PO_3H_2$, $-SO_3H$, -COOH, -OH, and



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-R_1$$

wherein R_1 is a hydrocarbon group or $-OR_2$ (R_2: hydrocarbon group), and cyclic acid anhydride-containing group:

General Formula (IV)

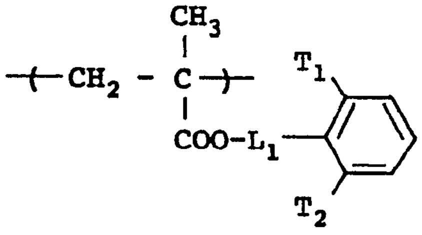


$$-(-CH_2-\overset{\overset{\displaystyle a_1}{|}}{C}\overset{\overset{\displaystyle a_2}{|}}{}\!\!\!\!\!\!\underset{\underset{\displaystyle COO-R_3}{|}}{C}-)-$$

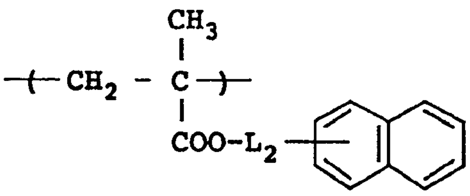
wherein a_1 and a_2 each represents a hydrogen atom, a halogen atom, a cyano group and a hydrocarbon group, $-COO-R_8$ or $-COO-R_8$ via a hydrocarbon group, wherein R_8 represents a hydrocarbon group, and R_3 represents a hydrocarbon group.

(6) The electrophotographic lithographic printing plate precursor as claimed in Claim 5, wherein the polymeric component represented by General Formula (IV) is at least one of aryl group-containing methacrylate components represented by the following General Formula (IIIa) and General Formula (IIIb):

General Formula (IIIa)

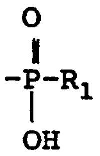


General Formula (IIIb)



wherein T_1 and T_2 each represents independently a hydrogen atom, a hydrocarbon group containing 1 to 10 carbon atoms, a chlorine atom, $-COR_4$ or $-COOR_5$ (R_4 and R_5 are hydrocarbon groups of 1 to 10 carbon atoms) and L_1 and L_2 each represents direct bonds for bonding -COO- and benzene ring or bonding groups containing 1 to 4 bonding atoms.

(7) The electrophotographic lithographic printing plate precursor as claimed in Claim 5, wherein the binder resin further contains 0.5 to 10% by weight of a copolymeric component containing at least one polar group selected from the group consisting of $-PO_3H_2$, $-SO_3H$, -COOH,



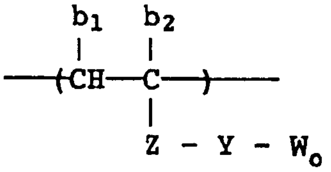
$$-\underset{\underset{\mathrm{OH}}{|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}-R_1$$

and cyclic acid anhydride-containing groups.

(8) The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the resin grains have a maximum grain diameter of at most 10 µm.

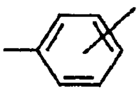
(9) The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the polymer component having at least one of functional groups represented by General Formula (I) and General Formula (II) is represented by the following repeating unit of General Formula (V):

General Formula (V)

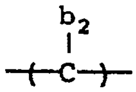


$$-\!\left(\overset{\overset{b_1}{|}}{\mathrm{CH}}-\underset{\underset{Z-Y-W_0}{|}}{\overset{\overset{b_2}{|}}{\mathrm{C}}}\right)\!-$$

wherein Z represents -COO-, -OCO, -O-, -CO-, $-\overset{\overset{r_1}{|}}{\mathrm{CON}}-$, $-\mathrm{SO_2}\overset{\overset{r_1}{|}}{\mathrm{N}}-$ wherein r_1 represents hydrogen atom or a hydrocarbon group, -CONHCOO-, CONHCONH-, $-CH_2COO-$, $-CH_2OCO-$ or

 ,

Y represents a direct bond or organic radical for connecting -Z- and $-W_o$, $\left(Z\text{-}Y\right)$ can directly connect



$$-\!\left(-\overset{\overset{\displaystyle b_2}{|}}{C}-\right)\!-$$

and -W_o, W_o represents the functional group represented by General Formula (I) or (II) and b_1 and b_2 may be same or different, each being a hydrogen atom, a halogen atom, cyano group, an alkyl group or an aryl group.

(10) The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein when processed with a processing solution containing at least one nucleophilic hydrophilic compound, the hydrophilic compound is added to the end of the functional group to render the binder resin hydrophilic.

(11) The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the resin grains containing at least one polymeric component having a functional group represented by General Formula (I) and/or (II) has a molecular weight of 10^3 to 10^6.

(12) The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the polymeric component having the functional group represented by General Formula (I) and/or General Formula (II) is present in a proportion of 30 to 99% by weight to the copolymer.

(13) The electrophotographic lithographic printing plate precursor and claimed in Claim 3, wherein the binder resin further contains a resin having a molecular weight of $3\text{x}10^4$ to $1\text{x}10^6$.

(14) The electrophotographic lithographic printing plate precursor as claimed in Claim 5, wherein the binder resin further contains a resin having a molecular weight of $3\text{x}10^4$ to $1\text{x}10^6$.

(15) The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the binder resin is present in a proportion of 10 to 100parts by weight to 100 parts by weight of the photoconductive zinc oxide.

(16) The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the photoconductive layer further contains a spectral sensitizer.