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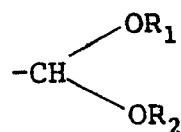
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(57) An electrophotographic lithographic printing plate precursor, in which the effect by the hydrophilic property of non-image areas is further improved, and which is stable during storage even under very severe conditions and capable of readily realizing the hydrophilic property in a short time during processing of rendering hydrophilic is provided, which utilizes an electrophotographic photoreceptor comprising a conductive support having provided thereon at least one photoconductive layer and further having provided thereon a surface layer as an outermost layer, wherein said surface layer comprises at least one resin containing at least one polymeric component having at least one of formyl group and functional groups represented by the following General Formula (I):

General Formula (I)



wherein R₁ and R₂ each represent, same or different, hydrocarbon groups or R₁ and R₂ are organic residual radicals which are combined with each other to form a ring.

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FIELD OF THE INVENTION

This invention relates to an electrophotographic lithographic printing plate precursor and, more particularly to a lithographic printing plate precursor having a photoconductive layer on which a surface layer having specific properties is provided.

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BACKGROUND OF THE INVENTION

A number of offset printing plate precursors 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 (e.g., zinc oxide) and a resin binder, is subjected to an ordinary electrophotographic processing to form a highly lipophilic toner image thereon. The surface of the photoreceptor is then treated with an oil-desensitizing solution called etching solution to selectively render non-image areas hydrophilic to obtain an offset printing plate.

Requirements of offset printing plate precursors for obtaining satisfactory prints are such that an original should be reproduced faithfully on the photoreceptor; the surface of a photoreceptor should have affinity with an oil-desensitizing solution, so as to render non-image areas sufficiently hydrophilic and, at the same time, should have water resistance; and that 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 hold the hydrophilic properties enough to be freed from stains even on printing a large number of prints.

For particular use as an offset printing plate precursor, formation of background stains due to insufficient oil-desensitization presents a serious problem. In order to solve this problem, various resins as binders for zinc oxide have been proposed. For example, such resins have been disclosed in Japanese Patent Publication No. 31011/75, Japanese Patent Laid-Open Publication Nos. 54027/78, 20735/79, 202544/82, and 68046/83. Nevertheless, actual evaluations of these resins proposed for improving oil-desensitization have revealed that none were satisfactory in terms of stain resistance and printing durability.

On the other hand, a photoconductive layer comprising particles of an organic photoconductive compound and a binder resin can be formed on a grained aluminum base. Printing plate precursors of this type can be produced by forming a toner image on a photo sensitive layer through the known electrophotographic processing such as described above and further removing the non-image areas by eluting with a processing solution, whereby the aluminum base corresponding to the non-image areas is exposed to form hydrophilic areas. The photosensitive layer using the organic photoconductive compound comprises, for example, an oxadiazole compound or oxazole compound and an alkali-soluble binder resin (e.g., a styrene-maleic anhydride copolymer, etc.), as disclosed in Japanese Patent Publication Nos. 17162/62 and 39405/71 and Japanese Patent Laid-Open Publication Nos. 2437/77 and 107246/81; or a phthalocyanine pigment or azo pigment and an alkali-soluble phenolic resin as disclosed in Japanese Patent Laid-Open Publication Nos. 105254/80, 16125/70, 150953/83, and 162961/83.

However, since the above-mentioned plate making process involves removal of the photosensitive layer corresponding to the non-image areas by dissolution, it requires a large-size apparatus and is too time-consuming to achieve a reasonable production rate.

It has been proposed to provide a specific resin layer capable of being rendered hydrophilic on a usual electrophotographic photoreceptor as described in Japanese Patent Publication No. 5606/70. According to this system, a surface layer comprising a vinyl ether-maleic anhydride copolymer and a hydrophobic resin compatible with the copolymer is provided on the photosensitive layer. After toner image formation, the non-image areas of the surface layer can be rendered hydrophilic by treating with an alkali to hydrolytically opening the acid anhydride ring.

However, since the vinyl ether-maleic anhydride copolymer used in the surface layer becomes water-soluble upon ring-opening, the surface layer is seriously inferior in water resistance even though the vinyl ether-maleic anhydride copolymer is combined with a compatible hydrophobic resin. Therefore, the printing durability of the resulting printing plate was about 500 to 600 prints at most.

It has also been proposed to form a surface layer capable of being rendered hydrophilic, which comprises silylated polyvinyl alcohol as main component and a crosslinking agent as disclosed in Japanese

Patent Laid-Open Publication Nos. 90343/85, 159756/85, and 217292/86. According to this proposal, after toner image formation, the surface layer can be rendered hydrophilic by hydrolysis of the silylated polyvinyl alcohol on the non-image areas. Further, in order to retain fine strength after becoming hydrophilic, the degree of silylation of polyvinyl alcohol is controlled, and the remaining hydroxyl group is crosslinked by the crosslinking agent.

The above publication describes that the provision of such a surface layer would prevent background stains of prints and increase printing durability. However, it has been shown by evaluation of actual use that the resulting printing plate still does not satisfy the stain resistance requirement. Further, due to the nature of the high-molecular reaction, it is difficult to stably produce the silylated polyvinyl alcohol having a controlled degree of silylation by silylating polyvinyl alcohol with a silylating agent to a desired degree. In addition, due to the limitations on the chemical structure of the hydrophilic polymer, it is difficult to exclude all adverse influences of the surface layer upon the functions of an electrophotographic photoreceptor, such as charging properties, quality of a reproduced image (e.g., dot reproducibility and resolving power of image areas, resistance to background fog of nonimage areas, etc.), and light sensitivity.

Furthermore, it has hitherto been studied to use, as a surface layer resin, resins containing functional groups capable of forming hydrophilic groups through decomposition jointly with compounds for crosslinking the resins in the light-sensitive layers. For example, the former are those having functional groups capable of forming hydroxyl groups through decomposition as disclosed in Japanese Patent Application Nos. 8217/1988 and 90185/1988, those having functional groups capable of forming carboxyl groups through decomposition as disclosed in Japanese Patent Application Nos. 112607/1988 and 113458/1988 and those having functional groups capable of forming thiol groups, amino groups, phosphono groups or sulfo groups through decomposition as disclosed in Japanese Patent Application Nos. 134357/1988 and 135705/1988.

These resins are those which form hydrophilic groups through hydrolysis or hydrogenolysis with an oil-desensitizing solution or dampening water used during printing. When using them as a surface layer resin for a lithographic printing plate precursor, a number of prints with clear image quality and without background stains can be obtained, since the hydrophilic property of non-image areas is further increased by the above described hydrophilic groups formed through decomposition 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, and a crosslinking structure is formed in the surface layer so that the resin rendered hydrophilic becomes water-insoluble, keeps water and swells through the crosslinking effect to give retention of water and to maintain the surface layer sufficiently hydrophilic.

In the resin of such a type as to form a hydrophilic group by the above described decomposition reaction, the carboxyl group or hydroxyl group previously masked with a protective group is subjected to decomposition reaction with a processing solution to release the protective group. For the resin 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.

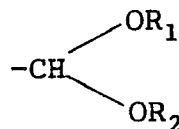
However, it is found that provision of a hydrophilic group-forming functional group (protective group) which is stably present without decomposition even under severer conditions, e.g., during storage at a high temperature and high humidity for a long time, results in difficulty in a rapid decomposition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

SUMMARY OF THE INVENTION

The present inventors have made studies in the field of electrophotographic lithographic printing plate precursors, with the aim of overcoming or reducing defects in the prior art, as noted above.

The present invention provides an electrophotographic lithographic printing plate precursor utilizing an electrophotographic photoreceptor comprising a conductive support having provided thereon at least one photoconductive layer and further provided thereon a surface layer as an outermost layer, wherein said surface layer comprises, as a predominant component, at least one resin containing at least one polymeric component having a formyl group and/or functional group represented by the following General Formula (I):

General Formula (I)



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10 wherein R_1 and R_2 each represent, same or different, hydrocarbon groups or R_1 and R_2 are organic residual radicals which are combined with each other to form a ring.

DETAILED DESCRIPTION OF THE INVENTION

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In the present invention, the resin containing at least one polymeric component having the above described formyl group and/or functional group represented by General Formula (I) can previously be crosslinked and in this case, the resin has water proof property, which is preferable when realizing the hydrophilic property through reaction with a processing solution for rendering hydrophilic.

20 The resin containing at least one polymeric component having the above described formyl group and/or functional group represented by General Formula (I) may be a resin further containing at least one functional group causing a hardening reaction by heat and/or light.

25 In a preferable embodiment of the present invention, in addition to the resin containing at least one polymeric component having formyl group and/or a functional group represented by General Formula (I), which will hereinafter be referred to as Resin A sometimes, at least one heat and/or light hardenable resin as Resin B is incorporated optionally with a crosslinking agent.

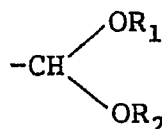
30 The feature of the electrophotographic lithographic printing plate precursor having a photoconductive layer according to the present invention consists in that the resin in the surface layer as the outermost layer comprises Resin A containing at least one of formyl group and functional groups represented by General Formula (I) and optionally Resin B consisting of a heat and/or light hardenable resin, preferably being at least partly crosslinked, whereby when processing with a processing solution containing at least one hydrophilic compound with nucleophilic reactivity, the hydrophilic compound with nucleophilic reactivity is additionally reacted with the end of the formyl group or the functional group represented by General Formula (I) of Resin A and the surface layer can thus reveal hydrophilic property while simultaneously, it is rendered not or hardly soluble in water with maintaining the hydrophilic property because of the crosslinked structure in the resin.

35 Thus, the lithographic printing plate precursor of the present invention has various advantages that an image faithful to an original can be reproduced 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 improved.

40 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.

45 The resin of the present invention or Resin A contains at least one copolymeric component containing at least one of formyl group and functional groups represented by General Formula (I):

General Formula (I)



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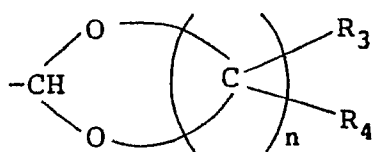
55 wherein R_1 and R_2 each represent, same or different, hydrocarbon groups or R_1 and R_2 each represent organic residual radicals which are connected with each other to form a ring.

When R_1 and R_2 each represent hydrocarbon groups, they are preferably optionally substituted aliphatic groups containing 1 to 12 carbon atoms, for example, optionally substituted alkyl groups containing

1 to 12 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, methoxymethyl, ethoxymethyl, 2-hydroxyethyl, 2-chloroethyl, 2-bromoethyl, 1-fluoroethyl, 2-cyanoethyl, 2-methoxyethyl, 2-ethoxyethyl, 3-hydroxypropyl, 3-methoxypropyl groups, etc., optionally substituted alkenyl groups containing 2 to 12 carbon atoms, such as propenyl, butenyl, hexenyl, octenyl, decenyl, dodecenyl groups, etc., optionally substituted aralkyl groups containing 7 to 12 carbon atoms, such as benzyl, phenethyl, 3-phenylpropyl, naphthylmethyl, 2-naphthylethyl, methylbenzyl, dimethylbenzyl, trimethylbenzyl, methoxybenzyl, dimethoxybenzyl, chlorobenzyl, bromobenzyl, fluorobenzyl, dichlorobenzyl groups, etc., optionally substituted alicyclic groups containing 3 to 12 carbon atoms, such as cyclopentyl, cyclohexyl, cycloheptyl, adamantyl groups, etc. and the like.

When R_1 and R_2 represent organic residual groups which are connected with each other to form a ring, they are preferably functional groups represented by the following general formula (Ia), that is, cyclic acetal groups:

General Formula (Ia)

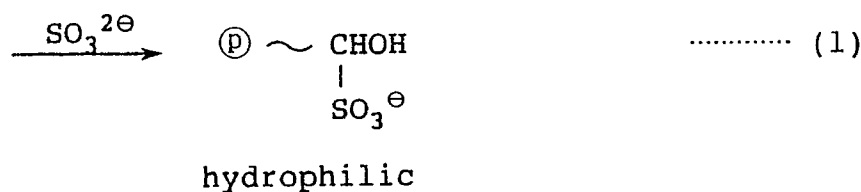
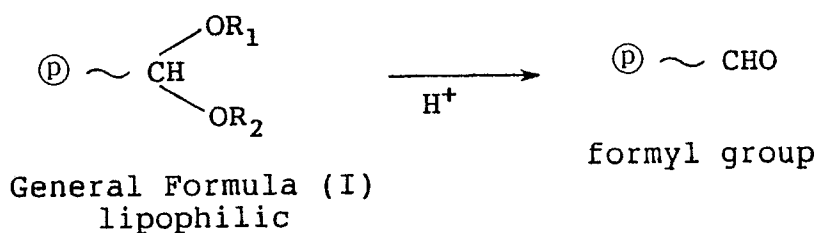


wherein R_3 and R_4 each represent, same or different, hydrogen atoms, optionally substituted hydrocarbon groups containing 1 to 12 carbon atoms or $-OR_5$ groups wherein R_5 represents an optionally substituted hydrocarbon group containing 1 to 12 carbon atoms and n represents an integer of 1 to 4.

Preferred examples of the optionally substituted hydrocarbon groups containing 1 to 12 carbon atoms, as R_3 , R_4 and R_5 , include aliphatic groups having the same contents as those defined in R_1 and R_2 and aromatic groups such as phenyl, tolyl, xylyl, methoxyphenyl, chlorophenyl, bromophenyl, methoxycarbonylphenyl, dimethoxyphenyl, chloromethylphenyl, naphthyl groups, etc.

In General Formulae (I) and (Ia), more preferably, R_1 to R_5 are aliphatic groups, for example, alkyl groups of 1 to 6 carbon atoms, alkenyl groups of 3 to 6 carbon atoms and aralkyl groups of 7 to 9 carbon atoms, and n is an integer of 1 to 3.

As described above, the surface layer resin of the present invention contains a polymeric component containing formyl group and/or a functional group represented by General Formula (I) and is modified from lipophilic to hydrophilic by processing with a processing solution containing a hydrophilic compound with nucleophilic reactivity. The mechanism of rendering hydrophilic is shown by the following reaction formula (I), for example, as to a case of using sulfite ion as the hydrophilic compound with nucleophilic reactivity. $\textcircled{P}$ represents a resin part except the formyl group or functional group of General Formula (I).



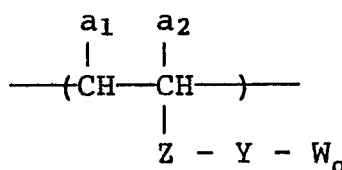
That is to say, Resin A of the present invention has the feature that only when non-image areas as a

lithographic printing plate precursor is subjected to oil-desensitization, it is reacted with a nucleophilic compound in a processing solution as described above, whereby the hydrophilic group is added to the end thereof and it is rendered hydrophilic. Since Resin A is 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 formyl group is a functional group which is very rapidly reactive with a nucleophilic compound, it is possible to rapidly render hydrophilic.

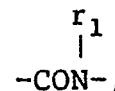
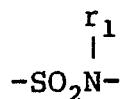
Furthermore, the functional group represented by General Formula (I) is a precursor of formyl group and this precursor can readily be converted into formyl group through acid decomposition as shown by Reaction Formula (1). As well known in the art, this functional group is very excellent in storage stability.

Specific, but not limiting, examples of the copolymer constituent containing the formyl group and/or the functional group represented by General Formula (I) used in the present invention include those represented by the following repeating unit of General Formula (II):

General Formula (II)



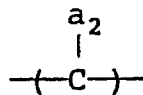
wherein Z represents -COO-, -OCO-, -O-, -CO-,



wherein R_1 represents hydrogen atom or a hydrocarbon group, -CONHCOO-, -CONHCONH-, -CH₂COO-, -CH₂OCO-or

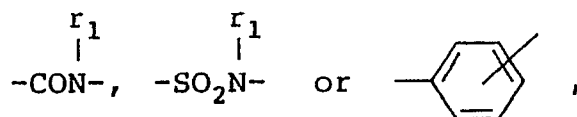


Y represents a direct bond or organic radical for connecting -Z- and -W₀, {Z-Y} can directly connect



and -W₀, W₀ represents the formyl group or the functional group represented by General Formula (I) and a_1 and a_2 may be same or different, each being hydrogen atom, a halogen atom, cyano group, an alkyl group or an aryl group.

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



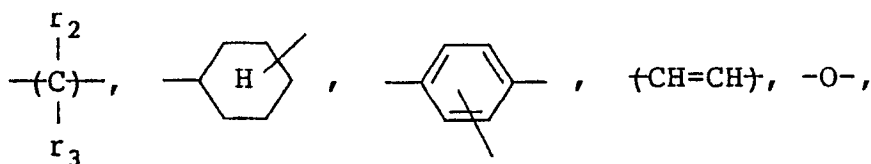
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wherein R_1 represents hydrogen atom, an optionally substituted alkyl group of 1 to 8 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, 2-chloroethyl, 2-bromoethyl, 2-cyanoethyl, 2-methoxyethyl, 2-hydroxyethyl, 3-bromopropyl 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.

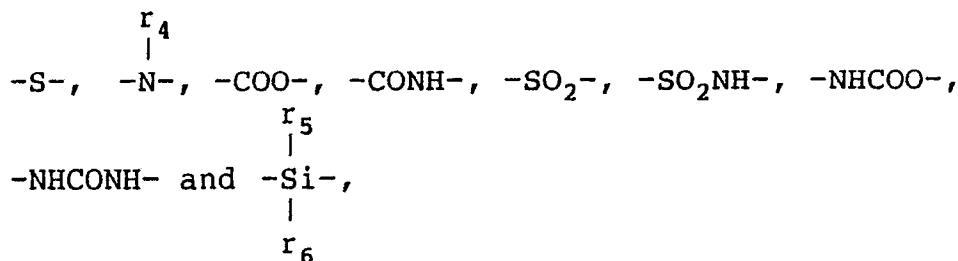
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Y represents a direct bond or an organic radical for connecting -Z- and -W₀. When Y represents the organic radical, this radical is a carbon-carbon bond, between which hetero atoms (including oxygen, sulfur and nitrogen atom) may be present, which specific examples include

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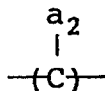
individually or in combination of these groups, wherein r_2 , r_3 , r_4 , r_5 and r_6 have the meaning as the foregoing r_1 .

a_1 and a_2 may be the same or different, each being a hydrogen atom, a halogen atom (e.g., chlorine, bromine), a cyano group, a hydrocarbon residue (e.g., an optionally 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, phenethyl, etc., and an aryl group such as phenyl, tolyl, xylyl, chlorophenyl, etc.

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In addition, the linkage moiety {Z-Y} in General Formula (II) may directly connect the moiety

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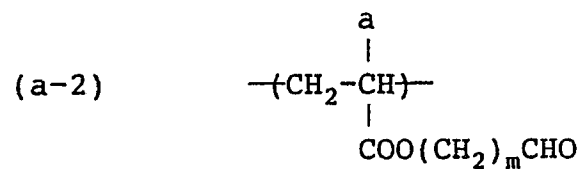
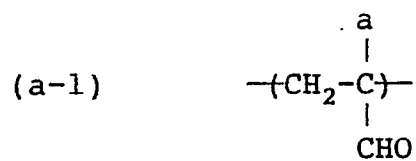
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to the moiety -W₀.

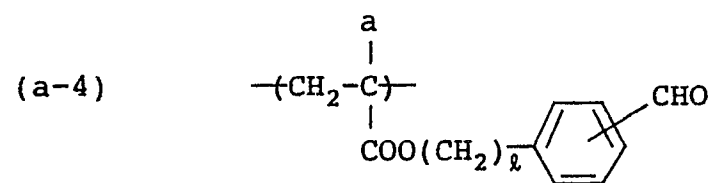
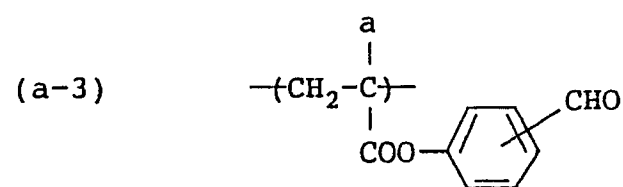
Specific, but not limiting examples of the polymeric constituent containing the formyl group will be illustrated below. In Examples (a-1) to (a-15), a represents -H or -CH₃.

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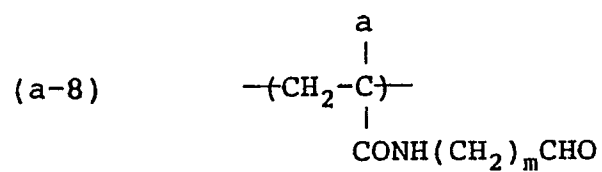
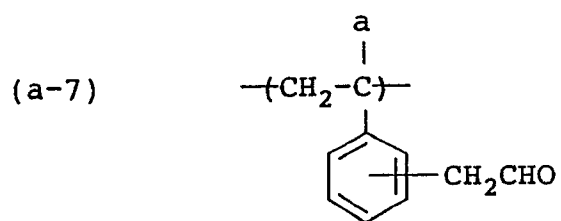
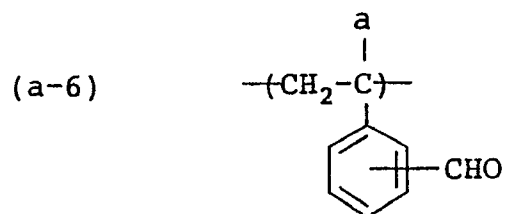
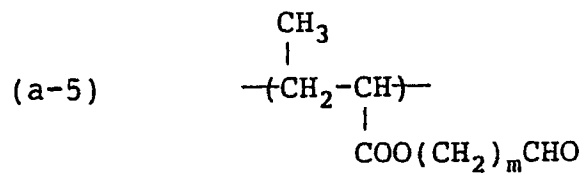
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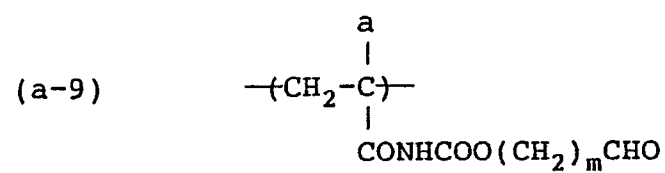
m: integer of 1~6



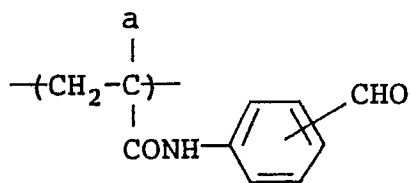
ℓ: integer of 1~4



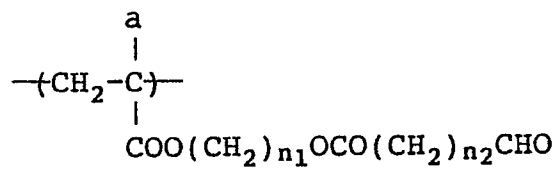
m: integer of 1~6



(a-10)

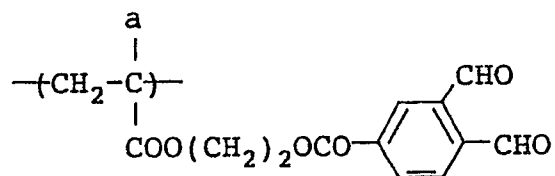


(a-11)

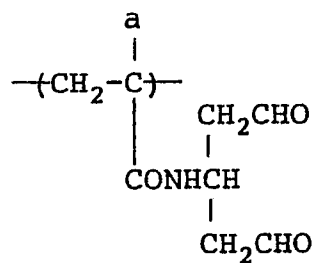


n_1 : integer of 1~4
 n_2 : integer of 1~3

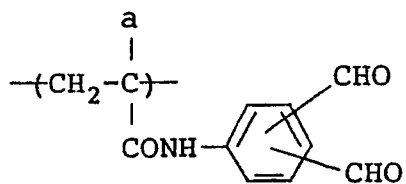
(a-12)



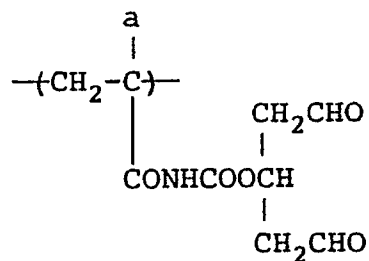
(a-13)



(a-14)

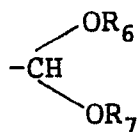


(a-15)

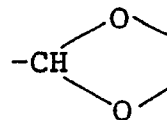


Specific, but not limiting examples of the functional group represented by General Formula (I) of the present invention will be illustrated below. In Examples (a'-1) to (a'-9), R_6 and R_7 each represent alkyl groups of 1 to 4 carbon atoms or $-\text{CH}_2\text{C}_6\text{H}_5$, and R_8 represents an alkyl group of C_1 to C_4 , $-\text{CH}_2\text{C}_6\text{H}_5$ or phenyl group.

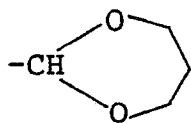
(a'-1)



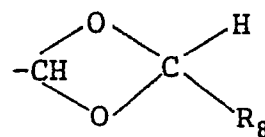
(a'-2)



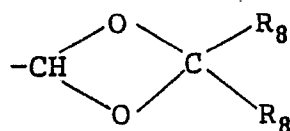
(a'-3)



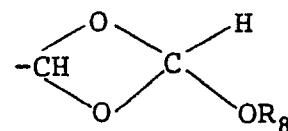
(a'-4)



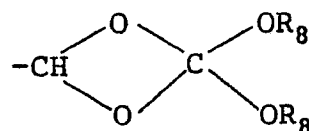
(a'-5)



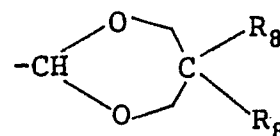
(a'-6)



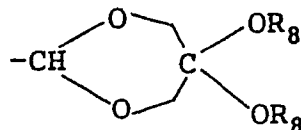
(a'-7)



(a'-8)



(a'-9)



Resin A containing the polymeric component containing formyl group and/or the functional group represented by General Formula (I) as described above can be synthesized by any of known methods, for example, by a method comprising subjecting to polymerization reaction a monomer containing formyl group or the functional group represented by General Formula (I) and a polymerizable double bond group in the molecule (e.g. monomer corresponding to the recurring unit of General Formula (II)) and a method comprising reacting a low molecular compound containing formyl group or the functional group represented by General Formula (I) 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, Resin A containing formyl group can be synthesized by synthesizing the resin containing the functional group represented by General Formula (I) and then subjecting to an acid decomposition.

In the above described synthesis by the monomer synthesis or polymer reaction, the formyl- or acetal-formation reaction can readily be carried out in known manner.

Synthesis of formyl group-containing compounds is described, for example, in Nippon Kagakukai Edition, Shin-Jikken Kagaku Koza, Vol. 14, 636 (1978), published by Maruzen KK, E. Muller "Methoden der Organischen Chemie", page 13 (1954), published by Georg Thieme Verlag, and Nippon Kagakukai Edition, Jikken Kagaku Koza, Vol. 19, page 231 (1957), published by Maruzen KK.

Synthesis of acetal group-containing compounds is described, for example, in Nippon Kagakukai Edition, Shin-Jikken Kagaku Koza, Vol. 14, page 611 (1978), published by Maruzen KK.

In Resin A of the present invention, the polymeric component containing formyl group and/or the functional group represented by General Formula (I) is generally in a proportion of 20 to 99% by weight, preferably 40 to 95% by weight based on the whole copolymer in a case where Resin A is of the copolymer. Preferably, this resin has a molecular weight of 10^3 to 10^6 , particularly, 3×10^3 to 5×10^5 .

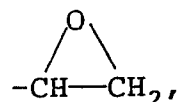
Resin A of the present invention may be crosslinked, at least in part, in an electrophotographic lithographic printing plate precursor. As such a resin, there can be used a previously crosslinked resin

during coating a light-sensitive layer-forming material in the plate-making step or a resin containing crosslinking functional groups causing a hardenable reaction by heat and/or light, which can be crosslinked in a process for producing a lithographic printing plate precursor (e.g. during drying). These resins can be used in combination.

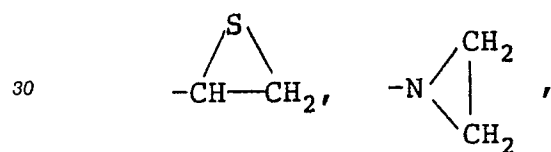
5 When using such a resin that at least a part of the polymer is previously crosslinked (resin having a crosslinked structure in the polymer), it is preferably a resin which is hardly soluble or insoluble in acidic or alkaline solutions when the above described functional group contained in the resin 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.

10 Introduction of a crosslinked structure in a polymer can be carried out by known methods, that is, a method comprising subjecting a monomer containing at least one of formyl group and the groups of General Formula (I) to polymerization reaction in the presence of a multifunctional monomer and a method comprising incorporating functional groups for effecting a crosslinking reaction in the polymer, then subjecting the polymer to polymer reaction with a compound containing formyl group or the group of

15 General Formula (I) and effecting the crosslinking.
Specifically, Resin A of the present invention can be prepared by a method comprising polymerizing a monomer containing two or more polymerizable functional groups (multifunctional monomer) with a monomer containing at least one of formyl group and the functional group General Formula (I) of the present invention, or a method comprising polymerizing the multifunctional monomer with a monomer
20 containing a polar group such as -OH, -Cl, -Br, -I, -NH₂, -COOH, -SH,



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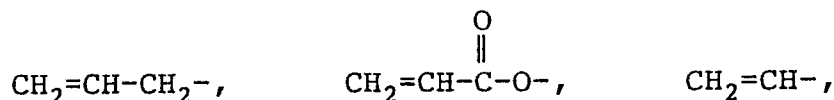


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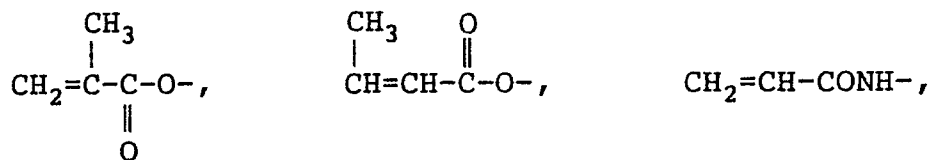
35 -N=C=O, -COCl, -SO₂Cl, etc., into which formyl group or the functional group of General Formula (I) can be introduced, to prepare a copolymer and then introducing therein a low molecular compound containing formyl group or the functional group of General Formula (I) by polymer reaction.

Examples of the polymerizable functional group are:

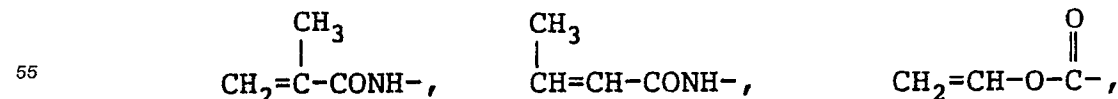
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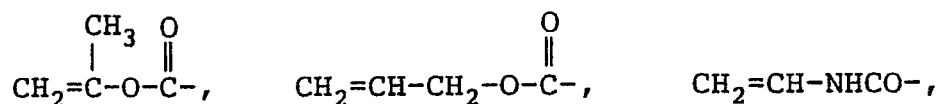
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$\text{CH}_2=\text{CH}-\text{CH}_2-\text{NHCO}-$, $\text{CH}_2=\text{CH}-\text{SO}_2-$, $\text{CH}_2=\text{CH}-\text{CO}-$, $\text{CH}_2=\text{CH}-\text{O}-$, $\text{CH}_2=\text{CH}-\text{S}-$.

Any of monomers containing two or more same or different ones of these polymerizable functional groups can be used in the present invention.

10

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.

15

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As the monomer having two or more 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, itaconyloxypropionic acid and itaconyloxypropionic 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, vinylloxycarbonylmethyl methacrylate, 2-(vinylloxycarbonyl)ethyl ester of acrylic acid, N-allylacrylamide, N-allyl methacrylamide, N-allylitaconamide, methacryloylpropionic 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.

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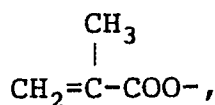
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The monomer containing two or more polymerizable functional groups of the present invention is generally used in a proportion of at most 10mole%, preferably at most 5 mole% to all monomers, which is polymerized to form a previously crosslinked resin.

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In the case of a polymer containing formyl group, however, it is preferable not to use $\text{CH}_2=\text{CH}-\text{COO}-$,

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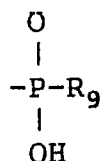


$\text{CH}_2=\text{CH}-\text{CONH}-$, $\text{CH}_2=\text{CH}-\text{SO}_2-$ and $\text{CH}_2=\text{CH}-\text{CO}-$ as the foregoing polymerizable functional group.

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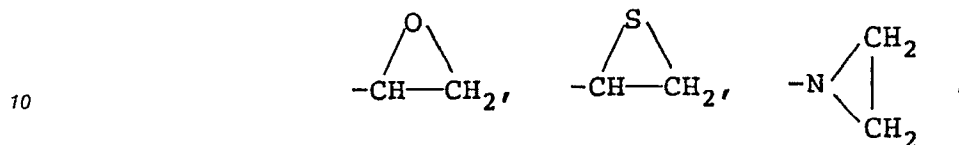
In the method comprising crosslinking a polymer containing functional groups for effecting a crosslinking reaction by polymer reaction, on the other hand, the functional group can be any group capable of causing a chemical reaction among the molecules to form chemical linkages. That is, the reaction mode of forming linkages among molecules by a condensation reaction or addition reaction, or crosslinkings by a polymerization reaction through heat and/or light can be utilized. Specifically, the functional groups include at least one combination selected from the group A consisting of functional groups containing dissociable hydrogen atoms, for example, $-\text{COOH}$, $-\text{PO}_3\text{H}_2$,

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wherein R_9 represents an aliphatic group, preferably optionally substituted linear or branched alkyl group containing 1 to 12 carbon atoms, such as methyl, ethyl, propyl, chloromethyl, dichloromethyl, trichloromethyl, trifluoromethyl, butyl, hexyl, octyl, decyl, hydroxyethyl or 3-chloropropyl group, or $-OR_9$, wherein R_9 has the same meaning as R_9 , $-OH$, $-SH$ and $-NH \cdot R_{10}$ wherein R_{10} represents hydrogen atom or an alkyl group containing 1 to 4 carbon atoms, such as methyl, ethyl, propyl or butyl group, and the group consisting of



$-NCO$ and $-NCS$ and cyclic dicarboxylic acid anhydrides, or $-CONHCH_2OR_{11}$ wherein R_{11} represents hydrogen atom or an alkyl group containing 1 to 6 carbon atoms, such as methyl, ethyl, propyl, butyl or hexyl group, or polymerizable double bond groups.

Examples of the polymerizable double bond group include those of the foregoing polymerizable functional group.

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-1, published by Sogogijutsu Center, 1985, Takayuki Otsu "Synthesis and Design of Acrylic Resins and Development of New Uses (Akuriru Jushi no Goseisekkei to Shin-yoto Kaihatsu)" published by Chubu Keiei Kaihatsu Center Shuppanbu, 1985, 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 Pub., 1982.

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

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

These vinyl compounds include those described in, for example, Kobunshi Gakkai Edition "Polymer Data Handbook -Kisohen-", published by Baihukan, 1986, for example, acrylic acid, α and/or β -substituted acrylic acid such as α -acetoxymethyl, α -acetoxymethyl, α -(2-aminomethyl), 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 or crosslinking functional groups in the substituents.

In Resin A of the present invention, the content of "the copolymeric components containing the hardenable functional groups" is preferably 1 to 80% by weight, more preferably 5 to 50 % by weight based on the whole quantity of the surface layer resin.

In a preferred embodiment of the present invention, Resin A of the present invention contains functional groups capable of undergoing a crosslinking reaction with Resin B by heating or irradiating. As these functional groups, there can be used those similar to the following crosslinking functional groups contained in Resin B (heat and/or light-hardenable functional groups: sometimes referred to as hardenable functional groups). In the case of Resin A containing the hardenable functional groups, "the content of copolymeric constituents containing the hardenable functional groups" is preferably 1 to 20% by weight, more preferably 3 to 10% by weight in Resin A.

In the present invention, incorporation of at least one functional group selected from the group consisting of the hardenable functional groups in Resin A is carried out by a method comprising introducing

a low molecular, hardenable functional group-containing compound into a polymer containing formyl group and/or functional groups represented by General Formula (I) by polymer reaction, or a method comprising copolymerizing at least one monomer corresponding to the copolymeric component containing at least one of the hardenable functional groups with a monomer corresponding to the repeating unit represented by General Formula (II) (monomer synthesis).

The former polymer reaction can be carried out by any of known methods, for example, Nippon Kagakukai Edition, Shin-Jikken Kagakukoza, Vol. 14, "Synthesis and Reaction of Organic Compounds (I) to (V) (Yuki Kagobutsu no Gosei to Hanno)" published by Maurzen KK, 1978, and Yoshio Iwakura and Keisuke Kurita "Reactive Polymers (Hannosei Kobunshi)" published by Kohdansha (1977).

As a monomer corresponding to the copolymeric component containing the hardenable functional group, used in the latter monomer synthesis method, there can be used vinyl compounds containing the crosslinking functional groups, which are copolymerizable with the polymeric component containing the hydrophilic group-forming functional group in Resin A (e.g. compound corresponding to General Formula (II)), such as those exemplified above as the monomer corresponding to the copolymeric component containing the crosslinking functional groups.

Resin B used in the present invention will now be illustrated in detail. Resin B is a hardenable resin causing a crosslinking reaction by heat and/or light, preferably causing a crosslinking reaction with the functional group described above in Resin A, and includes any of resins containing "heat and/or light-hardenable functional groups (sometimes referred to as hardenable functional groups in brief)" which will hereinafter be illustrated. As illustrated above, these hardenable functional groups may be contained in Resin A.

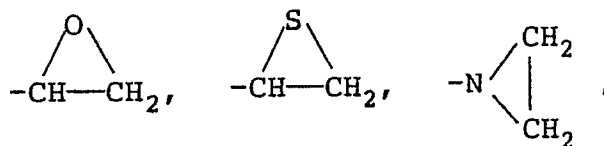
As the light-hardenable functional group of the hardenable functional groups of the present invention, there can be used functional groups used in light-sensitive resins of the prior art as light-hardenable resins, for example, describe in Hideo Inui and Gentaro Nagamatsu "Light-sensitive Polymers (Kankosei Kobunshi)" Kodansha KK, 1977, Takahiro Tsunoda "New Light-sensitive Resins (Shin-kankosei Jushi)" published by Insatsu Gakkai Shuppanbu, 1981, G.E. Green and B.P. Strark "J. Macro. Sci. Reas. Macro. Chem." C 21 (2), 187-273 (1981-82) and C.G. Rattey "Photopolymerization of Surface Coatings" published by A. Wiley Interscience Pub., 1982).

As the heat-hardenable functional group of the hardenable functional groups of the present invention, there can be used functional groups, for example, cited in the literatures described above to exemplify the polymerizable double bond groups.

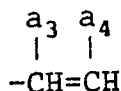
Specifically, there are functional groups (Group A) each having dissociable hydrogen and functional groups (Group B) capable of chemically reacting and bonding with Group A, or polymerizable double bond groups, which will hereinafter be exemplified.

As the functional group (Group A) having dissociable hydrogen atom, for example, there are given -OH group, -SH group, -NH₂ group, -NHR₉ group wherein R₉ represents a hydrocarbon group, e.g., optionally substituted alkyl group containing 1 to 10 carbon atoms, such as methyl, ethyl, propyl, butyl, hexyl, octyl, decyl, 2-chloroethyl, 2-methoxyethyl, 2-cyanoethyl, etc., optionally substituted cycloalkyl group containing 4 to 8 carbon atoms, such as cycloheptyl, cyclohexyl, etc., optionally substituted aralkyl group containing 7 to 12 carbon atoms, such as benzyl, phenethyl, 3-phenylpropyl, chlorobenzyl, methylbenzyl, methoxybenzyl group, etc., and optionally substituted aryl group such as phenyl, tolyl, xylyl, chlorophenyl, bromophenyl, methoxyphenyl, naphthyl group, etc., -COOH group, -PO₃H₂ group and the like.

As the functional group (Group B) capable of bonding with the functional group having dissociable hydrogen, for example, there are given groups of



-CONHCH₂OR₁₀ wherein R₁₀ represents hydrogen atom or an alkyl group having 1 to 8 carbon atoms, such as methyl, ethyl, propyl, butyl, hexyl, octyl group, etc., -N=C=O and



5

wherein a_3 and a_4 each represent hydrogen atoms, halogen atoms such as chlorine, bromine atom, etc., or alkyl groups containing 1 to 4 carbon atoms, such as methyl, ethyl group, etc.

10

A crosslinked structure can be formed by chemical bonding of the functional groups, Groups A and B, for example, selected so as to combine at least one member respectively selected from Groups A and B shown in the following Table 1:

15

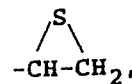
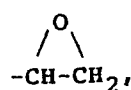
Table 1

20

Functional Groups (Group A)
(functional groups having
dissociable hydrogen atoms)

Functional Groups (Group B)
(functional groups capable of
chemically reacting and
bonding with Group A)

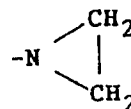
-OH, -SH or -NHR'



25

wherein R' is H or

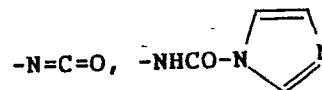
hydrocarbon,



30

-COOH,

-PO₃H



-N=C=S,

35

cyclic dicarboxylic acid

anhydrides

40

The crosslinking reaction can be carried out by a polymerizable reaction using polymerizable double bond groups, exemplified above as the polymerizable functional groups.

As the monomer containing "the heat and/or light hardenable functional group" according to the present invention, there can be used any of monomers containing hardenable functional groups in the substituents, which are copolymerizable with the monomer corresponding to the foregoing "polymeric component represented by General Formula (II)".

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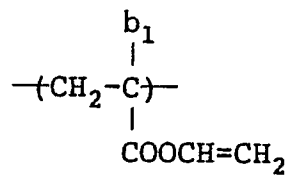
Examples of the copolymeric component containing the "heat and/or light-hardenable functional group" are the following repeating units (b-1) to (b-26):

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55

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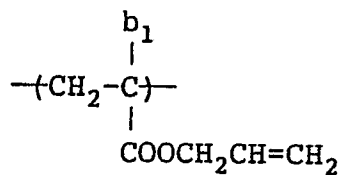
(b-1)



b_1 : -H, CH_3 (b_1 : same in the following)

10

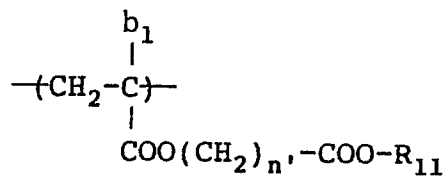
(b-2)



15

20

(b-3)



25

R_{11} : $-\text{CH}=\text{CH}_2$, $-\text{CH}_2\text{CH}=\text{CH}_2$

(R_{11} : same in the following)

30

n' : integer of 1~11

35

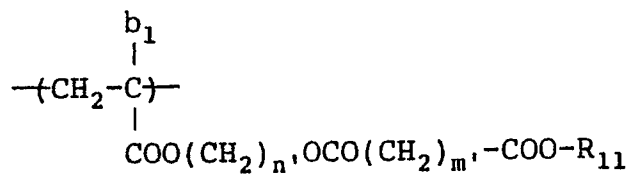
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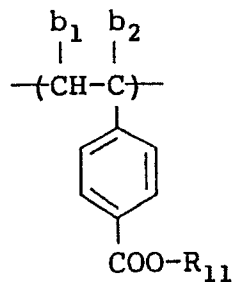
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(b-4)



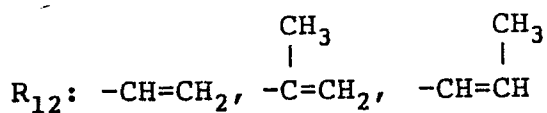
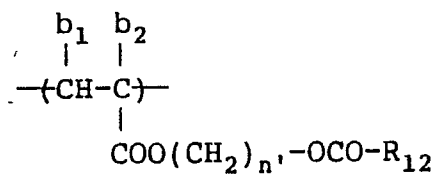
n', m' : integer of 1~11

(b-5)



b_2 : H, CH₃ (b_2 : same in the following)

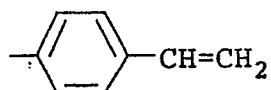
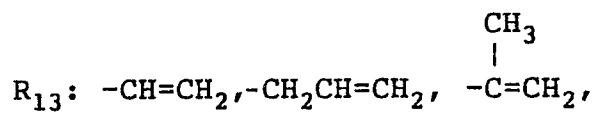
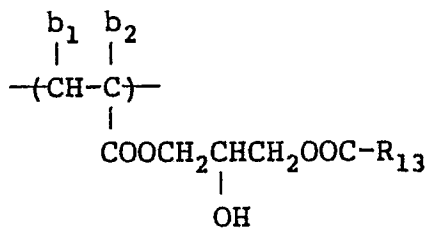
(b-6)



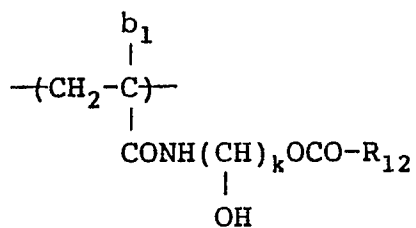
(R_{12} : same in the following)

n' : integer of 1~11

(b-7)

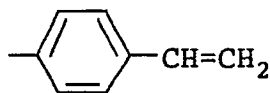
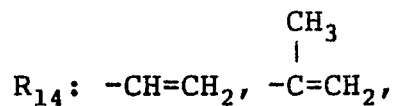
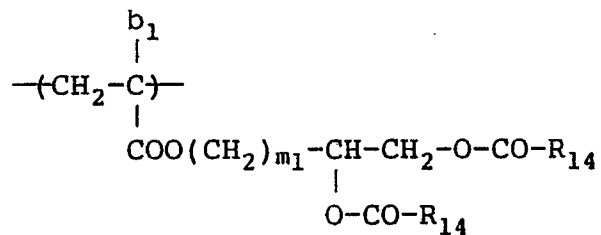
(R₁₃: same in the following)

(b-8)

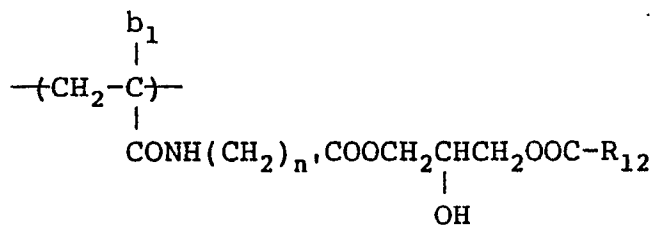


k: integer of 1~10

(b-9)

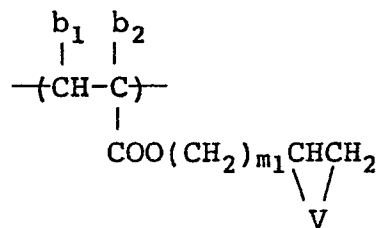
(R₁₄: same in the following)m₁: integer of 1~4

(b-10)

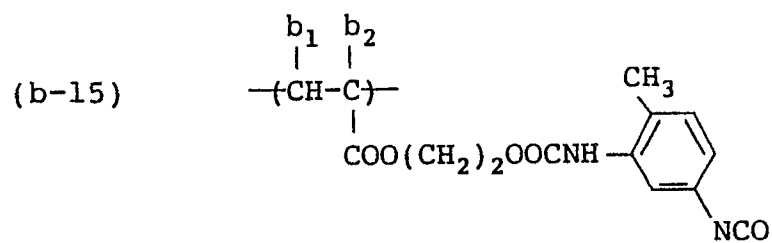
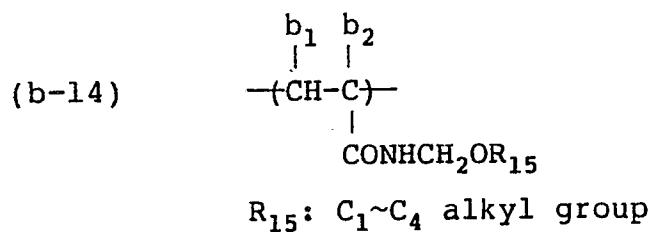
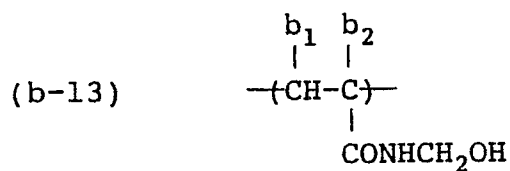
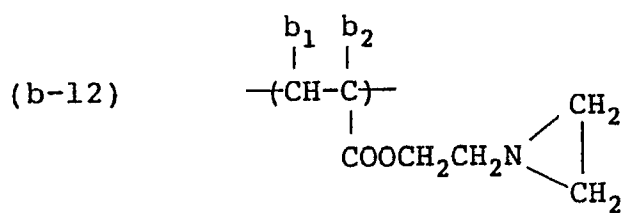


n': integer of 1~11

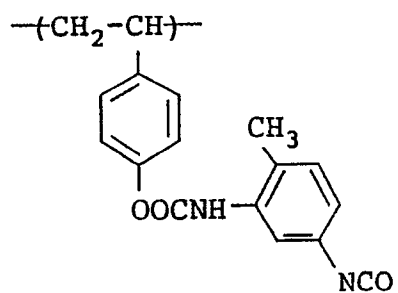
(b-11)

m₁: integer of 1~4

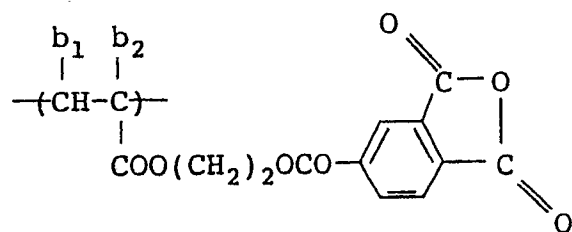
V: -S-, -O-



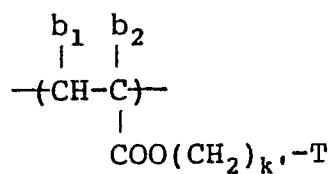
(b-16)



(b-17)



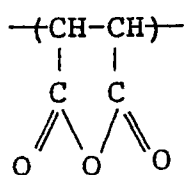
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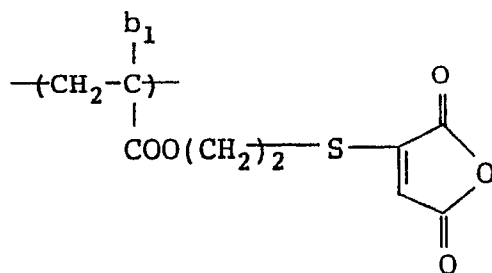
T: -OH, -NH₂

k!: integer of 2~11

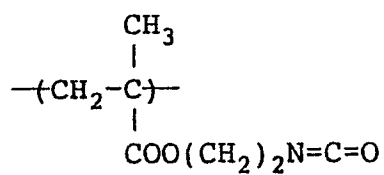
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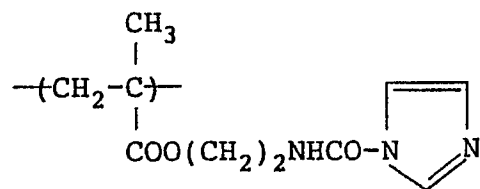
(b-20)



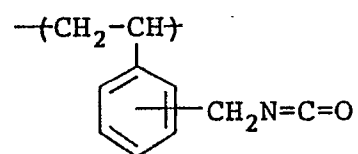
(b-21)



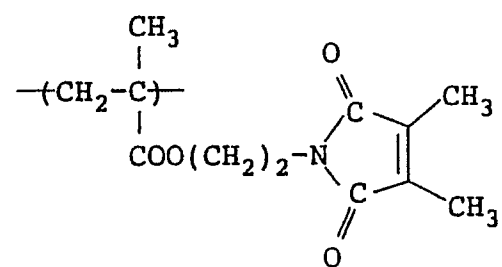
(b-22)

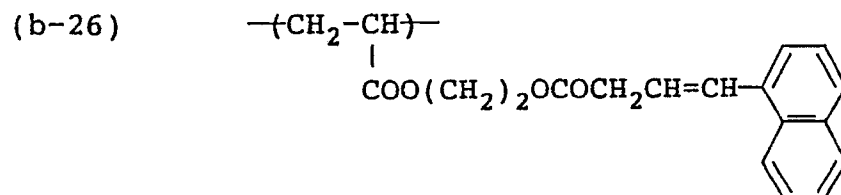
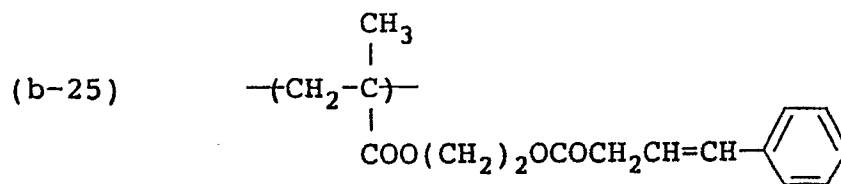


(b-23)



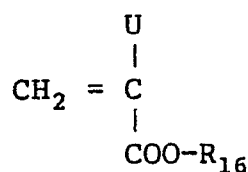
(b-24)





More specifically, there are given (meth)acrylic copolymers containing at least 30% by weight, based on the total amount of the copolymer, of a monomer represented by the following General Formula (III) as a copolymeric constituent, exemplified as Resin B:

General Formula (III)



wherein U is hydrogen atom, a halogen atom such as chlorine or bromine atom, cyano group, an alkyl group containing 1 to 4 carbon atoms, and R₁₆ is an alkyl group containing 1 to 18 carbon atoms, which can be substituted, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tridecyl, tetradecyl, 2-methoxyethyl or 2-ethoxyethyl group, an alkenyl group containing 2 to 18 carbon atoms, which can be substituted, such as vinyl, allyl, isopropenyl, butenyl, hexenyl, heptenyl or octenyl group, an aralkyl group containing 7 to 12 carbon atoms, which can be substituted, such as benzyl, phenethyl, methoxybenzyl, ethoxybenzyl or methylbenzyl group, a cycloalkyl group containing 5 to 8 carbon atoms, which can be substituted, such as cyclopentyl, cyclohexyl or cycloheptyl group, or an aryl group, which can be substituted, such as phenyl, tolyl, xylyl, mesityl, naphthyl, methoxyphenyl, ethoxyphenyl, chlorophenyl or dichlorophenyl group.

In Resin B, the content of "copolymeric components containing crosslinking (hardenable) functional groups" is preferably 0.5 to 40 wt%.

The weight average molecular weight of Resin B is preferably 1x10³ to 1x10⁵, more preferably 5x10³ to 5x10⁴.

The ratio of Resin A and Resin B, used in the present invention, depending on the kind, grain diameter and surface state of inorganic photoconductive materials used therewith, is generally 40-99 of the former 1-60 of the latter (by weight), preferably 60-95 to 5-40.

The surface layer resin of the present invention may further contain a crosslinking agent in addition to Resin A, or Resin A + Resin B. To this resin 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 (Kakyoza 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 -glycidoxypentyltrimethoxysilane, γ -mercaptopropyltriethoxysilane, γ -aminopropyltriethoxysilane and other silane coupling agents; polyisocyanate compounds such as tolylene diisocyanate, o-tolylene diisocyanate, diphenylmethane 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, trimethylolpropane triacrylate, pentaerythritol polyacrylate, bisphenol A-diglycidyl ether diacrylate, oligoester acrylate and methacrylates thereof and the like.

The quantity of the crosslinking agent used in the present invention is generally 0.5 to 30% by weight, preferably 1 to 10% by weight based on the resin used in the surface layer.

In a case where the crosslinking reaction is carried out by a reaction system for forming chemical bonds among functional groups, for example, organic acids such as acetic acid, propionic acid, butyric acid, benzenesulfonic acid and p-toluenesulfonic acid are used as the promoter, while in another case where the crosslinking reaction is carried out by a polymerizable reaction system, there are used polymerization initiators such as peroxides and azobis compounds, the latter being preferable, and multifunctional polymerizable group-containing monomers such as vinyl methacrylate, allyl methacrylate, ethylene glycol diacrylate, polyethylene glycol diacrylate, divinyl succinate, divinyl adipate, diallyl succinate, 2-methylvinyl methacrylate, divinylbenzene and the like.

In the case of containing functional groups with light-crosslinking reactivity, there can be used compounds described in the foregoing literatures cited relating to light-sensitive resins, for example, compounds containing allylester groups, cinnamoyl ester groups, dimethylmaleimide ring groups, etc.

In the present invention, other resins can jointly be used in addition to Resins A and B of the present invention, for example, alkyd resins, polybutylal resins, polyolefin resins, ethylene-vinyl acetate resins, styrene resins, styrene-butadiene resins, acrylate-butadiene resins, vinyl alkanate resins, polyester resins, acrylic resins and the like. For example, these resins are described in Takaharu Kurita and Jiro Ishiwataru "High Molecular Materials (Kobunshi)" 17, 278 (1968) and Harumi Miyamoto and Hidehiko Takei "Imaging" No. 8, page 9 (1973).

The resin of the present invention and the known resin can be mixed in optional proportions, but it is preferable to adjust the mixing proportion so that the content of the hydrophilic group-forming functional group-containing resin be 20 to 99% by weight, preferably 40 to 95% by weight based on the whole resin, since if less than 20% by weight, the resulting lithographic printing plate precursor meets with a problem that the hydrophilic property obtained by the oil-desensitization treatment with an oil-desensitizing solution or dampening water to result in background stains during printing, while if more than 99% by weight, the image-forming property during reproducing is not good and the film strength of the photoconductive layer during printing is lowered, resulting in deterioration of the durability.

The surface layer resin of the present invention is subjected to crosslinking after coating a surface layer forming composition. The crosslinking is preferably carried out, for example, by maintaining the drying conditions at a high temperature and/or for a long period of time, or by further subjecting to a heat treatment after drying the coating solvent, for example, at 60 to 120°C for 5 to 120 minutes.

When using a light-crosslinking resin, the crosslinking is carried out after coating by irradiating electron ray, X-rays, ultraviolet rays or plasma during, before or after drying and the reaction can further be promoted by the above described heating treatment during or after drying. Joint use of the above described reaction promoter results in that this treatment can be carried out under milder conditions.

Resin A of the surface layer of the present invention has such an action that hydrophilic groups appear by an oil-desensitizing treatment to render non-image areas more hydrophilic.

Furthermore, in the precursor of the present invention, the surface layer resin having a crosslinked structure at least in a part of the polymer is capable of preventing the hydrophilic group-containing resin formed by an oil-desensitization processing from being water-soluble and dissolved out of the non-image area, while maintaining the hydrophilic property.

Thus, the hydrophilic property of a non-image area can further be enhanced by hydrophilic groups formed in the resin, such as sulfo, phosphono, carboxyl and hydroxyl groups, and the durability is improved. Even if printing conditions become severer, for example, a printing machine is large-sized or printing pressure is fluctuated, a large number of prints with a clear image quality and free from background stains can be obtained.

Since in the prior art, the property of photosensitivity and rendering hydrophilic must be realized by one layer, only a limited material such as zinc oxide is used. In the printing plate precursor of the present invention, however, the functions are separately fulfilled by a photoconductive layer and a surface layer to be rendered hydrophilic and accordingly, severe control of printing is more relieved as compared with the system of the prior art which depends on the oil-desensitization reaction of zinc oxide. That is, the prior art system using zinc oxide presents difficult problems that ferrocyanide compounds are used as a predominant agent in an oil-desensitizing solution for oil-desensitizing zinc oxide, which compounds need a special control of handling from the standpoint of preventing the environmental pollution, and the kinds of available color inks are limited or it is difficult to use a neutral paper as a printing paper, because an oil-desensitizing agent is ordinarily added to the dampening water during printing so as to make up for the oil-desensitized hydrophilic material physically adhered to the surface layer of a printing plate precursor and consumed after printing a number of prints.

In the system of the present invention, these problems can readily be solved because the principles of oil-desensitization is fully different from that of the prior art.

In the present invention, inorganic compounds and organic compounds can be used as the photoconductive compound.

Examples of the inorganic photoconductive compound include zinc oxide, titanium oxide, zinc sulfide, cadmium sulfide, selenium, selenium alloys such as selenium-tellurium, lead sulfide and the like, well known in the art. From the standpoint of the environmental pollution, zinc oxide or titanium oxide is preferable. When using an inorganic photoconductive compound such as zinc oxide or titanium oxide as the photoconductive compound, a binder resin, as described above, is generally used in a proportion of 10 to 60 parts by weight, preferably 15 to 40 parts by weight to 100 parts by weight of the inorganic photoconductive compound.

On the other hand, as the organic compound, there can be used any of known compounds, specifically the following two kinds of compounds known as for an electrophotographic lithographic printing plate precursor. The first class has a photoconductive layer comprising an organic photoconductive compound, sensitizing dye and binder resin, as predominant components, as disclosed in Japanese Patent Publication Nos. 17162/1962 and 51462/1987, and Japanese Patent Laid-Open Publication Nos. 2437/1977, 19802/1979, 107246/1981 and 161863/1982 and the second class has a photoconductive layer comprising a charge generating agent, charge transporting agent and binder resin, as predominant components, as disclosed in Japanese Patent Laid-Open Publication Nos. 146145/1981, 17751/1985, 17752/1985, 17760/1985, 254142/1985 and 54266/1987. As a special case of the second class, a photoconductive layer of two-layer structure comprising a charge generating agent and a charge transporting agent respectively in separate layers has been known as disclosed in Japanese Patent Laid-Open Publication Nos. 230147/1985, 230148/1985 and 238853/1985. The electrophotographic lithographic printing plate precursor of the present invention can be in any form of the above described two kinds of photoconductive layers. In the case of the second example, the organic photoconductive compound of the present invention functions as a charge transporting agent.

Examples of the organic photoconductive compound used in the present invention are as follows:

- (a) Triazole derivatives as described in US Patent No. 3,112,197.
- (b) Oxadiazole derivatives as described in US Patent No. 3,189,447.
- (c) Imidazole derivatives as described in Japanese Patent Publication No. 16096/1962.
- (d) Polyaryalkane derivatives as described in US Patent Nos. 3,615,402, 3,820,989 and 3,542,544; Japanese Patent Publication Nos. 555/1970 and 10983/ 1976; and Japanese Patent Laid-Open Publication Nos. 93224/1976, 108667/1980, 156953/1980 and 36656/1981.
- (e) Pyrazoline derivatives and pyrazolone derivatives as described in US Patent Nos. 3,180,729 and 4,278,746; and Japanese Patent Laid-Open Publication Nos. 88064/1980, 88065/1980, 105537/1974, 51086/1980, 80051/1981, 88141/1981, 45545/1982, 112637/1979 and 74546/1980.
- (f) Phenylenediamine derivatives as described in US Patent No. 3,615,404; Japanese Patent Publication

Nos. 10105/1976, 3712/1971 and 28336/1972; and Japanese Patent Laid-Open Publication Nos. 83435/1979, 110836/1979 and 119925/1979.

(g) Arylamine derivatives as described in US Patent Nos. 3,567,450, 3,180,703, 3,240,597, 3,658,520, 4,232,103, 4,175,961 and 4,012,376; West German Patent (DAS) No. 1,110,518; Japanese Patent
5 Publication Nos. 35702/1974 and 27577/1964; and Japanese Patent Laid-Open Publication Nos. 144250/1980, 119132/1981 and 22437/1981.

(h) Amino-substituted chalcone derivatives as described in US Patent No. 3,526,501.

(i) N,N-bicarbazyl derivatives as described in US Patent No. 3,542,546.

(j) Oxazole derivatives as described in US Patent No. 3,257,203.

10 (k) Styrylanthracene derivatives as described in Japanese Patent Laid-Open Publication No. 46234/1981.

(l) Fluorenone derivatives as described in Japanese Patent Laid-Open Publication No. 110837/1979.

(m) Hydrazone derivatives as described in US Patent No. 3,717,462 and Japanese Patent Laid-Open Publication Nos. 59143/1979 (corresponding to US Patent No. 4,150,987), 52063/1980, 52064/1980, 46760/1980, 85495/1980, 11350/1982, 148749/1982 and 104144/1982.

15 (n) Benzidine derivatives as described in US Patent Nos. 4,047,948, 4,047,949, 4,265,990, 4,273,846, 4,299,897 and 4,306,008.

(o) Stilbene derivatives as described in Japanese Patent Laid-Open Publication Nos. 190953/1983, 95540/1984, 97148/1984, 195658/1984 and 36674/1987.

(p) Polyvinylcarbazole and derivatives thereof as described in Japanese Patent Publication No.
20 10966/1959.

(q) Vinyl polymers such as polyvinylpyrene, polyvinylanthracene, poly-2-vinyl-4-(4'-dimethylaminophenyl)-5-phenyloxazole and poly-3-vinyl-N-ethylcarbazole as described in Japanese Patent Publication Nos. 18674/1968 and 19192/1968.

25 (r) Polymers such as polyacenaphthylene, polyindene and acenaphthylene-styrene copolymers as described in Japanese Patent Publication No. 19193/1968.

(s) Condensed resins such as pyrene-formaldehyde resins, bromopyrene-formaldehyde resins and ethylcarbazole-formaldehyde resins as described in Japanese Patent Publication No. 13940/1981.

(t) Various triphenylmethane polymers as described in Japanese Patent Laid-Open Publication Nos. 90883/1981 and 161550/1981.

30 In the present invention, the organic photoconductive compounds are not limited to those exemplified in (a) to (t), but all other organic photoconductive compounds known in the art can be used. These organic photoconductive compounds can be used either alone or in combination of two or more thereof.

As a sensitizing dye contained in the photoconductive layer as the first example, there can be used the commonly used sensitizing dyes for electrophotographic photoreceptors described in "Denshi Shashin (Electrophotography)" 12 9 (1973), and "Yuki Gosei Kagaku (Organic Synthetic Chemistry)" 24 (11), 1010 (1966). Preferably examples thereof are pyrylium dyes as described in US Patent Nos. 3,141,770 and 4,283,475, Japanese Patent Publication No. 25658/1973 and Japanese Patent Laid-Open Publication No. 71965/1987, triarylmethane dyes as described in "Applied Optics Supplement" 3, 50 (1969) and Japanese Patent Laid-Open Publication No. 39548/1975, cyanine dyes as described in US Patent No. 3,597,196, and
40 styryl dyes as described in Japanese Patent Laid-Open Publication Nos. 163047/1985, 164588/1984 and 252517/1985.

As the charge generating agent contained in the photoconductive layer of the second example, there can be used the commonly used various organic and inorganic charge generating agents, for example, selenium, selenium-tellurium, cadmium sulfide, zinc oxide and organic pigments described below (1) to (9):

45 (1) Azo pigments such as monoazo, bisazo and trisazo pigments as described in US Patent Nos. 4,436,800 and 4,439,506; Japanese Patent Laid-Open Publication Nos. 37543/1972, 123541/1983, 192042/1983, 219263/1983, 78356/1984, 179746/1985, 14853/1986, and 238063/1986; Japanese Patent Publication Nos. 5941/1985 and 45664/19985.

(2) Phthalocyanine pigments such as metal-free or metal phthalocyanines as described in US Patent
50 Nos. 3,397,086 and 4,666,802 and Japanese Patent Laid-Open Publication Nos. 90827/1976 and 55643/1977.

(3) Perylene pigments as described in US Patent No. 3,371,884 and Japanese Patent Laid-Open Publication No. 30330/1972.

(4) Indigo and thioindigo derivatives as described in BP No. 2,237,680 and Japanese Patent Laid-Open
55 Publication No. 30331/1972.

(5) Quinacridone pigments as described in BP No. 2,237,679 and Japanese Patent Laid-Open Publication No. 30332/1974.

(6) Polycyclic quinone pigments as described in BP No. 2,237,678 and Japanese Patent Laid-Open

Publication Nos. 184348/1984, 28738/1987 and 18544/1972.

(7) Bisbenzimidazole pigments as described in Japanese Patent Laid-Open Publication Nos. 30331/1972 and 18543/1972.

(8) Squarium salt pigments as described in US Patent Nos. 3,296,610 and 4,644,082.

5 (9) Azulenium salt pigments as described in Japanese Patent Laid-Open Publication Nos. 53850/1984 and 212542/1986.

These pigments can be used either alone or in combination of two or more thereof.

The mixing ratio of the organic photoconductive compound and binder resin, i.e. the upper limit of the content of the organic photoconductive compound is determined by the compatibility of the organic
10 photoconductive compound and binder resin and addition of the organic photoconductive compound in an amount exceeding the upper limit results in crystallization thereof, which should be avoided. Since the electrophotographic sensitivity is lowered with the decrease of the content of the organic photoconductive compound, it is preferable to incorporate the organic photoconductive compound as much as possible in such a range that crystallization of the organic photoconductive compound does not take place. The content
15 of the organic photoconductive compound is generally 5 to 120 parts by weight, preferably 10 to 100 parts by weight per 100 parts by weight of the binder resin.

In the present invention, if necessary, various coloring matters or dyes can be used as a spectro sensitizer, illustrative of which are carbonium dyes, diphenylmethane dyes, triphenylmethane dyes, xan-
20 thene 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).

25 For example, those using carbonium dyes, triphenylmethane 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
30 dyes, there can be used dyes described in F.M. Hammer "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
35 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 27551/1986; U.S. Patent Nos. 3,619,154 and 4,175,956; and "Research Disclosure" 216, pages 117-118 (1982).

In the photoconductive layer of the electrophotographic lithographic printing plate precursor of the
40 present invention can be incorporated various known additives which have hitherto been used for electrophotographic photoreceptors. These additives include chemical sensitizers to improve the electrophotographic sensitivity, various plasticizers to improve the film property, surfactants, etc. Examples of the chemical sensitizer are electron accepting compounds such as p-benzoquinone, chloranil, fluoranil, bromanil, dinitrobenzene, anthraquinone, 2,5-dichlorobenzoquinone, nitrophenol, tetrachlorophthalic anhy-
45 dride, 2,3-dichloro-5,6-dicyanobenzoquinone, dinitrofluorenone, tetracyanoethylene and the like, and compounds as described in Japanese Patent Laid-Open Publication Nos. 65439/1983, 102239/1983, 129439/1983 and 71965/1987.

As the plasticizer, for example, dimethyl phthalate, dibutyl phthalate, dioctyl phthalate, triphenyl
50 phosphate, diisobutyl adipate, dimethyl sebacate, dibutyl sebacate, butyl laurate, methyl phthalyl ethyl glycolate, dimethylglycol phthalate, etc. can be added so as to improve the flexibility of the photoconductive layer in such a range that the static characteristics of the photoconductive layer are not deteriorated.

The quantity of the various additives is not particularly limited, but is generally in the range of 0.001 to 2.0 parts by weight per 100 parts by weight of the photoconductor.

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

55 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 generating layer is generally 0.01 to 1 μm , preferably 0.05 to 0.5 μm .

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 rendered 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 layers; and papers laminated with plastics which are made electroconductive, for example, by vapor deposition of A1 or the like thereon. Examples of the substrates or materials which are electroconductive or rendered 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.

The surface layer capable of being rendered hydrophilic according to the present invention has a thickness of 10 μm or less, and preferably from 0.1 to 5 μm particularly for use in Carlson's processing. Thickness of the surface layer more than 10 μm would result in disadvantages, such as reduced sensitivity and increased residual potential of the resulting electrophotographic photoreceptor.

The lithographic printing plate precursor according to the present invention can be generally produced as follows. An electrophotographic photosensitive layer (photoconductive layer) is first formed on a conductive support in a usual manner. A coating composition prepared by dissolving or dispersing the resin of the invention and, if desired, various additives as described above in a volatile hydrocarbon solvent having a boiling point of 200° C or lower is then coated on the photoconductive layer, followed by drying to form a surface layer. The hydrocarbon solvent to be used preferably includes halogenated hydrocarbon containing 1 to 3 carbon atoms, e.g., dichloromethane, chloroform, 1,2-dichloroethane, tetrachloroethane, dichloropropane, trichloroethane, etc. In addition, various solvents commonly employed for coating compositions, such as aromatic hydrocarbons, e.g., chlorobenzene, toluene, xylene, benzene, etc.; ketones, e.g., acetone, 2-butanone, etc.; ethers, e.g., tetrahydrofuran, etc.; methylene chloride; and mixtures thereof, can also be used.

Production of a lithographic printing plate using the electrophotographic lithographic printing plate precursor of the present invention can be carried out in known manner by forming a copying image thereon and then subjecting the non-image area to an oil-desensitization processing according to the present invention. The oil-desensitization (i.e. giving hydrophilic property) of the resin of the present invention, containing the formyl group 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 formyl group 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-hydroxyethylsulfinic 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-amino propionic 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 a photoconductor or in the foregoing processing solution of the binder resin.

5 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 an immersing period of time of 10 seconds to 5 minutes.

10 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.

15 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
20 "Synthesis 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.

25 The oil-desensitization of the resin of the present invention, containing the functional group represented by General Formula (I), is characterized in that it is rendered hydrophilic by carrying out the alcohol removing reaction through acid decomposition as shown in the foregoing Reaction Formula (1) and then subjecting the resulting formyl group to nucleophilic reaction with a nucleophilic reagent.

30 Since the alcohol removing reaction readily proceeds in a processing solution with a pH of at most 5, forming the formyl group and rendering hydrophilic through the nucleophilic reaction are accomplished by processing with the foregoing processing solution for the oil-desensitization of zinc oxide, adjusted to at most pH 5, or by processing with a processing solution with a pH of at most 5 before the nucleophilic reaction.

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

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Examples

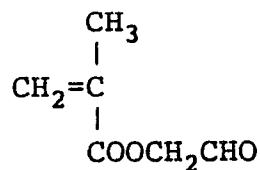
40 Synthetic Example 1 of Resin A: Resin A-1

A mixed solution of 39 g of benzyl methacrylate, 60 g of a monomer (M-1) having the following structure, 1.0 g of acrylic acid and 200 g of toluene was heated at a temperature of 75°C under a nitrogen stream. While stirring, 1.0 g of azobis(isobutyronitrile) (hereinafter referred to as A.I.B.N.) was added thereto,
45 followed by reacting for 4 hours, and 0.4 g of A.I.B.N. was further added, followed by reacting for 3 hours. The thus resulting polymer A-1 had a weight average molecular weight ($\bar{M}_w$) of 4.3×10^4 .

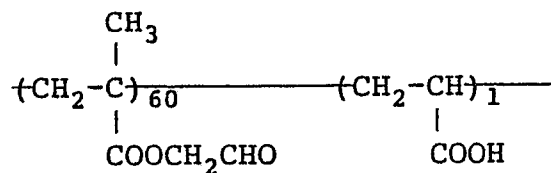
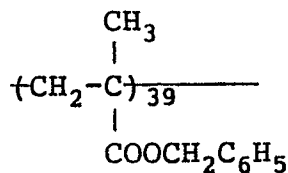
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Monomer M-1

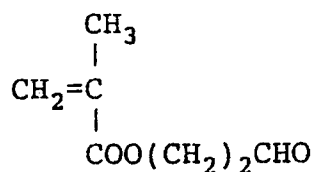


Resin A-1

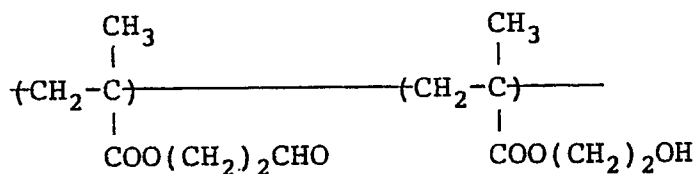
30 Synthetic Example 2 of Resin A: Resin A-2

A mixed solution of 90 g of a monomer (M-2) having the following structure, 10 g of 2-hydroxyethyl methacrylate and 200 g of toluene was heated at a temperature of 70° C under a nitrogen stream. While stirring, 1.5 g of A.I.B.N. was added thereto, followed by reacting for 5 hours, and 0.5 g of A.I.B.N. was further added, followed by reacting for 3 hours. The thus resulting polymer A-2 had a weight average molecular weight ($\bar{M}_w$) of 3.5×10^4 .

Monomer M-2

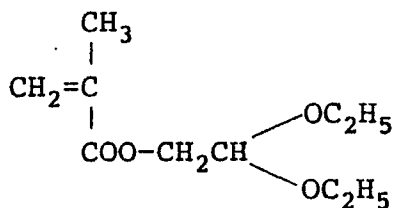
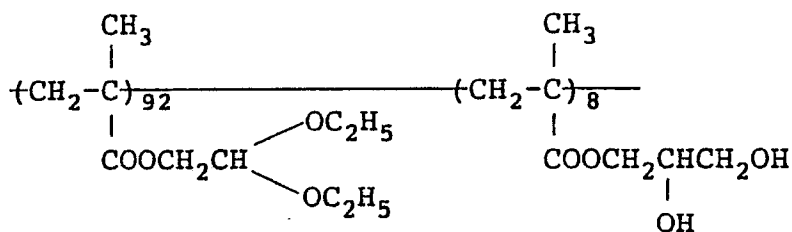


Resin A-2



Synthetic Example 3 of Resin A: Resin A-3

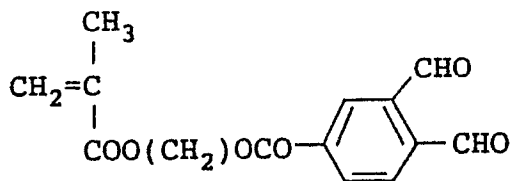
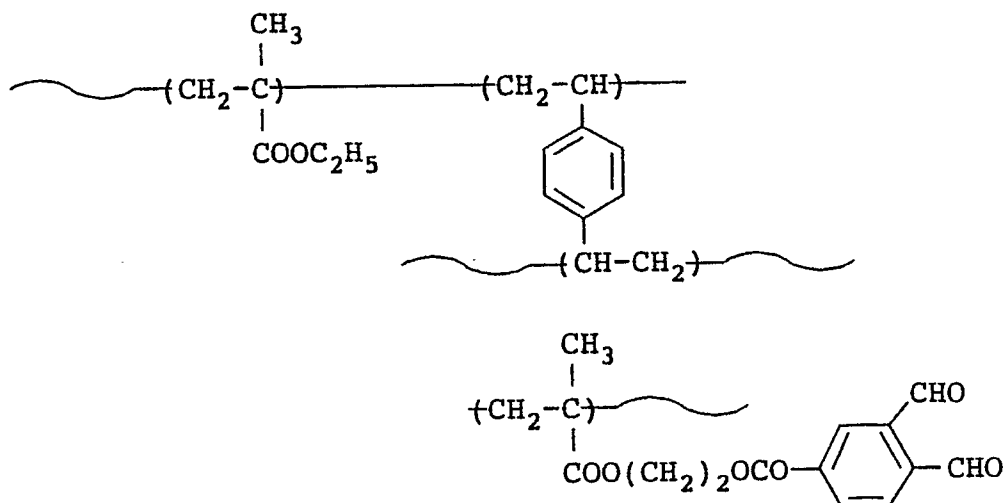
A mixed solution of 92 g of a monomer M-3 having the following structure, 8 g of 2,4-dihydroxypropyl methacrylate and 200 g of toluene was heated at a temperature of 75°C under a nitrogen stream. While stirring, 1.0 g of A.I.B.N. was added thereto, followed by reacting for 4 hours and 0.4 g of A.I.B.N. was further added, followed by reacting for 3 hours, thus obtaining the polymer A-3 with an $\bar{M}_w$ of 5.0×10^4 .

Monomer M-3**Resin A-3**Synthetic Example 4 of Resin A: Resin A-4

The mixture of the polymers obtained in Synthetic Example 3 of Resin was cooled to room temperature, to which 10 g of a methanol solution containing 10 wt% of 1N HCl was then added, followed by stirring for 30 minutes at room temperature, thus reprecipitated in 2000 ml of methanol. The precipitated white crystals was collected by filtering and dried under reduced pressure at room temperature, thus obtaining the polymer A-4 with a yield of 75 g and an $\bar{M}_w$ of 5.5×10^4 .

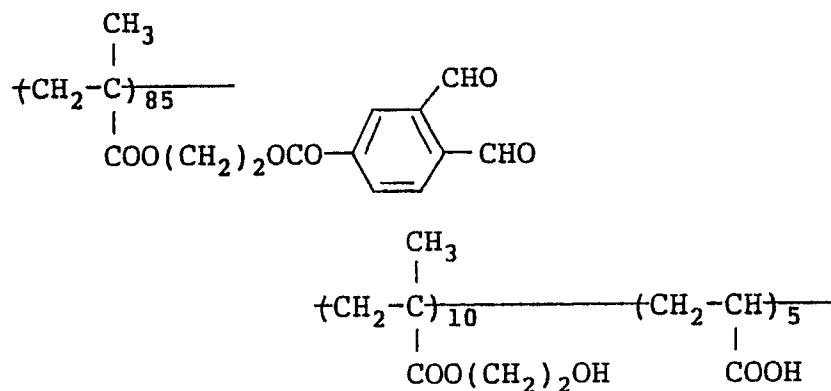
Synthetic Example 5 of Resin A: Resin A-5

A mixed solution of 18 g of ethyl methacrylate, 80 g of a monomer M-4 having the following structure, 2.0 g of divinylbenzene and 200 g of toluene was heated at a temperature of 70 °C under a nitrogen stream. While stirring, 1.5 g of azobis(isovaleronitrile) (hereinafter referred to as A.B.V.N.) was added thereto, followed by reacting for 4 hours and 0.5 g of A.B.V.N. was further added, followed by reacting for 3 hours. The thus resulting polymer A-5 had an ($\bar{M}_w$) of 1.5×10^5 .

Monomer M-4**Resin A-5 (estimated partial structure)**Synthetic Example 6 of Resin A: Resin A-6

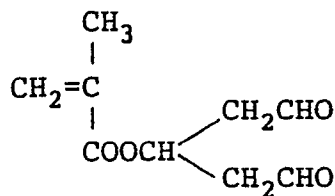
A mixed solution of 85 g of the monomer M-4, 10 g of 2-hydroxyethyl methacrylate, 5 g of acrylic acid and 200 g of toluene was heated at a temperature of 90 °C under a nitrogen stream, to which 6 g of A.I.B.N. was added, followed by reacting for 4 hours. The thus resulting polymer A-6 had an ($\bar{M}_w$) of 8.5×10^3 .

Resin A-6

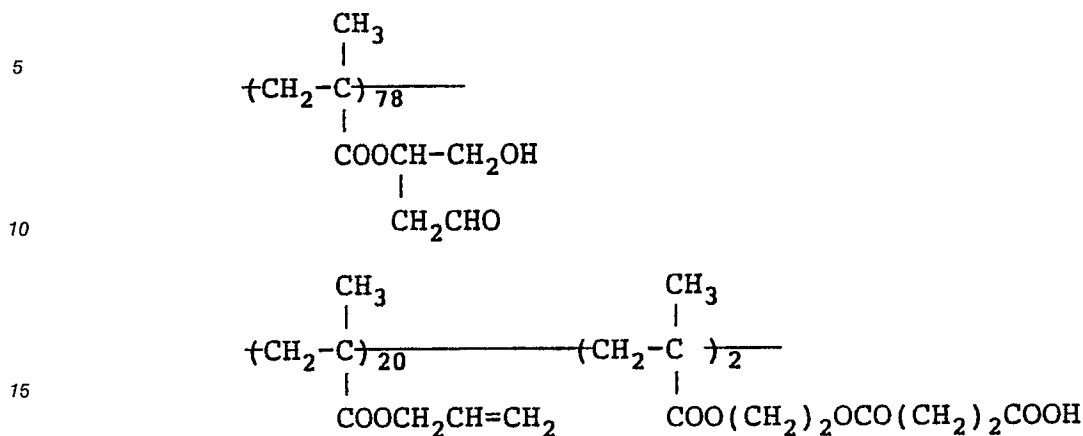
Synthetic Example 7 of Resin A: Resin A-7

A mixed solution of 78 g of a monomer M-5 having the following structure, 20 g of allyl methacrylate, 2 g of 2-(2-carboxyethylcarbonyloxy)ethyl methacrylate and 300 g of toluene was heated at a temperature of 60° C under a nitrogen stream, to which 1.5 g of A.B.V.N. was added, followed by reacting for 4 hours and 0.5 g of A.B.V.N. was further added, followed by reacting for 3 hours. The thus resulting polymer A-7 had an ($\bar{M}_w$) of 6.8×10^4 .

Monomer M-5

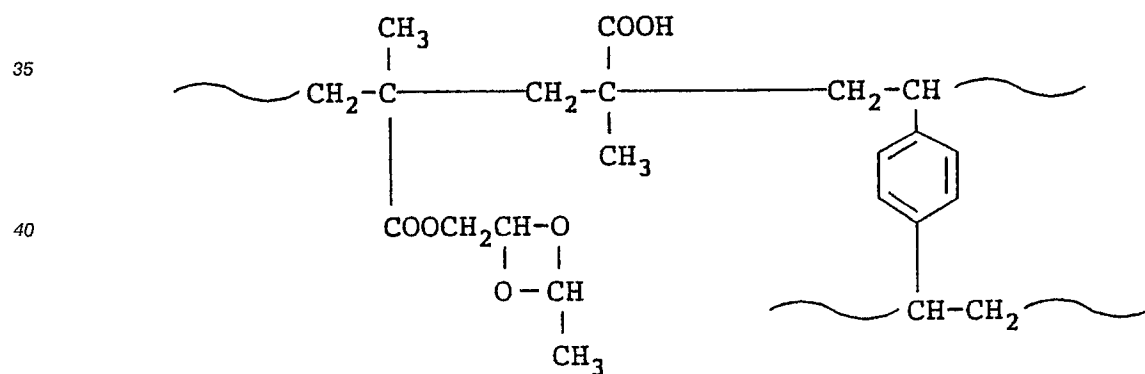


Resin A-7

Synthetic Example 8 of Resin A: Resin A-8

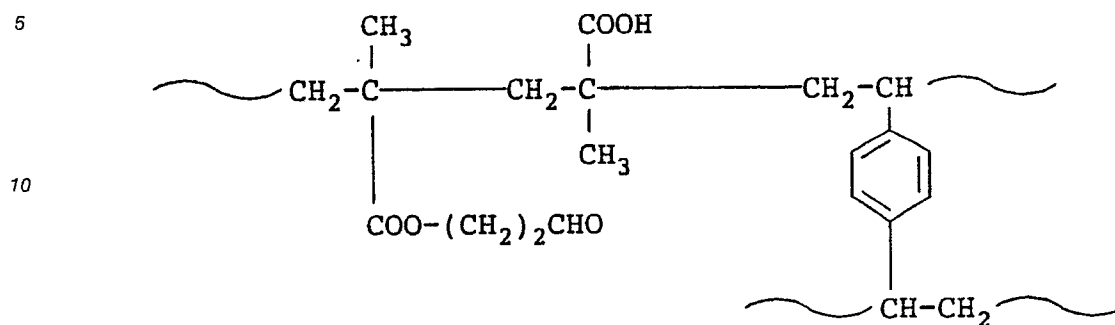
A mixed solution of 95 g of the monomer M-5, 5 g of methacrylic acid, 3 g of divinylbenzene, 1.5 g of n-dodecyl mercaptan and 200 g of toluene was heated at 75 °C under a nitrogen stream. 1 g of A.I.B.N. was added thereto, followed by reacting for 4 hours, 0.5 g of A.I.B.N. was further added, followed by reacting for 3 hours and 0.5 g of A.I.B.N. was further added, followed by reacting for 3 hours. The thus resulting polymer A-8 had an ($\bar{M}_w$) of 7.3×10^3 .

Resin A-8 (estimated partial structure)

Synthetic Example 9 of Resin A: Resin A-9

After the mixture of the polymers obtained according to Synthetic Example 8 of Resin A-8 was cooled, 10 g of an ethanol solution containing 10 wt% of 1N HCl was added to this mixture and stirred at a temperature of 30 °C for 30 minutes. The precipitated white crystals were separated by filtration, reprecipitated in 1500 ml of methanol, collected by filtration and dried under reduced pressure at room temperature. The thus resulting polymer A-9 had an $\bar{M}_w$ of 7.5×10^3 .

Resin A-9 (estimated partial structure)



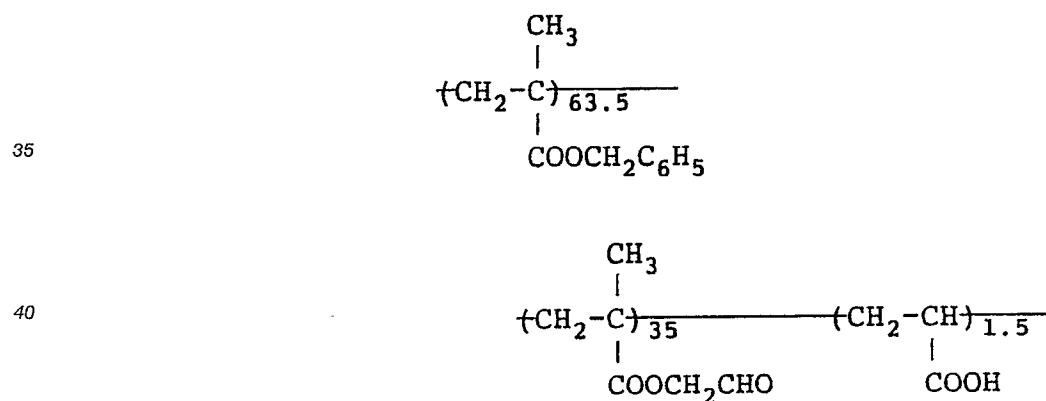
Synthetic Example 10 of Resin A: Resin A-10

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A mixed solution of 63.5 g of benzyl methacrylate, 35 g of the monomer (M-1), 1.5 g of acrylic acid and 200 g of toluene was heated at a temperature of 75°C under a nitrogen stream. While stirring, 1.0 g of A.I.B.N. was added thereto, followed by reacting for 4 hours, and 0.4 g of A.I.B.N. was further added, followed by reacting for 3 hours. The thus resulting polymer A-10 had a weight average molecular weight ($\bar{M}_w$) of 4.3×10^4 .

Resin A-10



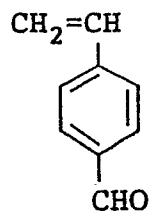
Synthetic Example 11 of Resin A: Resin A-11

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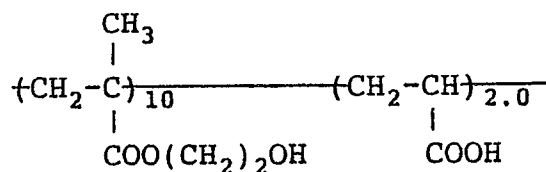
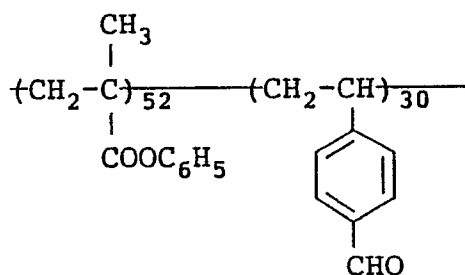
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A mixed solution of 52 g of phenyl methacrylate, 10 g of 2-hydroxyethyl methacrylate, 30 g of a monomer M-6 having the following structure, 2.0 g of acrylic acid and 200 g of toluene was heated at a temperature of 70°C under a nitrogen stream. While stirring, 1.5 g of A.I.B.N. was added thereto, followed by reacting for 5 hours and 0.5 g of A.I.B.N. was further added, followed by reacting for 3 hours. The thus resulting polymer A-11 had a ($\bar{M}_w$) of 3.5×10^4 .

Monomer M-6

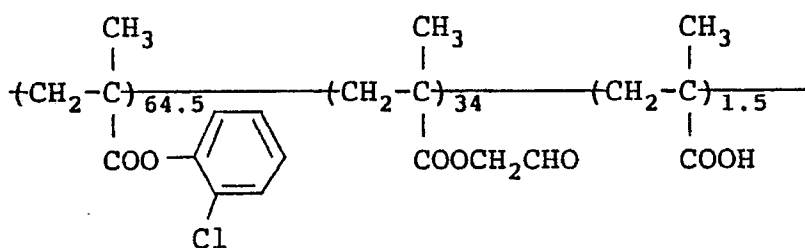


Resin A-11

Synthetic Example 12 of Resin A: Resin A-12

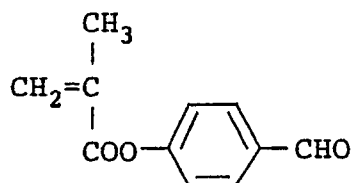
A mixed solution of 64.5 g of 2-chlorophenyl methacrylate, 34 g of the monomer M-3, 1.5 g of methacrylic acid and 200 g of toluene was heated at a temperature of 75° C under a nitrogen stream. While stirring, 1.0 g of A.I.B.N. was added thereto, followed by reacting for 4 hours and 0.4 g of A.I.B.N. was further added, followed by reacting for 3 hours. After cooling to room temperature, 10 g of an ethanol solution of 10 weight % of HCl was added to the resulting reaction mixture and stirred at room temperature for 1 hour, followed by reprecipitating in 2000 ml of methanol. The precipitated white crystals was collected by filtering and dried under reduced pressure at room temperature, thus obtaining the polymer A-12 with a yield of 75 g and an ($\bar{M}$ w) of 4.5×10^4 .

Resin A-13

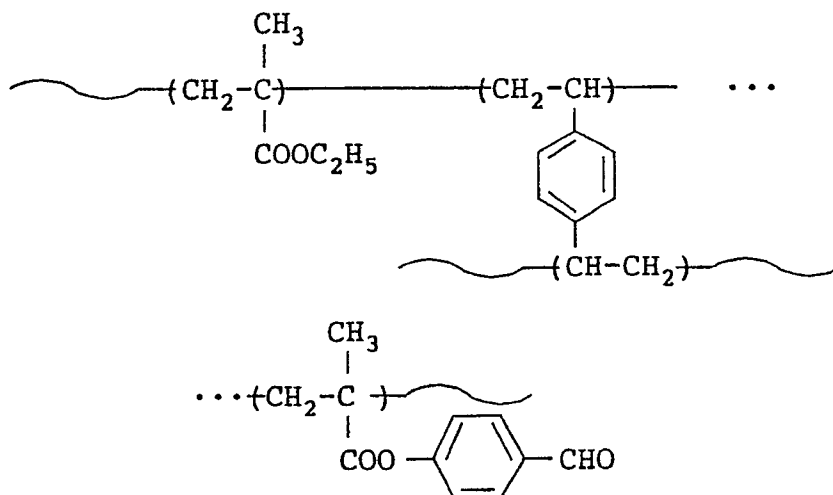
Synthetic Example 13 of Resin A: Resin A-13

A mixed solution of 18 g of ethyl methacrylate, 80 g of a monomer M-7 having the following structure, 2.0 g of divinylbenzene and 200 g of toluene was heated at a temperature of 70° C under a nitrogen stream. While stirring, 1.5 g of A.B.V.N. was added thereto, followed by reacting for 4 hours and 0.5 g of A.B.V.N. was further added, followed by reacting for 3 hours. The thus resulting polymer A-13 had an ($\bar{M}$ w) of 1.5×10^5 .

Monomer M-7

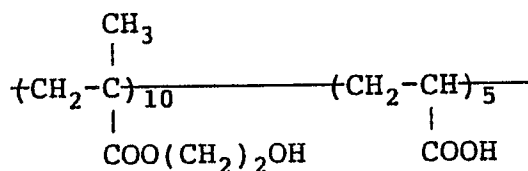
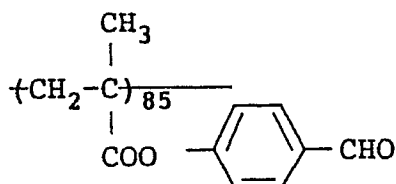


Resin A-13 (estimated partial structure)

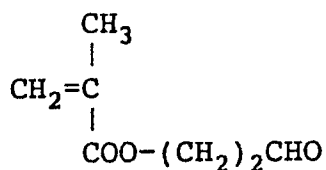


Synthetic Example 14 of Resin A: Resin A-14

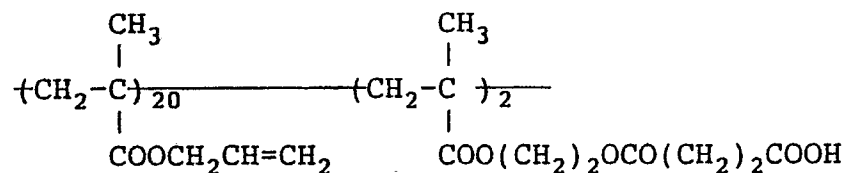
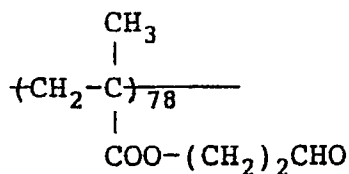
A mixed solution of 85 g of the monomer M-7, 10 g of 2-hydroxyethyl methacrylate, 5 g of acrylic acid
 5 and 200 g of toluene was heated at a temperature of 90° C under a nitrogen stream, to which 6 g of A.I.B.N. was added, followed by reacting for 4 hours. The thus resulting polymer A-14 had an ($\bar{M}$ w) of 8.5×10^3 .

Resin A-14Synthetic Example 15 of Resin A: Resin A-15

A mixed solution of 78 g of a monomer M-8 having the following structure, 20 g of allyl methacrylate, 2
 30 g of 2-(2-carboxyethylcarbonyloxy)ethyl methacrylate and 300 g of toluene was heated at a temperature of 60° C under a nitrogen stream, to which 1.5 g of A.B.V.N. was added, followed by reacting for 4 hours and 0.5 g of A.B.V.N. was further added, followed by reacting for 3 hours. The thus resulting polymer A-15 had
 35 an ($\bar{M}$ w) of 6.8×10^4 .

Monomer M-8

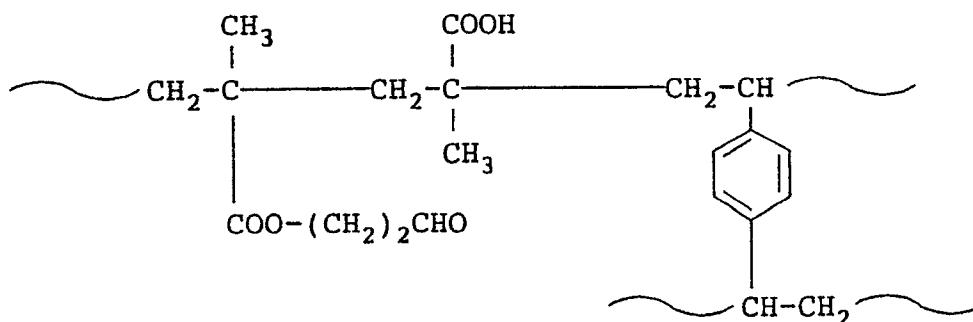
Resin A-15



Synthetic Example 16 of Resin A: Resin A-16

A mixed solution of 95 g of the monomer M-8, 5 g of methacrylic acid, 3 g of divinylbenzene, 1.5 g of n-dodecyl mercaptan and 200 g of toluene was heated at 75°C under a nitrogen stream. 1 g of A.I.B.N. was added thereto, followed by reacting for 4 hours, 0.5 g of A.I.B.N. was further added, followed by reacting for 3 hours and 0.5 g of A.I.B.N. was further added, followed by reacting for 3 hours. After cooling, 20 g of triethylamine was added and stirred at a temperature of 30°C for 1 hour. After the precipitated white crystals were separated by filtration, the crystals were reprecipitated in 1500 ml of methanol, collected by filtration and dried under reduced pressure at room temperature. The thus resulting polymer A-16 had an ($\bar{M}_w$) of 7.3×10^3 .

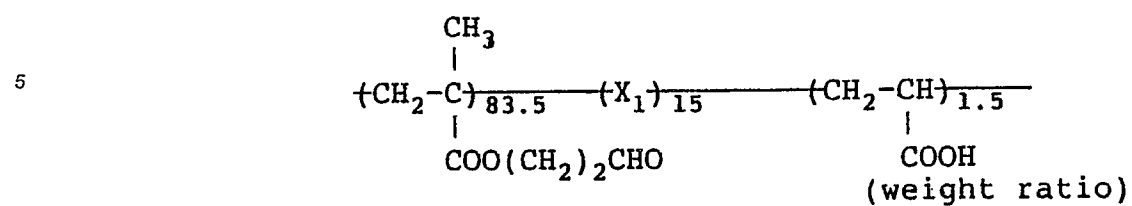
Resin A-16 (estimated partial structure)



Synthetic Examples 17 to 25 of Resins A: Resins A-17 to A-25

Synthetic Example 15 of Resin A was repeated except changing the copolymeric components as shown in Table 2 to synthesize copolymers having the following structures as shown in Table 2. The resulting polymers A-17 to A-25 each had an ($\bar{M}_w$) of 4×10^4 to 6×10^4 .

Table 2



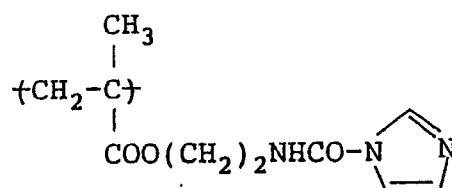
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Synthetic
ExamplesResin ACopolymeric Component:
Chemical structure of X₁

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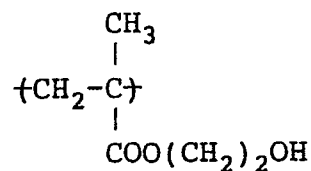
[A-17]



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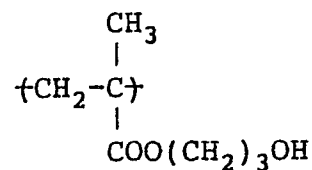
[A-18]



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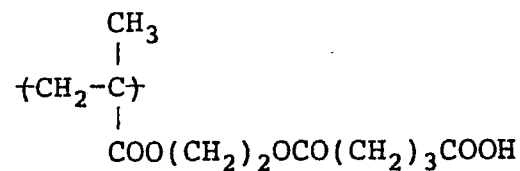
[A-19]



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[A-20]

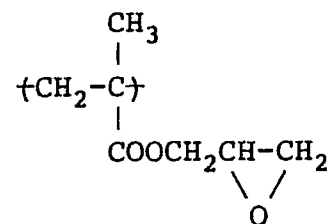


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[A-21]



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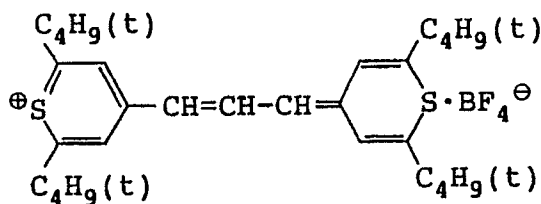
Table 2 (cont'd)

Synthetic Examples	Resin A	Copolymeric Component: Chemical structure of X ₁
22	[A-22]	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-} \\ \\ \text{COO(CH}_2\text{)}_2\text{S-} \end{array} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$
23	[A-23]	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-} \\ \\ \text{COO(CH}_2\text{)}_2\text{N=C=O} \end{array}$
24	[A-24]	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-} \\ \\ \text{COO(CH}_2\text{)}_6\text{N} \end{array} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{CH}_3 \\ \parallel \quad \parallel \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$
25	[A-25]	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-} \\ \\ \text{COO(CH}_2\text{)}_2\text{OCOCH}_2\text{-CH=CH-} \end{array} \text{C}_6\text{H}_5$

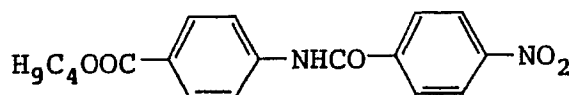
Example 1

5 grams of 4,4'-bis(diethylamino)-2,2'-dimethyltriphenylmethane as organic photoconductive substance,
 5 g of polycarbonate of bisphenol A ("Lexan 121" produced by G.E.), 40 mg of a spectral sensitizing dye
 (A) of the formula shown below, and 0.2 g of an anilide compound (B) of the formula shown below as
 chemical sensitizer were dissolved in 30 ml of methylene chloride and 30 ml of ethylene chloride to prepare
 a photosensitive composition.

Spectral Sensitizing Dye (A)



Anilide Compound (B)



The photosensitive composition was coated on a transparent conductive support (a 100 μm thick polyethylene terephthalate base having deposited thereon indium oxide; surface resistivity: $10^3 \Omega$) by means of a wire round rod to form a photosensitive layer having a thickness of about 4 μm .

A solution of 5% by weight (as solid content) of Resin A-2 and 0.5% by weight of 1,3-xylylene diisocyanate in toluene was coated onto the surface of this electrophotographic photoreceptor by a doctor blade and heated at 110° C for 2 hours to form a surface layer having a thickness of about 2 μm .

The resulting photosensitive material was subjected to oil-desensitization by immersing for 30 seconds in an oil-desensitizing solution (E-1) prepared by the following recipe:

Oil-desensitizing Processing Solution (E-1)	
Sodium Sulfite	52 g
Newcol B 4S N (made by Nippon Nyukazai KK)	10 g
Methyl Ethyl Ketone	100 g
Distilled Water	to 1000 ml

In order to evaluate the hydrophilic properties of the surface layer, a drop of 2 μl of distilled water was placed on the surface layer and the contact angle formed with water was measured by a goniometer to give less than 10°. In view of the contact angle of 88° before the oil-desensitization processing, it is apparent that the surface layer of the photosensitive material of the present invention was well rendered hydrophilic.

The above-prepared lithographic printing plate precursor was processed by an automatic printing plate making machine ("ELP 404V" manufactured by Fuji Photo Film Co., Ltd.) using a negatively chargeable liquid developer to form a toner image thereon. The precursor was then subjected to oil-desensitization under the same conditions as described above. The resulting printing plate (offset master plate) was mounted on an offset printing machine ("Hamada Star 800SX" manufactured by Hamada Star K.K.), and printing on fine paper was carried out.

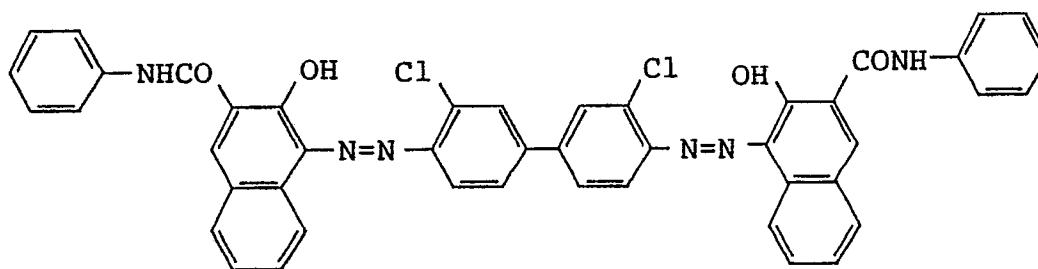
The number of prints that could be obtained with no problem of image quality and background stain formation on the non-image areas was 10,000.

When the light-sensitive material was further subjected to the same processings as described above, except after allowing to stand under conditions of 45° C and 75% RH for 3 weeks, no change occurred in the results.

Example 2

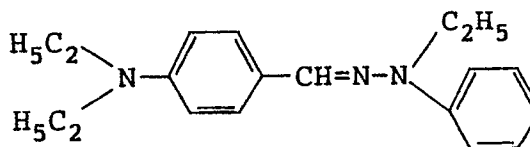
A mixture consisting of 5 g of a bisazo pigment of formula shown below, 95 g of tetrahydrofuran, and 30 g of a 5% by weight tetrahydrofuran solution of a polyvinyl butyral resin ("Denka Butyral #4000.1" produced by Electro Chemical Ind. Co., Ltd.) was thoroughly ground in a ball mill. The mixture was removed from the ball mill, and 520 g of tetrahydrofuran was added thereto with agitation. The resulting dispersion was coated on the same transparent conductive support as used in Example 1 with a wire round rod to form a charge generating layer having a thickness of about 0.7 μm .

Bisazo Pigment



A mixed solution consisting of 20 g of a hydrazone compound of formula shown below, 20 g of a polycarbonate resin (Lexan 121), and 160 g of tetrahydrofuran was coated on the charge generating layer with a wire round rod to form a charge transport layer having a thickness of about 18 μm . There was obtained an electrophotographic photoreceptor having a double-layered photosensitive layer.

Hydrazone Compound



A solution containing 5% by weight (as solid content) of Resin A-4 and 0.6% by weight of 1,6-hexane diisocyanate in toluene was coated on the resulting photoreceptor by a doctor blade to form a surface layer with a thickness of about 2 μm on the photosensitive layer.

The thus obtained light-sensitive material was negatively charged to -6 kV by means of a paper analyzer (Paper Analyzer SP-428 - commercial name- manufactured by Kawaguchi Denki KK) and subjected to measurement of the initial potential (V_0), retention of dark charge (D.R.R.) and half decay exposure ($E_{1/10}$) to obtain $V_0 = -550$ in, D.R.R. = 84% and $E_{1/10} = 10.0 \text{ lux} \cdot \text{sec}$.

Further, the light-sensitive material was processed by an automatic plate making machine (ELP 404V -commercial name- manufactured by Fuji Photo Film Co., Ltd.) using a toner (ELP-T -commercial name- manufactured by Fuji Photo Film Co., Ltd.) in the same manner as in Example 1. The resulting master plate for offset printing had a clear image having a density of at least 1.0.

Then, the plate was subjected to oil-desensitization by immersing for 30 seconds in an oil-desensitizing solution (E-2) prepared by the following recipe, followed by washing with water:

Oil-desensitizing Processing Solution (E-2)	
Thiosalicylic Acid	55 g
Benzyl Alcohol	100 g

These components were dissolved in distilled water to 1000 ml and the pH of the solution was adjusted to

12.0 with sodium hydroxide. The non-image area was sufficiently rendered hydrophilic as represented by a contact angle with distilled water of less than 10° .

When printing was carried out using the resulting offset master plate, the print obtaining 10000 prints had a clear image and no fog on the non-image area.

5 Evaluation of the above-described electrostatic characteristics was carried out as follows:

The light-sensitive material was subjected to corona discharge at -6kV 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- manufacture by Kawaguchi Denki KK) and then allowed to stand for 10 seconds, at which the surface potential V_{10} was measured. Then, the sample was further allowed to stand in the dark
10 room as it was for seconds to measure the surface potential V_{70} , thus obtaining the retention of potential after the dark decay for 60 seconds, i.e., dark decay retention ratio (DRR (%)) represented by $(V_{70}/V_{10}) \times 100$ (%). Moreover, the surface of the photoconductive layer was negatively charged to -400 V by corona discharge, then irradiated with a visible ray of an intensity of 2.0 lux and the time required for dark decay of the surface potential (V_{10}) to 1/10 was measured to evaluate an exposure quantity $E_{1/10}$ (lux·sec).

15

Example 3

A mixture of 45 g of a copolymer of methyl methacrylate, ethyl methacrylate and acrylic acid (39/60/1 weight ratio) having a weight average molecular weight of 42000, 200 g of zinc oxide, 0.03 g of Rose Bengal, 0.02 g of tetrabromophenol, 0.20 g of phthalic anhydride and 300 g of toluene was dispersed in a ball mill for 2 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 100°C for 1 minute.

25 A solution containing 5% by weight of Resin A-6 and 0.75% by weight of 1,4-xylylene diisocyanate in toluene was coated on the resulting photoreceptor by a doctor blade and heated at 90°C for 2 hours to form a surface layer with a thickness of about $2\text{ }\mu\text{m}$ on the light-sensitive layer. The thus coated paper was allowed to stand in a dark place at 20°C and 65% RH for 24 hours to prepare electrophotographic light-sensitive material.

30 This light-sensitive material was negatively charged at -6 kV and then subjected to evaluation of the electrostatic characteristics, thus obtaining an initial potential (V_0) of -550 V, dark charge retention (D.R.R.) of 88% and half decay exposure ($E_{1/10}$) of 11.0 (lux·sec).

Further, the light-sensitive material was subjected to plate making in an analogous manner to Example 1 and the resulting master plate for offset printing had a clear image having a density of at least 1.0.

35 Then, the plate was subjected to oil-desensitization by immersing for 30 seconds in the oil-desensitizing solution (E-1) used in Example 1 and washed with water. The non-image area of the resulting plate was sufficiently rendered hydrophilic as represented by a contact angle with distilled water of less than 10° .

When the plate for offset printing was subjected to printing by a printing machine using the processing solution E-1 diluted by 50 times with distilled water as a dampening water, the print obtaining 10000 prints
40 had a clear image and no fog on the non-image area.

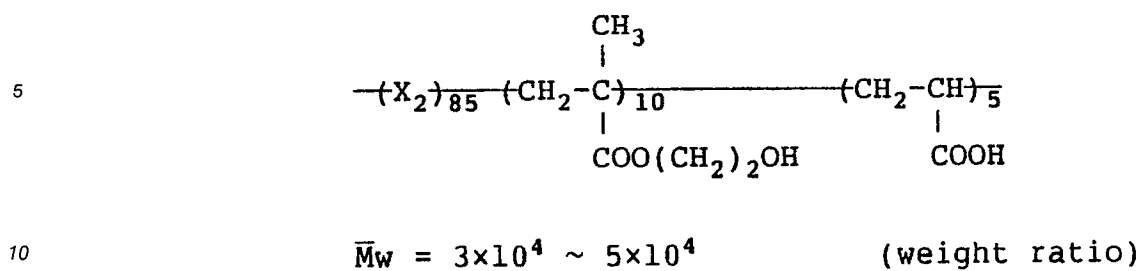
Examples 4 to 15

45 Example 1 was repeated except using copolymer resins (Resins A-26 to A-37 shown in Table 3) of the present invention instead of Resin A-2 of the present invention, thus obtaining electrophotographic light-sensitive materials, each Resin A having an $\bar{M}_w$ of 3×10^4 to 5×10^4 .

50

55

Table 3



15	<u>Example</u>	<u>Resin A of Present Invention</u>	<u>Copolymeric Component: Chemical Structure of X₂</u>
20	4	A-26	$\text{---CH}_2\text{---}\overset{\text{CH}_3}{\underset{\text{COO}(\text{CH}_2)_3\text{CHO}}{\text{C}}}\text{---}$
25	5	A-27	$\text{---CH}_2\text{---}\overset{\text{CH}_3}{\underset{\text{COO---}\text{C}_6\text{H}_4\text{---CHO}}{\text{CH}}}\text{---}$
30	6	A-28	$\text{---CH}_2\text{---}\overset{\text{CH}}{\underset{\text{C}_6\text{H}_3(\text{CHO})_2}{\text{C}}}\text{---}$
35			
40	7	A-29	$\text{---}\overset{\text{CH}_3}{\underset{\text{COOCH}_2\text{CHO}}{\text{CH}}}\text{---CH}\text{---}$

45

50

55

Table 3 (cont'd)

5	<u>Example</u>	<u>Resin of Present Invention</u>	<u>Copolymeric Component: Chemical Structure of X₂</u>
10	8	A-30	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C---} \\ \quad \\ \text{COOCHCH}_2\text{CHO} \end{array} $
15	9	A-31	$ \begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{CHO} \end{array} $
20	10	A-32	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C---} \\ \\ \text{CHO} \end{array} $
25	11	A-33	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C---} \\ \\ \text{CONHCOOCH}_2\text{CHO} \end{array} $
35	12	A-34	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C---} \\ \\ \text{COO(CH}_2)_2\text{CH} \begin{array}{l} \nearrow \text{OCH}_3 \\ \searrow \text{OCH}_3 \end{array} \end{array} $
40	13	A-35	$ \begin{array}{c} \text{---(CH}_2\text{---CH---)} \\ \\ \text{C}_6\text{H}_4\text{---CH}_2\text{CH} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \text{C} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array} \end{array} $

50

55

Table 4 (cont'd)

5	<u>Example</u>	<u>Resin of Present Invention</u>	<u>Copolymeric Component: Chemical Structure of X₂</u>
10	14	A-36	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{---CH}_2\text{---C---} \\ \\ \text{COO(CH}_2\text{)CH} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C} \begin{array}{c} \diagup \text{H} \\ \diagdown \text{OCH}_3 \end{array} \end{array} $
15	15	A-37	$ \begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{COO(CH}_2\text{)}_4\text{CHO} \end{array} $

20 When the resulting light-sensitive material was subjected to plate making by means of the same apparatus as that of Example 3, the resulting master plate had a density of at least 1.0 and clear image. When it was subjected to an etching treatment and printing, furthermore, 10000 or more prints with a clear image were obtained without occurrence of fog on non-image areas.

25 When the light-sensitive material was further subjected to the same processings as described above, except after allowing to stand under conditions of 45° C and 75% RH for 3 weeks, no change appeared in the results.

30 Examples 16 to 26

Example 3 was repeated except using compounds shown in Table 4 instead of Resin A-6 and 1,4-xylene diisocyanate to be coated as the surface layer of the photoreceptor, thus obtaining electrophotographic light-sensitive materials, each having an ($\bar{M}$ w) in the range of 3×10^4 to 6×10^4 .

Table 4

5					

Table 4 (cont'd)

5	<u>Example</u>	<u>Resin A</u>	Chemical Structure of Copolymeric Component X ₃	<u>Crosslinking Compound</u>
10	19	A-41	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{COOCH}_2\text{CHCH}_2 \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{S} \end{array}$	trimellitic anhydride mixture Rika Resin TMFG (made by Shin Nippon Rika KK)
15	20	A-42	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{COO}(\text{CH}_2)_2\text{N}=\text{C}=\text{O} \end{array}$	propylene glycol
20	21	A-43	$\begin{array}{c} -\text{CH}_2-\text{C}- \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \text{H}_2\text{C} \quad \text{C}=\text{O} \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \text{C}-\text{O} \\ \quad \quad \quad \parallel \\ \quad \quad \quad \text{O} \end{array}$	1,6-hexanediamine
30	22	A-44	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{COO}(\text{CH}_2)_2\text{OCO}-\text{C}_6\text{H}_4-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{C}=\text{O} \end{array}$	ethylene glycol
40	23	A-45	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{COO}(\text{CH}_2)_2\text{OCO}(\text{CH}_2)_2\text{COOH} \end{array}$	ethylene glycol diglycidyl ether

Table 4 (cont'd)

Example	Resin A	Chemical Structure of Copolymeric Component X ₁	Crosslinking Compound
24	A-46	$ \begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{COO}(\text{CH}_2)_2\text{N} \begin{array}{l} \text{CH}_2 \\ \text{CH}_2 \end{array} \end{array} $	1,4-butanediol
25	A-47	$ \begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{C}_6\text{H}_4-\text{CH}_2\text{NHCH}_3 \end{array} $	diphenylmethane diisocyanate
26	A-48	$ \begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{COOCH}_2\text{CHCH}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{O} \end{array} $	pyromellitic anhydride

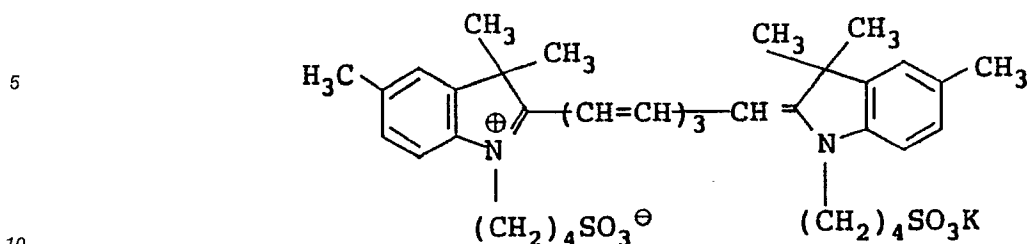
When the resulting light-sensitive material was subjected to plate making by means of the same apparatus as that of Example 3, the resulting master plate had a density of at least 1.0 and clear image. When it was subjected to an etching treatment and printing, furthermore, 10000 or more prints with a clear image were obtained without occurrence of fog on non-image areas.

When the light-sensitive materials were further subjected to the same processings as described above, except after allowing to stand under conditions of 45°C and 75% RH for 3 weeks, no change occurred in the results.

Example 27

A mixture of 6.5 g of a Resin R-1, copolymer of 2-chlorophenyl methacrylate/acrylic acid (95/5 by weight) having an $\bar{M}_w$ of 7.5×10^3 , 33.5 g of a Resin R-2, copolymer of methyl methacrylate/methyl acrylate/methacrylic acid (78.5/20/1.5 by weight) having an $\bar{M}_w$ of 5.6×10^4 , 200 g of zinc oxide, 0.018 g of a cyanine dye (I) having the following structure, 0.15 g of phthalic anhydride and 300 g of toluene was dispersed in a ball mill 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 20 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 20°C and 65% RH for 24 hours to prepare an electrophotographic light-sensitive material.

Cyanine Dye (I):



15 A solution of 5% by weight (as solid content) of Resin A-7, 0.8% by weight of ethylene glycol dimethacrylate and 0.05% by weight of 1,1'-azobis(cyclohexane-1-carbonitrile) in toluene was coated on the resulting photoreceptor by a doctor blade and heated at 100 °C for 3 hours to form a surface layer of about 2 μm thick. Then, the light-sensitive material was allowed to stand in a dark place at 20 °C and 65% RH for 24 hours to prepare an electrophotographic light-sensitive material.

The light-sensitive material was then subjected to evaluation of the electrostatic characteristics, image quality and printing property to thus obtain the following results:

20

25

Electrostatic Characteristics ¹⁾	V ₁₀ : -585 (V) D.R.R.: 86% E _{1/10} : 20 (erg/cm ²)
Image Quality ²⁾	I (20 °C, 65%): good II (30 °C, 80%): good
Contact Angle with Water	10 ° or less
Printing Durability ³⁾	8000 prints

30

As described above, the light-sensitive material of the present invention exhibited excellent electrostatic characteristics and printing property. The electrostatic characteristics and image quality were measured by the following procedures:

35

1) Electrostatic Characteristics

40 The light-sensitive material was subjected to corona discharge at -6kV 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- manufacture by Kawaguchi Denki KK) and then allowed to stand for 10 seconds, at which the surface potential V₁₀ was measured. Then, the sample was further allowed to stand in the dark room as it was for 60 seconds to measure the surface potential V₇₀, thus obtaining the retention of potential after the dark decay for 60 seconds, i.e., dark decay retention ratio (DRR (%)) represented by (V₇₀/V₁₀)-x100 (%). Moreover, the surface of the photoconductive layer was negatively charged to -400 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 (V₁₀) to 1/10 was measured to evaluate an exposure quantity E_{1/10}- (erg/cm²).

50 2) Image quality

55 The light-sensitive material 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 300 m/sec under irradiation of 64 erg/cm² 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

5

Printing Durability

- 10 The light-sensitive material was immersed in an oil-desensitizing processing solution (E-3), prepared by the following recipe, for 30 seconds, followed by washing with water:

15	Oil-desensitizing Processing Solution (E-3)	
	Potassium Sulfite	80 g
	Neosoap (commercial name, made by Takemoto Jushi KK)	15 g
	Benzyl Alcohol	100 g

- 20 These components were dissolved in distilled water to give a whole quantity of 1000 ml and the pH of the solution was adjusted to 11.5 with potassium hydroxide.

The plate thus oil-desensitized was subjected to printing in an analogous manner to Example 1 so as to examine the printing durability.

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

The light-sensitive material was excellent in the electrostatic characteristics, dark charge retention and photosensitivity and gave a clear image without occurrence of the background fog and disappearance of fine lines even under severer conditions, e.g. high temperature and high humidity (30 ° C, 80% RH).

- 30 When the plate making was carried out in an analogous manner to Example 1, the resulting master plate for offset printing had a concentration of at least 1.0 and clear image quality. When it was subjected to an etching treatment and printing by a printing machine, 10000 or more prints with a clear image were obtained without occurrence of fog or non-image areas.

35

Example 28

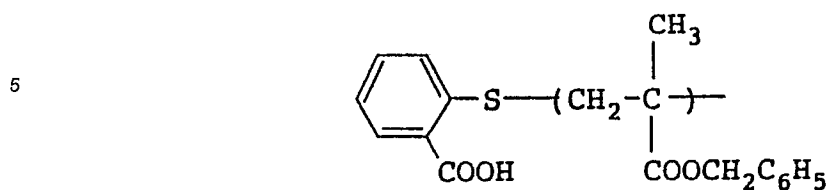
- 40 A mixture of 6.0 g of the following Resin (R-3), 34 g of the following Resin (R-4), 200 g of zinc oxide, 0.018 g of a cyanine dye (II) having the following structure, 0.20 g of maleic anhydride and 300 g of toluene was dispersed in a ball mill for 3 hours to prepare a light-sensitive layer-forming composition, which was then applied to a paper rendered electrically conductive to give a dry coverage of 25 g/m² by means of 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 20 ° C and 65% RH for 24 hours to prepare an electrophotographic light-sensitive material.

45

50

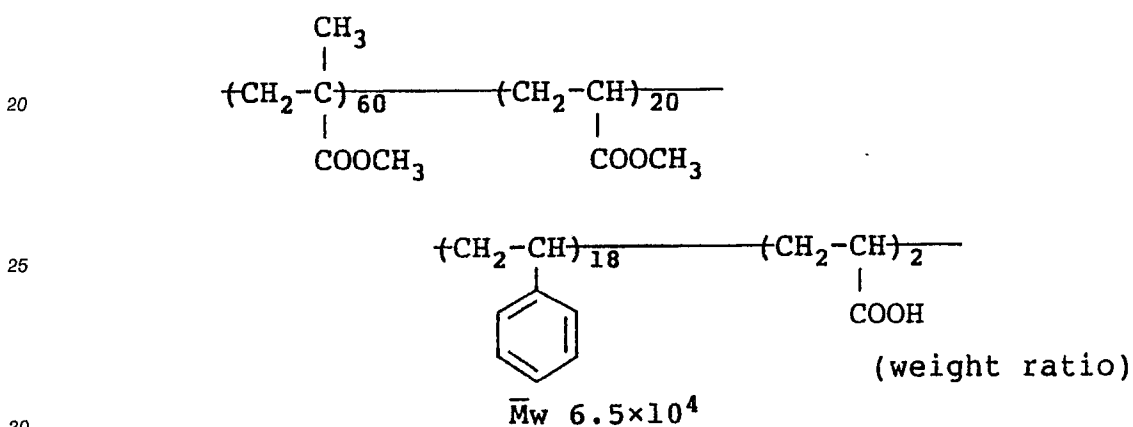
55

Resin R-3

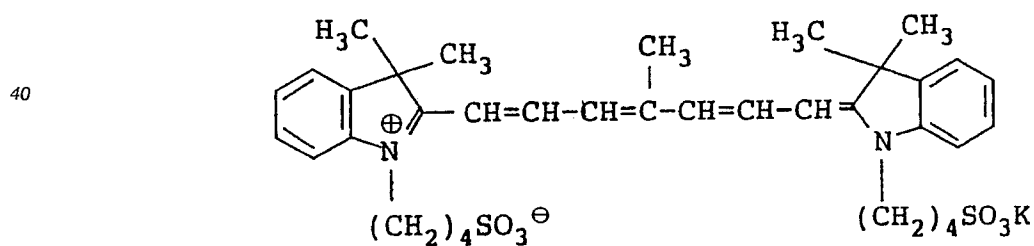


$$\bar{M}_w 7.8 \times 10^3$$

Resin R-4



Cyanine Dye II



A mixture of 10 g (as solid content) of Resin A-8, 10 g of zinc oxide and 100 g of toluene was dispersed in a ball mill for 2 hours, to which 2 g of ethylene glycol glycidyl ether was further added, and the mixture was then dispersed in the ball mill for 10 minutes to prepare a dispersion, which was applied to the surface of the resulting photoreceptor by a wire bar coater and heated at 110 °C for 2 hours to form a surface layer of about 2.5 μm thick. The thus coated paper was allowed to stand in a dark place at 20 °C and 65% RH for 24 hours to prepare an electrophotographic light-sensitive material.

The light-sensitive material was then subjected to evaluation of the electrostatic characteristics and image quality in an analogous manner to Example 27 to thus obtain the following results:

Electrostatic Characteristics	V ₁₀ : -560 (V) D.R.R.: 86% E _{1/10} : 25 (erg/cm ²)
Image Quality	I (20° C, 65%): good II (30° C, 80%): good

5

Then, the light-sensitive material subjected to plate making was immersed in an oil-desensitizing processing solution (E-4), prepared by the following recipe, for 20 seconds and washed with water.

10

Oil-desensitizing Processing Solution (E-4)	
Mixed Solution of	
ELP - FS (commercial name, made by Fuji Photo Film Co., Ltd.)	865 g
Ammonium Sulfite	85 g
Methyl Ethyl Keltone	50 g

15

20

The non-image area was sufficiently rendered hydrophilic as represented by a contact angle with water of less than 10°. When printing was carried out in an analogous manner to Example 1 using this light-sensitive material as a plate for offset printing and the processing solution E-4 diluted by 20 times with water as dampening water, the print obtaining 10000 prints had a good image quality.

25

As described above, the light-sensitive material of the present invention exhibited very excellent properties.

Examples 29 to 40

30

Master plates for offset printing were prepared by using the light-sensitive materials prepared in Examples 1 to 27 and carrying out an etching treatment as follows:

35

Distilled water was added to 0.5 mole of each of nucleophilic compounds shown in the following Table 5, 100 g of an organic solvent and 10 g of Newcol B4SN (commercial name, manufactured by Nippon Nyukazai KK) to 1000 ml and the pH thereof was adjusted to 10.0.

Each of the light-sensitive materials was immersed and etched in the solution ELP-E diluted by 2 times with distilled water for 20 seconds and then immersed in the above described processing solution at 25° C for 1 minute.

40

The thus resulting plate was subjected to printing in the same manner as in Example 1.

45

50

55

Table 5

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

The each material was sufficiently rendered hydrophilic as represented by a contact angle with water of less than 10° . The print obtaining 10000 prints had a clear image and no fog on the non-image area.

Examples 41 to 42

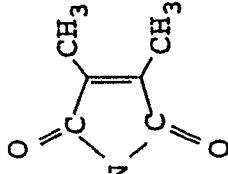
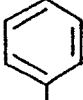
The electrophotographic photosensitive material obtained in Example 28 but before coating the surface layer was coated with a toluene solution containing 5% by weight of each of Resin A shown in the following Table 6 by a doctor blade and heated at 100°C for 30 seconds to form a surface layer with a thickness of about $2\text{ }\mu\text{m}$. Each of the light-sensitive materials was irradiated by a high voltage mercury lamp of 400 W at an interval of 30 cm and then allowed to stand in a dark place for 24 hours under conditions of 20°C and 65% RH to prepare a master plate for lithographic printing.

Table 6

Copolymer Composition (weight ratio)

Resin A

Example

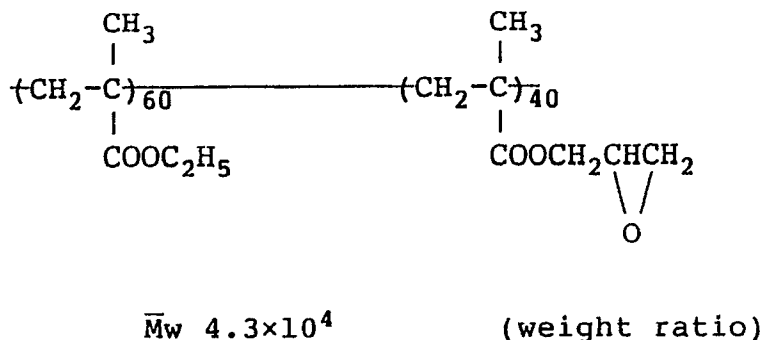
41	[A-49]	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-}_{80} \\ \\ \text{COO(CH}_2\text{)}_2\text{SO}_2\text{CH=CH}_2 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-CH)-}_{20} \\ \\ \text{COO(CH}_2\text{)}_6\text{-N} \end{array}$  $\bar{M}_w \ 4.0 \times 10^4$
42	[A-50]	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-}_{70} \\ \\ \text{COOCH}_2\text{COCH=CH}_2 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-}_{30} \\ \\ \text{COO(CH}_2\text{)}_2\text{OCOCH}_2\text{CH=CH-} \end{array}$  $\bar{M}_w \ 6.5 \times 10^4$

When these printing plates were processed in an analogous manner to Example 27 to examine the electrostatic characteristics and printing property, they exhibited good electrostatic characteristics and a printing durability of at least 10000 prints.

Example 43

The procedure of Example 1 was repeated except using Resin A-14 and 1% by weight of Resin B-1 having the following structure for forming the surface layer instead of Resin A-2 and 0.5% by weight of 1,3-xylylene diisocyanate, thus obtaining the similar results thereto.

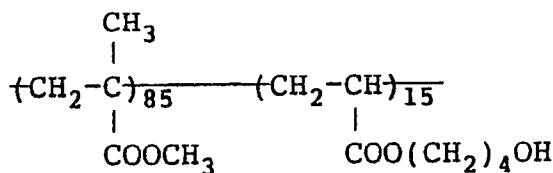
Resin B-1



Example 44

The procedure of Example 2 was repeated except using, for forming the surface layer, 5% by weight of Resin A-13, 1% by weight of Resin B-2 having the following structure and 0.6% by weight of 1,3-xylylene diisocyanate instead of 5% by weight of Resin A-4 and 0.6% by weight of 1,6-hexane diisocyanate, and for oil-desensitizing, an oil-desensitizing processing solution (E-5) prepared by the following recipe instead of Oil-desensitizing Processing Solution E-2:

Resin B-2



$$\bar{M}_w \ 3.3 \times 10^4$$

Oil-desensitizing Processing Solution E-5

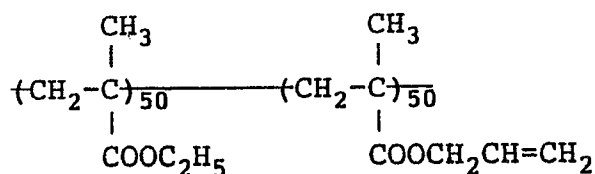
Thiomalic Acid	55 g
Benzyl Alcohol	100 g
Distilled Water	to 1000 ml
pH adjusted with NaOH	11.5

Thus, the similar results were obtained to Example 2.

Example 45

The procedure of Example 3 was repeated except using, for forming the surface layer, 5% by weight of

Resin A-15, 0.8% by weight of Resin B-3 having the following structure and 0.02% by weight of 2,2'-azobisisobutyronitrile instead of 5% by weight of Resin A-6 and 0.75% by weight of 1,4-xylylene diisocyanate used in Example 3:



$$\bar{M}_w \ 7.5 \times 10^4$$

Examples 46 to 57

Example 43 was repeated except using copolymers A-26 to A-37 shown in Table 3 instead of Resin A-14 of the present invention, thus obtaining electrophotographic light-sensitive materials.

When each of the resulting light-sensitive materials was subjected to plate making by means of the same apparatus as that of Example 43, the resulting master plate had a density of at least 1.2 and clear image. When it was subjected to an etching treatment with the processing solution E-1 and printing, further more, 10000 or more prints with a clear image were obtained without occurrence of fog on non-image areas.

When the light-sensitive material was further subjected to the same processings as described above, except after allowing to stand under conditions of 45° C and 75% RH for 3 weeks, no change appeared in the results.

Examples 58 to 63

Example 45 was repeated except using compounds shown in the following Table 7 instead of Resin A-15, Resin B-3 and the asobis compound, coated as the surface layer of the photoreceptor in Example 45, thus obtaining electrophotographic light-sensitive materials. During the same time, the crosslinking compounds were used in the predetermined amounts shown in Table 7 and the others were used in the same amounts as described in Example 45.

Table 7

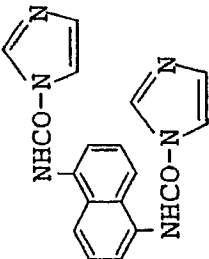
Example	Resin A	Resin B (weight ratio)	Crosslinking Compound	Amount
58	[A-17]	$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2-\text{C})_{95} \\ \\ \text{COOC}_2\text{H}_5 \end{array} \quad \begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2-\text{C})_5 \\ \\ \text{COO}(\text{CH}_2)_2\text{NHCON} \end{array} \quad \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{C} \end{array}$ $\bar{M}_w 1.0 \times 10^4$	1,6-hexadecamine	3 g
59	[A-18]	$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2-\text{C})_{89} \\ \\ \text{COO}-\text{C}_6\text{H}_4-\text{COO}(\text{CH}_2)_2\text{OH} \end{array} \quad \begin{array}{c} (\text{CH}_2-\text{CH})_{10} \\ \\ \text{COOH} \end{array}$ $\bar{M}_w 3.8 \times 10^4$	1,3-xylylene diisocyanate	4 g
60	[A-19]	$\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2-\text{C})_{91} \\ \\ \text{COOCH}_2\text{C}_6\text{H}_5 \end{array} \quad \begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2-\text{C})_8 \\ \\ \text{COOCH}_2\text{CHCH}_2\text{OH} \\ \\ \text{OH} \end{array} \quad \begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2-\text{C})_{1.0} \\ \\ \text{COOH} \end{array}$ $\bar{M}_w 3.5 \times 10^4$		3.5 g

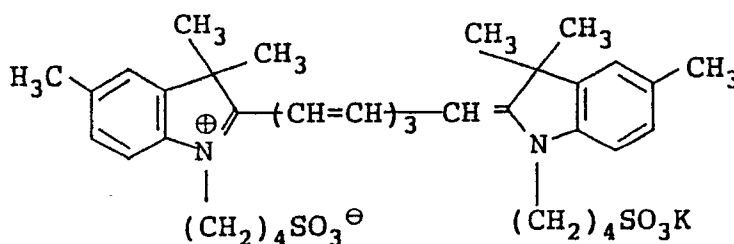
Table 7 (cont'd)

Example	Resin A	Resin B (weight ratio)	Crosslinking Compound	Amount
61	[A-20]	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-}_{92} \\ \\ \text{COOC}_3\text{H}_7 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-}_8 \\ \\ \text{COO(CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_2\text{COOH} \end{array}$ $\bar{M}_w 8.5 \times 10^3$	ethylene glycol diglycidyl ether	6 g
62	[A-21]	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-}_{90} \\ \\ \text{COOCH}_2\text{C}_6\text{H}_5 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-}_{10} \\ \\ \text{COOCH}_2\text{CH-CH}_2 \\ \quad \quad \\ \text{O} \quad \quad \text{O} \end{array}$ $\bar{M}_w 4.5 \times 10^4$	pyromellitic anhydride	2 g
63	[A-22]	$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-}_{90} \\ \\ \text{COOCH}_2\text{C}_6\text{H}_5 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-C)-}_{10} \\ \\ \text{COO(CH}_2\text{)}_2\text{OCO} \end{array}$ $\begin{array}{c} \text{O} \\ \\ \text{C-O} \\ \\ \text{C} \\ \\ \text{O} \end{array}$ $\bar{M}_w 3.0 \times 10^4$	-	-

Example 64

A mixture of 6.5 g of a Resin R-1, copolymer of 2-chlorophenyl methacrylate/acrylic acid (95/5 by weight) having an $\bar{M}_w$ of 7.5×10^3 , 33.5 g of a Resin R-2, copolymer of methyl methacrylate/methyl acrylate/methacrylic acid (78.5/20/1.5 by weight) having an $\bar{M}_w$ of 5.6×10^4 , 200 g of zinc oxide, 0.018 g of a cyanine dye (I) having the following structure, 0.15 g of phthalic anhydride and 300 g of toluene was dispersed in a ball mill 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 20 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 20 °C and 65% RH for 24 hours to prepare an electrophotographic light-sensitive material.

Cyanine Dye (I):



A solution of 5% by weight (as solid content) of Resin A-17, 1% by weight of Resin B-3 and 0.05% by weight of 1,4-tetramethylenediamine in toluene was coated on the resulting photoreceptor by a doctor blade and heated at 100 °C for 30 seconds and at 120 °C for 1 hour to form a surface layer of about 2 μm thick. Then, the light-sensitive material was allowed to stand in a dark place at 20 °C and 65% RH for 24 hours to prepare an electrophotographic light-sensitive material.

The light-sensitive material was then subjected to evaluation of the electrostatic characteristics, image quality and printing property to thus obtain the following results:

Electrostatic Characteristics	V_{10} : -585 (V) D.R.R.: 86% $E_{1/10}$: 20 (erg/cm ²)
Image Quality	I (20 °C, 65%): good II (30 °C, 80%): good
Contact Angle with Water	10 ° or less
Printing Durability	10000 prints

As described above, the light-sensitive material of the present invention exhibited excellent electrostatic characteristics and printing property. The electrostatic characteristics and image quality were measured in the same manner as in Example 27.

Example 65

A mixture of 6.0 g of Resin R-3, 34 g of Resin R-4, 200 g of zinc oxide, 0.018 g of the cyanine dye (II), 0.20 g of maleic anhydride and 300 g of toluene was dispersed in a ball mill 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/m² by means of 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 20 °C and 65% RH for 24 hours to prepare an electrophotographic light-sensitive material.

A mixture of 10 g (as solid content) of Resin A-15, 1.5 g of Resin B-3, 10 g of zinc oxide and 100 g of

toluene was dispersed in a ball mill for 2 hours, to which 1 g of ethylene glycol diglycidyl ether was further added, and the mixture was then dispersed in the ball mill for 10 minutes to prepare a dispersion, which was applied to the surface of the resulting photoreceptor by a wire bar coater and heated at 110 °C for 2 hours to form a surface layer of about 2.5 μm thick. The thus coated paper was allowed to stand in a dark place at 20 °C and 65% RH for 24 hours to prepare an electrophotographic light-sensitive material.

The light-sensitive material was then subjected to evaluation of the electrostatic characteristics and image quality in an analogous manner to Example 64 to thus obtain the following results:

Electrostatic Characteristics	V ₁₀ : -560 (V) D.R.R.: 86% E _{1/10} : 25 (erg/cm ²)
Image Quality	I (20 °C, 65%): good II (30 °C, 80%): good

Then, the light-sensitive material subjected to plate making was immersed in the oil-desensitizing processing solution (E-4), prepared in Example 28, for 20 seconds and washed with water. The non-image area was sufficiently rendered hydrophilic as represented by a contact angle with water of less than 10°. When printing was carried out in an analogous manner to Example 43 using this light-sensitive material as a plate for offset printing and the processing solution E-4 diluted by 20 times with water as dampening water, the print obtaining 10000 prints had a good image quality.

As described above, the light-sensitive material of the present invention exhibited very excellent properties.

Examples 66 to 77

Master plates for offset printing were prepared by using the light-sensitive materials prepared in Examples 43 to 65 and carrying out an etching treatment as follows:

Distilled water was added to 0.5 mole of each of nucleophilic compounds shown in the following Table 8, 100 g of an organic solvent and 10 g of Newcol B4SN (commercial name, manufactured by Nippon Nyukazai KK) to 1000 ml and the pH thereof was adjusted to 10.0.

Each of the light-sensitive materials was immersed and etched in the solution ELP-E diluted by 2 times with distilled water for 20 seconds and then immersed in the above described processing solution at 25 °C for 1 minute.

The thus resulting plate was subjected to printing in the same manner as in Example 43.

Table 8

Example	Light sensitive Material	Nucleophilic Compound	Organic Solvent
66	Example 44	sodium sulfite	benzyl alcohol
67	Example 45	monoethanolamine	-do-
68	Example 47	diethanolamine	methyl ethyl ketone
69	Example 48	thiomalic acid	ethylene glycol
70	Example 50	thiosalicylic acid	benzyl alcohol
71	Example 51	taurine	isopropyl alcohol
72	Example 53	4-sulfobenzenesulfinic acid	benzyl alcohol
73	Example 54	thioglycolic acid	ethanol
74	Example 58	2-mercaptoethylphosphonic acid	dioxane
75	Example 60	serine	-
76	Example 62	sodium thiosulfate	methyl ethyl ketone
77	Example 63	ammonium sulfite	benzyl alcohol

The each material was sufficiently rendered hydrophilic as represented by a contact angle with water of less than 10° . The print obtaining 10000 prints had a clear image and no fog on the non-image area.

5 Examples 78 to 79

Example 64 was repeated except using resins shown in Table 9 instead of Resin A-17 and Resin B-3, used for forming the surface layer in Example 64, and omitting 1,4-tetramethylenediamine, thus preparing printing plate precursors. Each of the light-sensitive materials was irradiated by a high voltage mercury
 10 lamp of 400 W at an interval of 30 cm and then allowed to stand in a dark place for 24 hours under conditions of 20°C and 65% RH to prepare a master plate for lithographic printing.

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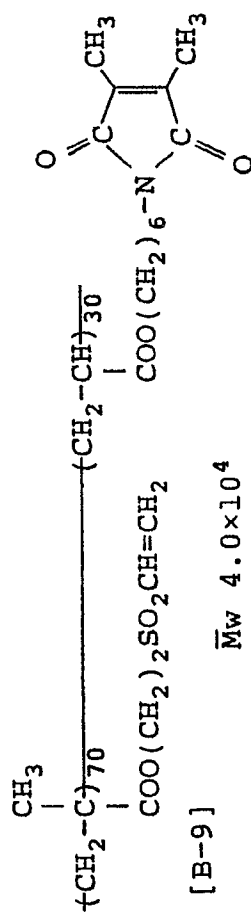
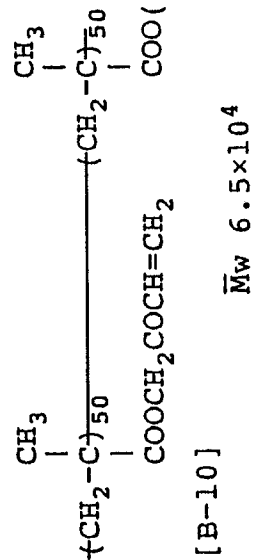
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Table 9

Resin B

 $\bar{M}_w \ 4.0 \times 10^4$  $\bar{M}_w \ 6.5 \times 10^4$

Resin A

[A-24]

[A-25]

Further, the light-sensitive material was subjected to plate making in an analogous manner to Example 64 and the resulting master plate for offset printing had a clear image having a density of at least 1.2.

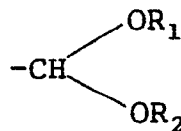
According to the present invention, there can be obtained an electrophotographic lithographic printing plate precursor, which does not deteriorate during long storage under severer conditions and which has excellent electrostatic characteristics as well as good printing properties.

Claims

1. An electrophotographic lithographic printing plate precursor comprising a conductive support having

provided thereon at least one photoconductive layer and further provided thereon a surface layer as an outermost layer, wherein said surface layer comprises at least one resin containing at least one polymeric component having at least one formyl group and functional groups represented by the following General Formula (I):

General Formula (I)



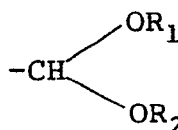
wherein R_1 and R_2 each represent, same or different, hydrocarbon groups or R_1 and R_2 are organic residual radicals which are combined with each other to form a ring.

2. An electrophotographic lithographic printing plate precursor comprising a conductive support having provided thereon at least one photoconductive layer and further provided thereon a surface layer as an outermost layer, wherein said surface layer comprises at least one resin A, at least one resin B and optionally a crosslinking agent:

Resin A

resin containing at least one polymeric component having at least one of formyl group and functional groups represented by the following General Formula (I):

General Formula (I)



wherein R_1 and R_2 each represent, same or different, hydrocarbon groups or R_1 and R_2 are organic residual radicals which are combined with each other to form a ring, and

Resin B

heat- and/or light-hardenable resin.

3. The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the resin containing at least one polymeric component having at least one of formyl group and functional groups represented by General Formula (I) is previously crosslinked.

4. The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the resin containing at least one polymeric component having at least one of formyl group and functional groups represented by General Formula (I) further contains at least one functional group causing a hardening reaction by heat and/or light.

5. The electrophotographic lithographic printing plate precursor as claimed in Claim 1 or Claim 2, wherein when processed with a processing solution containing at least one nucleophilic hydrophilic compound, the hydrophilic compound is added to the end of the formyl group or the functional group to render the binder resin hydrophilic.

6. The electrophotographic lithographic printing plate precursor as claimed in Claim 1 or Claim 2, wherein the polymeric component having at least one of formyl group and functional groups represented by General Formula (I) is represented by the following repeating unit of General Formula (II):

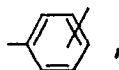
General Formula (II)



wherein Z represent -COO-, -OCO-, -O-, -CO-,



wherein r_1 represents hydrogen atom or a hydrocarbon group, -CONHCOO-, -CONHCONH-, -CH₂COO-,
-CH₂OCO- or



Y represents a direct bond or organic radical for connecting -Z- and -W_o, {Z-Y} can directly connect



and -W_o, W_o represents formyl group or the functional group represented by General Formula (I) and a_1 and a_2 may be same or different, each being hydrogen atom, a halogen atom, cyano group, an alkyl group or an aryl group.

7. The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the polymeric component having at least one of formyl group and functional groups represented by General Formula (I) is in a proportion of 20 to 99% by weight to the binder resin consisting of a copolymer.

8. The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the polymeric component contains a hardenable functional group in a copolymeric component containing at least one of formyl group and the functional group represented by General Formula (I) or in another copolymeric component therefrom.

9. The electrophotographic lithographic printing plate precursor as claimed in Claim 8, wherein the copolymeric component containing a hardenable functional group is in a proportion of 1 to 80% by weight to the surface layer.

10. The electrophotographic lithographic printing plate precursor as claimed in Claim 2, wherein the heat- and/or light-hardenable resin contains a copolymeric component having a heat- and/or light-hardenable functional group.

11. The electrophotographic lithographic printing plate precursor as claimed in Claim 2, wherein Resin B consists of a (meth)acrylic copolymer.

12. The electrophotographic lithographic printing plate precursor as claimed in Claim 2, wherein Resin B contains a copolymeric component containing a crosslinking (hardenable) functional group in a proportion of 0.5 to 40 mole% to Resin B.

13. The electrophotographic lithographic printing plate precursor as claimed in Claim 1 or Claim 2, wherein the resin containing at least one polymeric component having at least one of formyl group and the functional group represented by General Formula (I) has a molecular weight of 10^3 to 10^6 .
14. The electrophotographic lithographic printing plate precursor as claimed in Claim 2, wherein Resin A
5 contains a copolymeric component containing a heat and/or light hardenable functional group in a proportion of 1 to 20% by weight to Resin A.
15. The electrophotographic lithographic printing plate precursor as claimed in Claim 2, wherein Resin A and Resin B are mixed with a Resin A to Resin B ratio of 40-99 to 1-60 by weight.
16. The electrophotographic lithographic printing plate precursor as claimed in Claim 1 or Claim 2, wherein
10 the surface layer resin further contains a crosslinking agent.
17. The electrophotographic lithographic printing plate precursor as claimed in Claim 16, wherein the crosslinking agent is in a proportion of 0.5 to 30% by weight to the resin of the surface layer.
18. The electrophotographic lithographic printing plate precursor as claimed in Claim 1, wherein the photoconductive layer further contains at least one dye as spectral sensitizer.
19. The electrophotographic lithographic printing plate precursor as claimed in Claim 1 or Claim 2, wherein
15 the photoconductive layer contains at least one photoconductive compound selected from the group consisting of inorganic compounds and organic compounds.
20. The electrophotographic lithographic printing plate precursor as claimed in Claim 1 or Claim 2, wherein the photoconductive layer contains 10 to 60 parts by weight of a binder resin to 100 parts by weight of the
20 inorganic photoconductive compound.
21. The electrophotographic lithographic printing plate precursor as claimed in Claim 1 or Claim 2, wherein the photoconductive layer contains 5 to 120 parts by weight of an organic photoconductive compound to 100 parts by weight of a binder resin.
22. The electrophotographic lithographic printing plate precursor as claimed in Claim 1 or Claim 2, wherein
25 the surface layer has a thickness of at most 10 μm .
23. The electrophotographic lithographic printing plate precursor as claimed in Claim 1 or Claim 2, wherein the surface layer is crosslinked after coated.
24. The electrophotographic lithographic printing plate obtained by image-wise exposure and development of a precursor as claimed in any one of the preceding claims.

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European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 31 1567

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
A	EP-A-0 284 748 (FUJI PHOTO FILM CO.,LTD.) * abstract; claims 1-16 * - - -	1-24	G 03 G 5/147 G 03 G 13/28		
A	DE-A-2 533 371 (CANON K.K.) * page 6, line 20 - page 10; claim 1 * - - -	1-24			
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 15 (P-989)(3958) 12 January 1990, & JP-A-1 262556 (FUJI PHOTO FILM CO.,LTD.) 19 October 1989, * the whole document * - - - - -	1-24			
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
			G 03 G 5 G 03 G 13		
The present search report has been drawn up for all claims					
Place of search The Hague		Date of completion of search 06 February 91	Examiner HINDIAS E.		
<table border="0"><tr><td>CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</td><td>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document</td></tr></table>				CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention	E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document
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