

Description

The present invention relates to a process for the application of protective layers or relief images to a substrate, wherein a radiation-sensitive layer consisting of a solid film-forming epoxy resin and of a photoinitiator which can be activated by radiation is transferred to the substrate, then exposed directly or under a photomask and then hardened by the action of heat, after which, if appropriate, the unexposed parts are developed with a solvent.

German Patent 1,522,515 describes a process for the production of printed circuits, wherein a photosensitive layer is transferred from a support to a substrate and then the customary photographic process steps for the production of a relief image are carried out. This process has considerable technological advantages over the direct application of the photosensitive layer to a substrate, for example by means of a coating solution.

However, the photoresist laminates disclosed hitherto, consisting of support and photosensitive layer, have disadvantages attributable mainly to the use of liquid polyfunctional acrylate or methacrylate monomers as photocross-linkable compounds, if appropriate together with binders. The hardened protective layers or relief structures produced with the aid of these laminates do not meet the high thermal requirements which arise, for example, when printed circuit boards are subjected to further processing in soldering baths, and this disadvantage cannot be completely overcome by the addition of crosslinking agents (cf., for example, EP-A-0,073,444). Moreover, the known laminates have the disadvantage that the photocrosslinkable layer is oxygen-sensitive because of the monomers present in it, and can therefore be processed only by taking special protective measures. Thus, for example, exposure must be carried out through a transparent protective film covering the photosensitive layer, which, due to the light scattering which occurs, results in a reduction in the definition. The cold flow characteristic of thermoplastic resist layers furthermore causes the adhesive photosensitive layers to come out at the edges of the normally rolled-up laminates, rendering the material unusable.

It is also known that epoxy resins can be crosslinked with cationic photoinitiators and that these mixtures can be used for the photographic

(= photomechanical) production of relief images, cf. E. Irving et al., Brit. Polym. J., 15, 24 et seq. (1983). There is no mention, however, of the fact that such mixtures can be used as thermally transferable radiation-sensitive layers.

It has now been found, surprisingly, that solid epoxy resins which contain a radiation-sensitive photoinitiator for the polyaddition reaction are outstandingly suitable as photosensitive layers which can easily be transferred from a support to a substrate and can be irradiated directly, without the use of a protective film (in the present case the carrier film) to cover them, optimum definitions being achieved. The laminate used in the process is also characterized by a high storage stability.

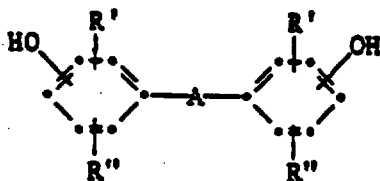
The present invention relates to a process for the production of a protective layer or a relief image on a substrate, wherein a radiation-sensitive layer is transferred from a support to the substrate, then exposed directly or under a photomask and then hardened by the action of heat, after which, if appropriate, the unexposed parts are developed with a solvent, and wherein the radiation-sensitive layer consists of a solid film-forming epoxy resin which contains a photoinitiator, which can be activated by radiation, for the polyaddition reaction.

The solid epoxy resin preferably has an epoxy equivalent weight of 1 to 5 equivalents per kg of resin.

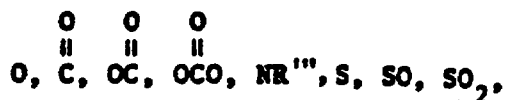
The epoxy resins can be, for example, glycidyl ethers of novolaks of substituted or unsubstituted phenols, for example xylenol, cresol, resorcinol and particularly phenol, and aldehydes, for example acetaldehyde and particularly formaldehyde.

Another preferred group of epoxy resins are the glycidyl ethers of bisphenols. These can be monomers, oligomers or, preferably, low-molecular polymers with an average molecular weight $\bar{M}_w$ of about 1000 to 10,000. The molecular weight is preferably 1000 to 6000.

The bisphenols can be represented by the following formula:



The hydroxyl groups can be in the m-position, but are particularly in the p-position. R' and R'' in this formula can be alkyl having 1 to 6 C atoms, halogen such as chlorine or bromine, and in particular hydrogen atoms. A can be a direct bond or



substituted or unsubstituted alkylidene, cycloalkylidene or alkylene. R''' is a hydrogen atom, phenyl or alkyl having 1 to 6 C atoms.

Examples of substituted or unsubstituted alkylidene are ethylidene, 1,1- or 2,2-propylidene, 2,2-butylidene, 1,1-isobutylidene, dichloroethylidene and trichloroethylidene. Examples of substituted or unsubstituted alkylene are methylene, ethylene, phenylmethylene, diphenylmethylene and methylphenylmethylene. Examples of cycloalkylidene are cyclopentylidene and cyclohexylidene.

Examples of bisphenols are: bis(p-hydroxyphenyl) ether or thioether, bis(p-hydroxyphenyl) sulfone, bis(p-hydroxyphenyl)methane, 1,2-bis(p-hydroxyphenyl)ethane, phenylbis(p-hydroxyphenyl)methane, diphenylbis(p-hydroxyphenyl)methane, 2,2-bis(4'-hydroxy-3',5'-dimethylphenyl)propane, 1,1- or 2,2-bis(p-hydroxyphenyl)butane, 1,1-dichloro- or 1,1,1-trichloro-2,2-bis(p-hydroxyphenyl)ethane, 1,1-bis(p-hydroxyphenyl)cyclopentane and particularly 2,2-bis(p-hydroxyphenyl)propane (bisphenol A) and 1,1-bis(p-hydroxyphenyl)-cyclohexane (bisphenol C).

The epoxy resins also include solid prereacted resins obtainable by the reaction of polyepoxy compounds with suitable hardeners, for example aliphatic, cycloaliphatic or aromatic polyamines, polyols and polycarboxylic acids. Examples of polyepoxy compounds suitable for this purpose are aliphatic, cycloaliphatic or aromatic compounds. Examples of such compounds are the glycidyl ethers and β -methylglycidyl ethers of aliphatic or cycloaliphatic diols or polyols, for example those of ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, diethylene glycol, polyethylene glycol, polypropylene glycol, glycerol, trimethylolpropane, 1,4-dimethylolcyclohexane, 2,2-bis(4-hydroxycyclohexyl)-propane and N,N-bis(2-hydroxyethyl)aniline; and the glycidyl ethers of diphenols and polyphenols, for example resorcinol, 4,4'-dihydroxydiphenylmethane, 4,4'-dihydroxydiphenyl-2,2-propane, novolaks and 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane. Additional examples are N-glycidyl compounds, for example the diglycidyl compounds of ethyleneurea, 1,3-propyleneurea, 5-dimethylhydantoin or 4,4'-methylene-5,5'-tetramethyldihydantoin, or those like triglycidyl isocyanurate.

Other glycidyl compounds of industrial importance are the glycidyl esters of carboxylic acids, in particular dicarboxylic and polycarboxylic acids. Examples of these are the glycidyl esters of succinic acid, adipic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, tetrahydrophthalic and hexahydrophthalic acids, isophthalic acid or trimellitic acid, or of fatty acid dimers.

Examples of polyepoxides other than glycidyl compounds are the diepoxides of vinylcyclohexene and dicyclopentadiene, 3-(3',4'-epoxycyclohexyl)-8,9-epoxy-2,4-dioxaspiro[5.5]undecane, the 3',4'-epoxycyclohexylmethyl ester of 3,4-epoxycyclohexanecarboxylic acid, butadiene diepoxide or isoprene diepoxide, epoxidized linoleic acid derivatives or epoxidized polybutadiene.

The said epoxides can also be prereacted on their own, by catalytic hardening, to give film-forming solid epoxy resins.

Other preferred epoxy resins are epoxy compounds which have been lengthened

beforehand, particularly diglycidyl ethers of dihydric phenols or dihydric aliphatic alcohols having 2 to 4 carbon atoms. The diglycidyl ethers, which have been lengthened beforehand, of 2,2-bis(4-hydroxyphenyl)propane and bis-(4-hydroxyphenyl)methane are particularly preferred. Bisphenols, for example those of the type defined previously, particularly bisphenol A and tetrabromobisphenol A, are preferably used as "advancing" agents.

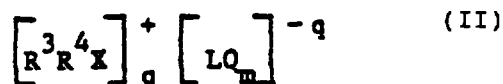
The solid film-forming epoxy resins to be used in the process according to the invention are known or purchasable or can be obtained by known processes. The radiation-sensitive layers produced with these epoxy resins are also preferably non-adhesive so that the photomask which may have been used during exposure can be removed from the layer undamaged and without leaving a residue.

A large number of different cationic compounds have been disclosed as photoinitiators which can be activated by radiation and which are suitable for the polyaddition reaction leading to the crosslinking of the epoxy resins, cf. Brit. Polymer J. 15, pages 24 et seq. (1983) and J. Macromol. Sci. Macromol. Rev. C21, pages 187 et seq. (1981).

Onium salts, particularly those with weakly nucleophilic anions, have proved particularly suitable. Examples of such anions are the halogen complex anions of divalent to heptavalent metals or non-metals, for example Sb, Sn, Fe, Bi, Al, Ga, In, Ti, Zr, Sc, V, Cr, Hf and Cu, as well as B, P and As. The halogen is preferably F. Examples are BF_4^- , PF_6^- , AsF_6^- and SbF_6^- .

Examples of suitable onium salts are aryldiazonium salts and onium salts of groups Va, VIa and VIIa of the periodic table, for example halonium salts, particularly aromatic iodonium and iodoxonium salts, quaternary ammonium, phosphonium and arsonium salts, aromatic sulfonium salts and sulfoxonium salts or selenonium salts.

Preferred halonium salts are those of the formula II



wherein R^3 and R^4 independently of one another are a carbocyclic or heterocyclic aromatic radical having 6 to 20 C atoms, or R^3 and R^4 together are a divalent carbocyclic or heterocyclic aromatic radical, X is a halogen atom, m is a number corresponding to the sum of the values of L and q, L is a divalent to heptavalent metal or non-metal, Q is a halogen atom and q is a number from 1 to 3.

R^3 and R^4 can be substituted by one or more monovalent radicals, for example alkyl or alkoxy having 1 to 8 C atoms, halogen such as F, Cl or Br, nitro or cyano. Examples are phenyl, toluyl, xylyl, chlorophenyl, nitrophenyl, methoxyphenyl and pyridyl. R^3 and R^4 together can be, for example, 2,2'-biphenylene or 2,2'-bipyridyl. Preferred anions are those mentioned above. X is particularly iodine and q is particularly 1. Q is preferably Cl and particularly F. The iodonium salts are described, for example, in patent document DE-A-2,518,639. Diphenyliodonium hexafluorophosphate is particularly preferred.

Another preferred group consists of iodosyl salts of the formula IV

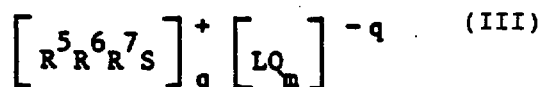


wherein R^7 and R^8 are a carbocyclic or heterocyclic aromatic radical having 6 to 20 C atoms, m is a number corresponding to the sum of the values of L and q, L is a divalent to heptavalent metal or non-metal, Q is a halogen atom and q is a number from 1 to 3.

R^8 and R^9 are preferably phenyl or naphthyl which can be monosubstituted or polysubstituted, for example by C_1 - C_4 alkyl or C_1 - C_4 alkoxy, phenyl,

nitro or halogen. Preferred anions are those mentioned above. Q is preferably Cl and particularly F and q is preferably 1. Diphenyliodosyl hexafluorophosphate or hexafluoroantimonate are examples of these salts. The iodosyl salts can be obtained, for example, by the reaction of diaryliodosyl hydroxide with an acid $H_q [LQ_m]^{q-}$ or ammonium salts thereof, in aqueous or aqueous-organic solutions, at temperatures from about 0°C to 30°C.

Another preferred group consists of sulfonium salts of the formula III



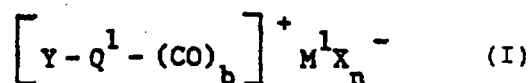
wherein R^5 , R^6 and R^7 independently of one another are a carbocyclic or heterocyclic aromatic radical having 6 to 20 C atoms, or one of R^5 , R^6 and R^7 is this aromatic radical and the other two together are a divalent carbocyclic or heterocyclic aromatic radical, m is a number corresponding to the sum of the values of L and q, L is a divalent to heptavalent metal or non-metal, Q is a halogen atom and q is a number from 1 to 3.

R^5 , R^6 and R^7 are preferably carbocyclic aromatic radicals such as phenyl or naphthyl. These can be monosubstituted or polysubstituted, for example by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, phenyl, nitro or halogen. Q is preferably Cl and particularly F and q is preferably 1. Examples are triphenylsulfonium hexafluorophosphate or hexafluoroantimonate.

Suitable sulfoxonium salts are described, for example, in U.S. Patents 4,383,025, 4,398,014 and 4,299,938.

Other suitable photoinitiators are metal carbonyl compounds, metallocenes and metallocene carbonyl complexes.

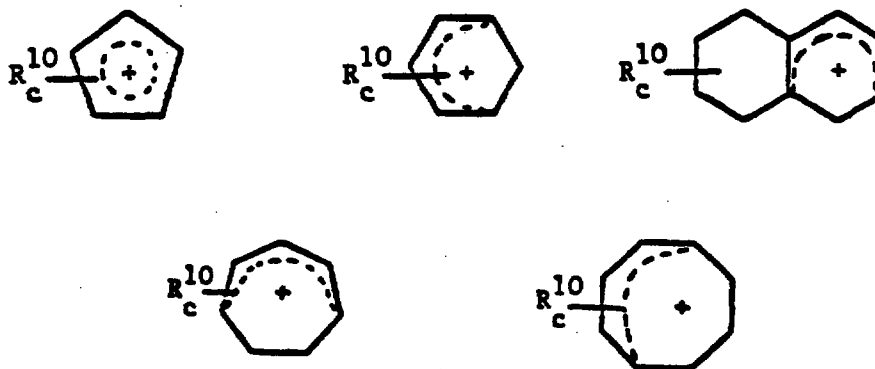
A preferred group consists of salts of the formula I



wherein Y is an arene group or a dienylium group, Q^1 is an atom of a d-block transition metal selected from titanium, vanadium, chromium, manganese, iron, cobalt, nickel and copper; niobium, molybdenum, ruthenium, rhodium, palladium and silver; and tantalum, tungsten, rhenium, osmium, iridium, platinum and gold, b is a positive integer such that the atom Q^1 has a closed electron shell configuration, M^1 is an atom of a metal or non-metal, n is 4, 5 or 6 and is one greater than the valency of M^1 , and X is a fluorine or chlorine atom, with the proviso that if M^1 is antimony, n is 6 and five of the symbols X are fluorine, one of them can also be a hydroxyl group.

If Y denotes an arene group, i.e. is itself a 6-electron ligand, it can be a mononuclear or polynuclear group, including a fused cyclic group. It is preferably a hydrocarbon group which is unsubstituted or substituted by one or more alkoxy groups and preferably contains 6 to 18 carbon atoms, such as benzene, toluene, mesitylene, naphthalene, biphenyl, phenanthrene, fluorene and anthracene.

If Y is a dienylium group, it is preferably a cyclic group of one of the following formulae



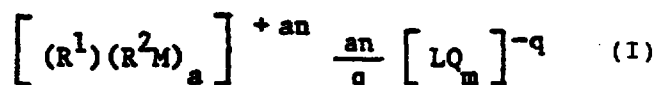
wherein R^{10} is an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 to 4 carbon atoms or an alkyl group having up to 12 carbon atoms, interrupted by one or more oxycarbonyl groups, and c is zero, 1, 2 or 3.

Q^1 is preferably chromium, cobalt, nickel and especially iron or manganese.

The atom M^1 can be, for example, iron, tin, bismuth, aluminium, gallium, indium, titanium, zirconium, scandium, vanadium, chromium or manganese, but is preferably antimony, arsenic, boron or phosphorus. The anion $M^1X_n^-$ can thus be, for example, tetrachloroaluminate or hexachloroferrate, but it is preferably tetrafluoroborate, hexafluoroarsenate, hydroxypentafluoroantimonate, hexafluoroantimonate or hexafluorophosphate.

Salts of these types are described, for example, in EP-A-0,094,914.

A particularly preferred group of photoinitiators consists of those of the formula



wherein a is 1 or 2 and n and q independently of one another are each an integer from 1 to 3, M is the cation of a monovalent to trivalent metal from group Ivb to VIIb, VIII or Ib of the periodic table, m is an integer corresponding to the sum of the values of L and q, Q is a halogen atom, L is a divalent to heptavalent metal or non-metal, R^1 is a π -arene and R^2 is a π -arene or the anion of a π -arene.

Suitable π -arenes R^1 and R^2 are, in particular, aromatic groups having 6 to 24 carbon atoms or heteroaromatic groups having 3 to 30 carbon atoms, it being possible for these groups to be unsubstituted or monosubstituted or polysubstituted by identical or different monovalent radicals such as halogen atoms, preferably chlorine or bromine atoms, or C_1-C_8 alkyl,

C_1-C_8 alkoxy, cyano, C_1-C_8 alkylthio, C_2-C_6 monocarboxylic acid alkyl ester, phenyl, C_2-C_5 alkanoyl or benzoyl groups. These π -arene groups can be mononuclear, fused polynuclear or non-fused polynuclear systems, it being possible in the last-mentioned systems for the nuclei to be linked directly or via bridge members such as -S- or -O-.

As the anion of a π -arene, R^2 can be an anion of a π -arene of the abovementioned type, for example the indenyl anion and especially the cyclopentadienyl anion, it also being possible for these anions to be unsubstituted or monosubstituted or polysubstituted by identical or different monovalent radicals such as C_1-C_8 alkyl, C_2-C_6 monocarboxylic acid alkyl ester, cyano, C_2-C_5 alkanoyl or benzoyl groups.

The abovementioned alkyl, alkoxy, alkylthio, monocarboxylic acid alkyl ester and alkanoyl substituents can be straight-chain or branched. Typical alkyl, alkoxy, alkylthio, monocarboxylic acid alkyl ester and alkanoyl substituents are, respectively, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl and n-octyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, n-hexyloxy and n-octyloxy, methylthio, ethylthio, n-propylthio, isopropylthio, n-butylthio, n-pentylthio and n-hexylthio, carboxylic acid methyl, ethyl, n-propyl, isopropyl, n-butyl and n-pentyl esters, and acetyl, propionyl, butyryl and valeryl. The abovementioned alkyl, alkoxy, alkylthio and monocarboxylic acid alkyl ester groups preferably have 1 to 4 and especially 1 or 2 carbon atoms in the alkyl moieties and the abovementioned alkanoyl groups preferably have 2 or 3 carbon atoms. Preferred substituted π -arenes or anions of substituted π -arenes are those containing one or two of the abovementioned substituents, especially chlorine or bromine atoms, methyl, ethyl, methoxy, ethoxy, cyano or carboxylic acid methyl or ethyl ester groups and acetyl groups.

Identical or different π -arenes can be present as R^1 and R^2 . Suitable heteroaromatic π -arenes are systems containing S, N and/or O atoms. Heteroaromatic π -arenes containing S and/or O atoms are preferred. Examples of suitable π -arenes are benzene, toluene, xylenes, ethylbenzene, methoxybenzene, ethoxybenzene, dimethoxybenzene, p-chlorotoluene, chloro-

benzene, bromobenzene, dichlorobenzene, acetylbenzene, trimethylbenzene, trimethoxybenzene, naphthalene, 1,2-dihydronaphthalene, 1,2,3,4-tetrahydronaphthalene, methylnaphthalenes, methoxynaphthalenes, ethoxynaphthalenes, chloronaphthalenes, bromonaphthalenes, biphenyl, indene, biphenylene, fluorene, phenanthrene, anthracene, 9,10-dihydroanthracene, triphenylene, pyrene, naphthacene, coronene, thiophene, chromene, xanthene, thioxanthene, benzothiophene, naphthothiophene, thianthrene, diphenyl ether, diphenyl sulfide, acridine and carbazole.

If a is 2, both the R^2 groups are preferably the anion of a π -arene and both the M atoms are atoms of the same metal. Examples of anions of substituted π -arenes are the anions of methylcyclopentadiene, ethylcyclopentadiene, n -propylcyclopentadiene and n -butylcyclopentadiene, and the anions of dimethylcyclopentadiene, of cyclopentadienecarboxylic acid methyl and ethyl esters and of acetylcyclopentadiene, propionylcyclopentadiene, cyanocyclopentadiene and benzoylcyclopentadiene. Preferred anions are the anion of unsubstituted indene and especially of unsubstituted cyclopentadiene.

Preferably, a has the value 1, R^1 is benzene, toluene, xylene, methoxybenzene, chlorobenzene, p -chlorotoluene, naphthalene, methylnaphthalene, chloronaphthalene, methoxynaphthalene, biphenyl, indene, pyrene or diphenylene sulfide, and R^2 is the anion of cyclopentadiene, acetylcyclopentadiene or indene or is benzene, toluene, xylene, trimethylbenzene, naphthalene or methylnaphthalene.

Particularly preferred complexes of the formula I are those in which a is 1, R^1 is η^6 -pyrene or η^6 -naphthalene, R^2 is the anion of η^5 -cyclopentadiene, n is preferably 1 or 2, especially 1, and q is preferably 1. M is, for example, Ti^+ , Ti^{2+} , Ti^{3+} , Zr^+ , Zr^{2+} , Zr^{3+} , Hf^+ , Hf^{2+} , Hf^{3+} , Nb^+ , Nb^{3+} , Cr^+ , Mo^+ , Mo^{2+} , W^+ , W^{2+} , Mn^+ , Mn^{2+} , Re^+ , Fe^{2+} , Co^{2+} , Co^{3+} , Ni^{2+} or Cu^{2+} . M is preferably a chromium, cobalt, manganese, tungsten or molybdenum cation, especially an iron cation and particularly preferably Fe^{2+} .

Examples of suitable metals or non-metals L are Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, Sc, V, Cr, Mn and Cu, lanthanides such as Ce, Pr and Nd, or actinides such as Th, Pa, U or Np. Suitable non-metals are especially B, P and As. L is preferably P, As, B or Sb, P being particularly preferred.

Examples of complex anions $[LQ_m]^{-q}$ are BF_4^- , PF_6^- , AsF_6^- and SbF_6^- .

Examples of compounds of the formula II are $(\eta^6\text{-toluene})(\eta^5\text{-indenyl})\text{-iron(II) hexafluorophosphate}$, $(\eta^6\text{-pyrene})(\eta^5\text{-cyclopentadienyl})\text{iron(II) hexafluoroantimonate}$, $(\eta^6\text{-toluene})(\eta^5\text{-cyclopentadienyl})\text{iron(II) hexafluorophosphate}$, $(\eta^6\text{-naphthalene})(\eta^5\text{-cyclopentadienyl})\text{iron(II) hexafluoroarsenate}$ and $(\eta^6\text{-benzene})(\eta^5\text{-cyclopentadienyl})\text{-cobalt(III) bis(tetrafluoroborate)}$. Such metallocene salts are described, for example, in patent document EP-A-0,094, 915.

The photoinitiators can be used in a quantity of 0.1-15% by weight, preferably 0.1-10% by weight and especially 0.5-5% by weight based on the epoxy resin.

The resist laminates used in the process according to the invention are prepared by customary processes, for example by initially dissolving the individual components in a suitable inert solvent.

Suitable organic solvents are polar solvents, particularly polar aprotic solvents, which can be used by themselves or in mixtures of at least two solvents. Examples of suitable solvents are: ethers such as diethyl ether, dibutyl ether, tetrahydrofuran, dioxane, methylethylene glycol, dimethylethylene glycol, dimethyldiethylene glycol, diethyldiethylene glycol, dibutyldiethylene glycol and dimethyltriethylene glycol, halogenohydrocarbons such as methylene chloride, chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane, carboxylic acid esters and lactones, such as propylene carbonate, ethyl acetate, methyl propionate, ethyl benzoate, ethylglycol acetate, 2-methoxyethyl acetate, γ -butyrolactone, γ -valerolactone and mevalolactone, sulfoxides such as dimethyl sulfoxide and tetramethyl sulfoxide, sulfones

such as dimethyl sulfone, diethyl sulfone, trimethylenesulfone and tetramethylenesulfone, ketones such as dimethyl ketone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone, and substituted benzenes such as chlorobenzene and nitrobenzene.

Other customary additives can be incorporated at this stage, for example fillers, adhesion promoters and dyes, which do not have an adverse effect on the action of the initiators, and sensitizers. Examples of sensitizers are: perylene, 9,10-dichloroanthracene, 9,10-diphenylanthracene, 3,4-benzopyrene, 1-chloroanthracene, 2-methylanthracene, 9-methylanthracene, 2-t-butylanthracene, anthracene, 1,12-benzperylene, trans-1,3,5-hexatriene, 1,2-benzanthracene, pyrene, pentaphene, diphenyltetraacetylene, trans-stilbene, 1,2,3,4-dibenzanthracene, 1,2,5,6-dibenzanthracene, 1,3-cyclohexadiene, 1,2,7,8-dibenzanthracene, 1,2-benzopyrene, fluoroanthene, 1,2-benzochrysene, tetraacetylene glycol, diethyltetraacetylene, 1-aminonaphthalene, benzil, coronene, 1-nitronaphthalene, 3,4-benzofluorene, diphenyltriacetylene, 2,2'-binaphthyl, 1-naphthaldehyde, 5,6-benzochrysene, 1-acetylnaphthalene, 3,4,5,6-dibenzophenanthrene, cis-stilbene, 2,3-butanedione, chrysene, 1,2-benzofluorene, 2,3-benzofluorene, 1-benzoylnaphthalene, 1-naphthonitrile, naphthalene-1-carboxylic acid, diphenyldiacetylene, 1,2,6,7-dibenzopyrene, cyclopentadiene, 9-acetylphenanthrene, p-terphenyl, 1-naphthol, 1-iodonaphthalene, 2-phenylnaphthalene, 3,4-benzophenanthrene, 3-acetylphenanthrene, 1-bromonaphthalene, 1-chloronaphthalene, 2-naphthonitrile, acenaphthene, trans-1,3-pentadiene, 2-naphthaldehyde, naphthalene-2-carboxylic acid, 2-acetylnaphthalene, 2-benzoylnaphthalene, 2,4-hexadien-1-ol, 1-methylnaphthalene, 1-methoxynaphthalene, 1,3-butadiene, 1-fluoronaphthalene, isoprene, 2-iodonaphthalene, 2-bromonaphthalene, 2-chloronaphthalene, 2-naphthol, 4-phenylbenzophenone, 4-phenylacetophenone, 2-methylnaphthalene, naphthalene, o-terphenyl, styrene, phenanthrene, 4,4'-bis-dimethylaminobenzophenone, diphenylacetylene, anthraquinone, 4,4'-dichlorobiphenyl, triacetylene glycol, 4-hydroxybiphenyl, 2,4,6-octatriyne, m-terphenyl, 2-bromobiphenyl, thioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-dodecylthioxanthone, 1-methoxycarbonylthioxanthone, 2-ethoxycarbonylthioxanthone, 3-(2-methoxyethoxycarbonyl)thioxanthone, 4-butoxycarbonylthioxanthone, 1-cyano-3-chloro-thioxanthone, biphenyl, 3,4-methylenedioxyacetophenone, 4-cyanobenzophenone, triphenylene, 4-benzoylpyridine, 2-benzoylpyridine,

fluorene, 4,4'-dichlorobenzophenone, 4-trifluoromethylbenzophenone, 3-methoxybenzophenone, 4-chlorobenzophenone, 3-chlorobenzophenone, 4,4'-dibromobenzophenone, 3-benzoylpyridine, 4-methoxybenzophenone, 3,4-dimethylbenzophenone, 4-methylenebenzophenone, benzophenone, 2-methylbenzophenone, 4,4'-dimethylbenzophenone, 2,5-dimethylbenzophenone, 2,4-dimethylbenzophenone, 4-cyanoacetophenone, 4-fluorobenzophenone, o-benzylbenzophenone, α -chloroacetophenone, diphenylene ether, carbazole, 4,4'-dimethoxybenzophenone, 4-acetylpyridine, 3,4,5-trimethylacetophenone, p-dicyanobenzene, 4-methoxybenzaldehyde, 4-methylbenzaldehyde, 3,5-dimethylacetophenone, 4-bromoacetophenone, 4-methoxyacetophenone, 3,4-dimethylacetophenone, benzaldehyde, triphenylmethylacetophenone, anthrone, 4-chloroacetophenone, 4-trifluoromethylacetophenone, phenylacetylene, 2,4,6-trimethylacetophenone, 3-methoxyacetophenone, 3-methylacetophenone, o-dicyanobenzene, 1-tetralone, 3-bromoacetophenone, 4-methylacetophenone, 3-cyanoacetophenone, 3-trifluoromethylacetophenone, hexachlorobenzene, xanthone, acetophenone, 2-phenylbutyrophenone, allylacetophenone, β -phenylpropiophenone, valero-phenone, propiophenone, butyrophenone, 2-ethoxycarbonyl-3-nitrothioxanthone, 3-thiophenylphthalimide and N-methyl-4-thiophenylphthalimide.

Preference is given to thioxanthenes, phthalimide thioethers and particularly anthracenes. These are preferably added in a quantity of 0.1-10% by weight, preferably 0.1-5% by weight, based on the epoxy resin.

The solution is applied to the support by means of conventional methods, for example by dipping, coating, spraying or centrifuging, with the aid of a feed hopper with a slot die, or by means of roll coating. The layer thicknesses are in the range from 10 to about 200 μm according to the intended use. After coating, the solvent is removed, for example by heating and, if appropriate, also in vacuo.

The support can be transparent or opaque and is preferably flexible. Preference is given to special papers and particularly plastic films, especially those made of polyethylene terephthalate, which can also be pigmented.

The layer present on the support can be protected by a covering film against

dust and mechanical damage; polyolefin films or silicone-coated paper, for example, are suitable for this purpose. If the support and the covering film are impermeable to actinic radiation, the laminate can safely be handled in daylight. It may therefore be advantageous to tint the support and covering film accordingly.

The process according to the invention can be carried out, for example, according to the following details. The surface of the substrate is first cleaned. The substrate can be made of a variety of materials according to the intended use, for example plastics, metals, metal alloys, metalloids, semiconductors, glass, ceramic, SiO_2 or Si_3N_4 .

The radiation-sensitive layer is then transferred from the support to the substrate, if appropriate after removal of the covering film, the transfer generally taking place under the application of pressure and heat. In this process, heating can be effected up to 150°C .

It is a particular advantage of the process according to the invention that the support can be removed after lamination, because the radiation-sensitive layer is non-adhesive, and the said layer can then be further modified by irradiation.

In the continuation of the process according to the invention, the layer, after irradiation, is hardened by the action of heat, preferably at temperatures of 50 to 150°C , particularly 80 to 130°C . In practice, only the already exposed parts are hardened by the action of heat in this step.

Irradiation and subsequent thermal hardening make it possible to produce particularly resistant protective layers on substrates. To produce photographic images, the irradiation is effected through a photomask and the image is then developed by treatment with a solvent.

The hardenable mixtures are advantageously irradiated with electron beams or actinic light, preferably having a wavelength of 200 to 600 nm and an intensity of 150 to 8000 Watts. Examples of suitable light sources are xenon lamps, argon lamps, tungsten lamps, carbon arcs, metal halide lamps, and

metal arc lamps such as low-pressure, medium-pressure and high-pressure mercury discharge lamps. The irradiation is preferably carried out with metal halide lamps or high-pressure mercury discharge lamps. The irradiation time depends on a variety of factors, for example the thickness of the copying layer used, the type of light source and its distance from the composite irradiated. The irradiation time can preferably be, for example, 10-120 seconds.

For the thermal after-treatment, the exposed compositions can be heated in conventional convection ovens. If short heating or reaction times are required, the heating can be effected by exposure with, for example, IR radiation, IR lasers or microwave devices. The hardening time is in the range between approx. 1 and 10 minutes.

Developing is carried out with organic solvents in which the epoxy resins used are soluble. This process step can be mechanized and carried out, for example, with a spray developer or a continuous developer. Developing can also be carried out simply by wiping or by treatment with solvent vapour. Suitable solvents have already been mentioned above.

The surface revealed in the non-image areas can then be after-treated or modified according to the intended use. The surfaces can be, for example, etched, coated with metal by electroplating or electroless plating, implanted with ions, rendered hydrophilic, anodized, soldered or lacquered.

Principal fields of application for the process according to the invention are the manufacture of printed circuits, solder resist masks, high-pressure and low-pressure mouldings, nameplates, offset printing plates and templates.

Hardened epoxy resins are characterized by good thermomechanical, chemical and electrical properties, for example heat stability, good adhesion to substrates, high volume resistivity, and good resistance to electroplating, etching and soldering baths.

The process according to the invention makes it possible to combine these

advantages, over direct coating with solutions, with a technologically less expensive and simple operation, the radiation-sensitive photoresist laminates used according to the invention additionally having the following advantages: reduced cold flow of the radiation-sensitive layer and hence elimination of adhesion of the film edges; high photosensitivity; good storage stability and direct exposure of the layer, achieving a better definition. It has furthermore been found that a better covering of the edges of conductor tracks formed is also achieved by means of the lamination process.

The examples which follow illustrate the invention in greater detail:

Examples 1-4: A solution consisting of 10 g of an epoxy resin and 0.06 mmol of (⁶-1-methylnaphthalene)(η ⁵-cyclopentadienyl)iron(II) hexafluorophosphate in 4 g of 1-acetoxy-2-ethoxyethane is applied to a polyester film (polyethylene terephthalate) with a 75 μm wire doctor. After drying at 80°C, the resulting film (thickness: 150 μm) is applied to a copper-coated epoxy board at 130°C with a roller laminator. Exposure is then carried out under a 21 step Stouffer sensitivity guide with a 500 W metal halide lamp at a distance of 50 cm, and this is followed by hardening. A 1:1 mixture of 1,1,1-trichloroethane and ethyl methyl ketone is used as the developer. The last step of which a complete image is formed is taken as a measure of the photosensitivity.

Example	Epoxy resin	Epoxy value (Eq/kg)	Exposure time (seconds)	Hardening time (minutes)	Hardening temperature (°C)	Developing time (seconds)	Step
1	epoxycresol novolak	4.5	30	2	100	15	4
			30	2	120	15	5
			60	2	100	15	5
			120	5	120	30	10
2	bisphenol A diglycidyl ether	1.35	30	2	100	15	3
			30	2	120	15	3
			60	2	100	15	4
			120	5	120	30	7
3	bisphenol A diglycidyl ether	2.41	30	2	100	15	4
			60	2	100	100	6
			30	2	120	15	4
			120	5	120	30	8
4	bisphenol A diglycidyl ether leng- thened with tetrabromo- bisphenol A beforehand		30	2	110	30	4
			120	5	110	30	9
			120	5	100	30	10

Examples 5-8: 10 g of an industrial epoxycresol novolak (epoxy content: 4.5 eq/kg) and 0.25 g of photoinitiator are dissolved in 4 g of 1-acetoxy-2-ethoxyethane and applied to a polyester film with a 75 μm wire doctor. After drying at 80°C, the resulting film (thickness: $\sim 50 \mu\text{m}$) is laminated onto a copper-coated epoxy board at 130°C. Exposure is carried out under a 21 step Stouffer sensitivity guide with a 5000 W metal halide lamp (distance 50 cm), and this is followed by hardening. A 1:1 mixture of 1,1,1-trichloroethane and ethyl methyl ketone is used as the developer. The last step of which a complete image is formed is taken as a measure of the photo-sensitivity.

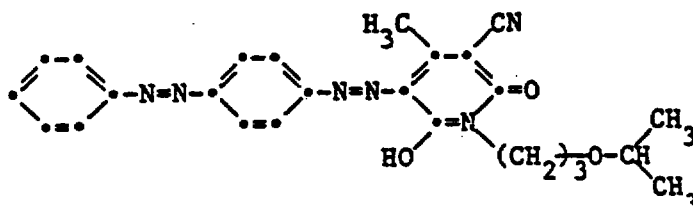
Example	Initiator	Exposure time (seconds)	Hardening time (minutes)	Hardening temperature (°C)	Developing time (seconds)	Step
5	(η ⁶ -naphthalene)- (η ⁵ -cyclopentadienyl)- iron(II) hexafluoro- antimonate	30	2	110	1	11
		5	2	110	1	7
6	triphenylsulfonium hexafluorophosphate 2-methylantracene*)	30	10	110	1	4
		30	2	110	1	1
7	diphenyliodonium hexafluoro- antimonate 2-methylantracene*)	30	10	110	1	15
		30	2	110	1	15
		5	2	110	1	9
8	diphenyliodosyl hexafluorophosphate 2-methylantracene*)	30	10	110	1	2

*) 2.5% by weight based on epoxycresol novolak

Examples 9-12: 10 g of an industrial epoxycresol novolak (epoxy content: 4.5 eq/kg) and 0.06 mmol of (η^6 -1-methylnaphthalene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate are dissolved in 4 g of 1-acetoxy-2-ethoxyethane and applied to a polyester film with a 75 μ m wire doctor. The resulting film is dried at 80°C and laminated onto various substrates at 130°C with a roller laminator. Exposure is then carried out under a 21 step Stouffer sensitivity guide with a 5000 W metal halide lamp (distance $\sim$ 50 cm), and this is followed by hardening at 110°C. A 1:1 mixture of 1,1,1-trichloroethane and ethyl methyl ketone is used as the developer. The last step of which a complete image is formed is taken as a measure of the photosensitivity.

Example	Exposure time and hardening time Substrate	Exposure time (seconds)			
		30		60	
		Hardening time (minutes)		Hardening time (minutes)	
		2	10	2	10
9	electrochemically roughened aluminium (from Rotaprint)	4	11	7	13
10	polyester film (Mylar)	6	8	8	12
11	paper impregnated with phenol/form- aldehyde resin (specification FR2)	2	4	6	8
12	Cu-coated epoxy laminate (Cu vetronite)	2	6	8	9

Example 13: 10g of an industrial epoxycresol novolak (epoxy content 4.5 eq/kg), 0.15 g of (η^6 -1-methylnaphthalene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate and 0.3 g of a dye of the formula



are dissolved in a mixture of 4 g of 1-acetoxy-2-ethoxyethane and 1 g of cyclohexanone and applied to a polyester film with a 75 μ m wire doctor. The resulting film is dried at 80°C and then laminated onto a copper-coated epoxy board at 130°C with a roller laminator. (Dry film thickness 30 μ m). Exposure is then carried out through a negative pattern of a printed circuit with a high-pressure mercury discharge lamp (5000 W, distance from the lamp 50 cm) and the exposed board is completely hardened for 5 minutes at 110°C. Developing of the exposed and hardened board is carried out in 1-acetoxy-2-ethoxyethane, the unexposed areas being dissolved away. This gives the image of the pattern. By etching in a 50% FeCl₃ solution, the blank copper parts are dissolved away, resulting in the conductive pattern of the desired circuit.

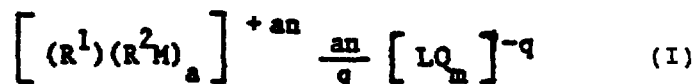
Example 14: 6 g of an industrial epoxycresol novolak (epoxy content 4.5 eq/kg), 4 g of allyl glycidyl ether, 0.15 g (3.68×10^{-4} mol) of (η^6 -1-methylnaphthalene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate and 1.5 g of a chlorinated phthalocyanine dye (Colour Index No. 74260) are dissolved in a mixture of 4 g of 1-acetoxy-2-ethoxyethane and 1 g of cyclohexanone and applied to a polyester film with a 75 μ m wire doctor. The resulting film is dried at 80°C (dry film thickness 30 μ m). The film is then laminated onto a copper-coated epoxy board by means of a roller laminator. This board is then exposed through a negative pattern of a solder resist mask with a high-pressure mercury discharge lamp (5000 W, distance from the lamp 50 cm). The exposed board is hardened

at 110°C for approx. 5 minutes and, after cooling, is developed in 1-acetoxy-2-ethoxyethane. This gives the image of the desired pattern, the lands being free. The board is then tinned in a soldering bath at 250°C, only the free copper areas being tinned. The hardened photoresist withstands this treatment even when the tinning cycle is repeated 10 times.



Patent Claims:

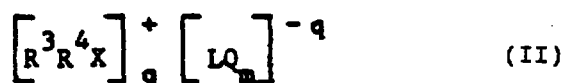
1. A process for the production of a protective layer or a relief image on a substrate, wherein a radiation-sensitive layer is transferred from a support to the substrate, then exposed directly or under a photomask and then hardened by the action of heat, after which, if appropriate, unexposed parts are developed with a solvent, and wherein the radiation-sensitive layer consists of a solid film-forming epoxy resin containing a photoinitiator, which can be activated by radiation, for the polyaddition reaction.
2. The process according to claim 1, wherein a dye is contained in the photosensitive layer.
3. The process according to claim 1, wherein the hardening temperature is in the range from 50°C to 150°C.
4. The process according to claim 1, wherein the epoxy resin has an epoxy equivalent weight of 1 to 5 equivalents per kg of resin.
5. The process according to claim 1, wherein the photo-initiator is incorporated in a quantity of 0.1 to 15% by weight based on the epoxy resin.
6. The process according to claim 1, wherein the photo-initiator corresponds to a compound of the formula I





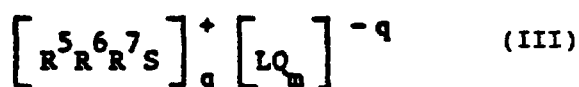
wherein a is 1 or 2 and n and q independently of one another are each an integer from 1 to 3, M is the cation of a monovalent to trivalent metal from group Ivb to VIIb, VIII or Ib of the periodic table, m is an integer corresponding to the sum of the values of L and q, Q is a halogen atom, L is a divalent to heptavalent metal or non-metal, R¹ is a π-arene and R² is a π-arene and R² is a π-arene or the anion of a π-arene.

7. The process according to claim 1, wherein the photo-initiator is a halonium salt of the formula II



wherein R³ and R⁴ independently of one another are a carbocyclic or heterocyclic aromatic radical having 6 to 20 C atoms, or R³ and R⁴ together are a divalent carbocyclic or heterocyclic aromatic radical, X is a halogen atom, m is a number corresponding to the sum of the values of L and q, L is a divalent to heptavalent metal or non-metal, Q is a halogen atom and q is a number from 1 to 3.

8. The process according to claim 1, wherein the photo-initiator is a sulfonium salt of the formula III



wherein R⁵, R⁶ and R⁷ independently of one another are a carbocyclic or heterocyclic aromatic radical having 6 to 20 C atoms, or one of R⁵, R⁶ and R⁷ is this aromatic radical and the other two together are a divalent carbocyclic or heterocyclic aromatic radical, m is a number corresponding to the sum of the values of L and q, L is a divalent to heptavalent metal or non-metal, Q is a halogen atom and q is a number from 1 to 3.

9. The process according to claim 1, wherein the photo-initiator is an iodosyl salt of the formula IV



wherein R^7 and R^8 are a carbocyclic or heterocyclic aromatic radical having 6 to 20 C atoms, m is a number corresponding to the sum of the values of L and q , L is a divalent to heptavalent metal or non-metal, Q is a halogen atom and q is a number from 1 to 3.

10. The process according to claim 1, wherein a sensitizer is additionally contained in the photosensitive layer.

11. The process according to claim 1, wherein the epoxy resin is a diglycidyl ether, lengthened with dihydric phenols beforehand, of aliphatic diols having 2 to 4 C atoms, or a bisphenol diglycidyl ether lengthened with dihydric phenols beforehand, or wherein the epoxy resin is a glycidyl ether of a novolak or of a bisphenol.



As printed

Claims

1. A process for the production of a protective layer or a relief image on a substrate, wherein a radiation-sensitive layer is transferred from a support to the substrate, then exposed directly or under a photomask and then hardened by the action of heat, after which, if appropriate, unexposed parts are developed with a solvent, and wherein the radiation-sensitive layer consists of a solid film-forming epoxy resin containing a photoinitiator, which can be activated by radiation, for the polyaddition reaction.

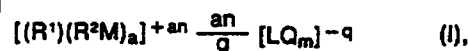
2. The process according to claim 1, wherein a dye is contained in the photosensitive layer.

3. The process according to claim 1, wherein the hardening temperature is in the range from 50 °C to 150 °C.

4. The process according to claim 1, wherein the epoxy resin has an epoxy equivalent weight of 1 to 5 equivalents per kg of resin.

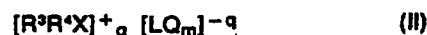
5. The process according to claim 1, wherein the photo-initiator is incorporated in a quantity of 0.1 to 15% by weight based on the epoxy resin.

6. The process according to claim 1, wherein the photo-initiator corresponds to a compound of the formula I



wherein a is 1 or 2 and n and q independently of one another are each an integer from 1 to 3, M is the cation of a monovalent to trivalent metal from group IVb to VIIb, VIII or Ib of the periodic table, m is an integer corresponding to the sum of the values of L and q, Q is a halogen atom, L is a divalent to heptavalent metal or non-metal, R¹ is a π-arene and R² is a π-arene and R² is a π-arene or the anion of a π-arene.

7. The process according to claim 1, wherein the photo-initiator is a halonium salt of the formula II



wherein R³ and R⁴ independently of one another are a carbocyclic or heterocyclic aromatic radical having 6 to 20 C atoms, or R³ and R⁴ together are a divalent carbocyclic or heterocyclic aromatic radical, X is a halogen atom, m is a number corresponding to the sum of the values of L and q, L is a divalent to heptavalent metal or non-metal, Q is a halogen atom and q is a number from 1 to 3.

8. The process according to claim 1, wherein the photo-initiator is a sulfonium salt of the formula III



wherein R⁵, R⁶ and R⁷ independently of one another are a carbocyclic or heterocyclic aromatic radical



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having 6 to 20 C atoms, or one of R⁵, R⁶ and R⁷ is this aromatic radical and the other two together are a divalent carbocyclic or heterocyclic aromatic radical, m is a number corresponding to the sum of the values of L and q, L is a divalent to heptavalent metal or non-metal, Q is a halogen atom and q is a number from 1 to 3.

9. The process according to claim 1, wherein the photo-initiator is an iodosyl salt of the formula IV



wherein R⁷ and R⁶ are a carbocyclic or heterocyclic aromatic radical having 6 to 20 C atoms, m is a number corresponding to the sum of the values of L and q, L is a divalent to heptavalent metal or non-metal, Q is a halogen atom and q is a number from 1 to 3.

10. The process according to claim 1, wherein a sensitizer is additionally contained in the photosensitive layer.

11. The process according to claim 1, wherein the epoxy resin is a diglycidyl ether, lengthened with dihydric phenols beforehand, of aliphatic diols having 2 to 4 C atoms, or a bisphenol diglycidyl ether lengthened with dihydric phenols beforehand, or wherein the epoxy resin is a glycidyl ether of a novolak or of a bisphenol.

Revendications

1. Procédé pour réaliser une couche protectrice ou une image en relief selon lequel on transfère une couche photosensible d'une matière support au substrat, puis on expose la couche à un rayonnement directement ou sous un photomasque et ensuite on la durcit par voie thermique, après quoi, le cas échéant, on élimine les parties qui n'ont pas été touchées par la lumière en effectuant un développement au moyen d'un solvant, ce procédé étant caractérisé en ce que la couche photosensible est constituée d'une résine époxydique feuillonnée solide qui contient un photo-amorceur photo-activable pour la polyaddition.

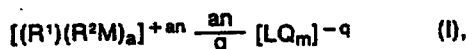
2. Procédé selon la revendication 1 caractérisé en ce qu'il y a un colorant dans la couche photosensible.

3. Procédé selon la revendication 1 caractérisé en ce que la température de durcissement est située dans l'intervalle allant de 50 à 150 °C.

4. Procédé selon la revendication 1 caractérisé en ce que la résine époxydique a un poids équivalent d'époxy de 1 et 5 équivalents par kilogramme de la résine.

5. Procédé selon la revendication 1 caractérisé en ce que le photo-amorceur est incorporé en une quantité de 0,1 à 15% en poids par rapport à la résine époxydique.

6. Procédé selon la revendication 1 caractérisé en ce que le photo-amorceur est un composé répondant à la formule I:



dans laquelle

a est égal à 1 ou à 2,

n et q représentent chacun, indépendamment l'un de l'autre, un nombre entier de 1 à 3,

M représente le cation d'un métal univalent à trivalent pris dans l'un des groupes IVb à VIIb, VIII et Ib de la classification périodique,

m désigne un nombre entier égal à la somme de q et de la valence de L,

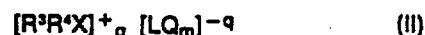
Q représente un atome d'halogène,

L représente un métal ou un non-métal dont la valence peut aller de 2 à 7,

R¹ représente un π -arène et

R² représente un π -arène ou l'anion d'un π -arène.

7. Procédé selon la revendication 1 caractérisé en ce que le photo-amorceur est un sel d'halonium répondant à la formule II:



dans laquelle R³ et R⁴ représentent chacun, indépendamment l'un de l'autre, un radical aromatique carbocyclique ou hétérocyclique qui contient de 6 à 20 atomes de carbone, ou encore R³ et R⁴ forment ensemble un radical aromatique carbocyclique ou hétérocyclique bivalent, X représente un atome d'halogène, m désigne un nombre égal à la somme de q et de la valence de L, L représente un métal ou un non-métal dont la valence peut aller de 2 à 7, Q représente un atome d'halogène et q représente un nombre de 1 à 3.

8. Procédé selon la revendication 1 caractérisé en ce que le photo-amorceur est un sel de sulfonium répondant à la formule III:



dans laquelle R⁵, R⁶ et R⁷ représentent chacun, indépendamment les uns des autres, un radical aromatique carbocyclique ou hétérocyclique qui contient de 6 à 20 atomes de carbone, ou l'un des symboles R⁵, R⁶ et R⁷ représente un tel radical aromatique et les deux autres forment ensemble un radical aromatique carbocyclique ou hétérocyclique bivalent, m désigne un nombre égal à la somme de q et de la valence de L, L représente un métal ou un non-métal dont la valence peut aller de 2 à 7, Q représente un atome d'halogène et q désigne un nombre de 1 à 3.

9. Procédé selon la revendication 1 caractérisé en ce que le photo-amorceur est un sel d'iodosyle répondant à la formule IV:



dans laquelle R⁷ et R⁶ représentent chacun un radical aromatique carbocyclique ou hétérocyclique contenant de 6 à 20 atomes de carbone, m désigne un nombre entier égal à la somme de q et de la valence de L, L représente un métal ou un non-métal dont la valence peut aller de 2 à 7, Q représente un atome d'halogène et q désigne un nombre de 1 à 3.

10. Procédé selon la revendication 1 caractérisé en ce que la couche photosensible contient en outre un sensibilisateur.

11. Procédé selon la revendication 1 caractérisé en ce que la résine époxydique est un éther diglyci-



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dylique qui dérive d'un diol aliphatique contenant de 2 à 4 atomes de carbone et qui a été pré-allongé par un diphénol, ou est un éther diglycidylique d'un bis-

phénol qui a été pré-allongé par un diphénol, ou est un éther glycidylique d'une novolaque ou d'un bis-phénol.