

Description

The present invention relates to novel curable compositions containing metallocene complexes, to the activated precursors (active types) obtainable therefrom and to the use thereof.

Various iodonium, sulfonium and diazonium salts are known from the literature as photoinitiators for cationically polymerizable organic materials (see, for example, DE-B 2,518,639, J. Polym. Sci., Polymer Chemistry Ed., 17, 1059 (1979), Makromol. Chem., Suppl. 3, 348 (1979), DE-A 2,520,489 and 2,854,011 and 3,021,376, US-A 4,210,449 and GB-A 2,046,269). Owing to the relatively low level of their absorption range (about 190 to 400 nm), these known photoinitiators require the use of sensitizers, such as coloured polycyclic hydrocarbons, for example perylene dyestuffs, aromatic amines, benzoin alkyl ethers or alkoxyacetophenones, in order to cure cationically polymerizable systems under the action of light. The curing by heat of systems containing such photoinitiators is expediently carried out in the presence of reducing agents, such as copper, tin, iron or cobalt salts, thiophenols, ascorbic acid and the like.

Epoxide curing compositions containing a metallocene, preferably a ferrocene, as a latent curing agent by heat are described in DE-A 2,025,814. Curing by radiation is not suggested. The organometallic compounds contain two cyclopentadienyl anions, but no π -arene, as ligands. The preparation of iron-arene complexes by ligand exchange in the presence of Lewis acids is described in Chem. Comm., 1971, 1071 and in Can. J. Chem., 57, 933 (1979). The Lewis acids employed are $AlCl_3$ or BF_3 -etherate.

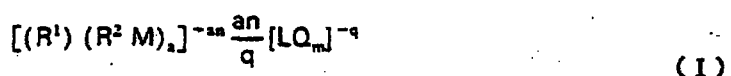
The stereospecific ring protonization of bisindenyl iron and the subsequent isolation of the corresponding hexafluorophosphate salt is disclosed in J. Organomet. Chem., 88, 207 (1975). A reference to the use of metallocene salts as initiators for cationic polymerization is not to be found in any of these publications.

The object of the present invention consists in

providing novel curable compositions which can be cured under the action of light and/or heat without the addition of sensitizers.

Accordingly, the invention relates to curable compositions containing

- A) a cationically polymerizable organic material and
- B) at least one 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 represents the cation of a monovalent to trivalent metal from group IVb to VIb, VIII or Ib of the periodic system, m is an integer corresponding to the valency of L + q and Q denotes a halogen atom, L denotes a divalent to heptavalent metal or non-metal, R¹ denotes a π-arene and R² denotes a π-arene or the anion of a π-arene.

Suitable π-arenes R¹ and R² 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 optionally monosubstituted or polysubstituted by identical or different monovalent radicals, such as halogen atoms, preferably chlorine or bromine atoms, or by C₁-C₈-alkyl, C₁-C₈-alkoxy, cyano, C₁-C₈-alkylthio, alkyl C₂-C₆-monocarboxylate, phenyl, C₂-C₅-alkanoyl or benzoyl groups. These π-arene groups can be mononuclear, condensed polynuclear or non-condensed polynuclear systems, it being possible in the last-mentioned groups for the nuclei to be attached directly or via bridge members such as -S- or -O-.

As the anion of a π-arene, R² can be an anion of a π-arene of the abovementioned type, for example the indenyl anion and especially the cyclopentadienyl anion, it being also possible for these anions to be optionally monosubstituted or polysubstituted by identical or different monovalent radicals, such as C₁-C₈-alkyl, alkyl C₂-C₆-monocarboxylate,

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cyano, C₂-C₅-alkanoyl or benzoyl groups.

The alkyl, alkoxy, alkylthio, alkyl monocarboxylate and alkanoyl substituents can be linear or branched in this connection. Typical alkyl, alkoxy, alkylthio, alkyl monocarboxylate or alkanoyl substituents which may be mentioned are 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, methyl, ethyl, n-propyl, isopropyl, n-butyl and n-pentyl carboxylate and acetyl, propionyl, butyryl and valeroyl, respectively. In this regard, alkyl, alkoxy, alkylthio and alkyl monocarboxylate groups having 1 to 4 and particularly 1 or 2 carbon atoms in the alkyl moieties and also alkanoyl groups having 2 or 3 carbon atoms are preferred. Substituted π -arenes or anions of substituted π -arenes which are preferred are those containing one or two of the abovementioned substituents, in particular chlorine or bromine atoms or methyl, ethyl, methoxy, ethoxy, cyano, methyl or ethyl carboxylate groups and acetyl groups.

R¹ and R² can be identical or different π -arenes. 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, chlorobenzene, 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, diphenylene oxide, diphenylene sulfide, acridine and carbazole.

If a is 2, R^2 preferably represents in each case the anion of a π -arene and M is in each case the same metal atom. Examples of anions of substituted π -arenes are the anions of methylcyclopentadiene, ethylcyclopentadiene, n -propylcyclopentadiene and n -butylcyclopentadiene, and the anions of dimethylcyclopentadiene, methyl and ethyl cyclopentadienecarboxylate, acetylcyclopentadiene, propionylcyclopentadiene, cyanocyclopentadiene and benzoylcyclopentadiene. Preferred anions are the anion of unsubstituted indene and, especially, of unsubstituted cyclopentadiene.

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

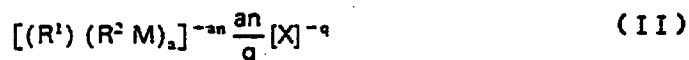
Examples of M are Ti^+ , Ti^{2+} , Ti^{3+} , Zr^+ , Zr^{2+} , Zr^{3+} , Hf^+ , Hf^{2+} , Hf^{3+} , Nb^+ , Nb^{2+} , Nb^{3+} , Cr^+ , Mo^+ , Mo^{2+} , W^+ , W^{2+} , Mn^+ , Mn^{2+} , Re^+ , Fe^{2+} , Co^{2+} , Co^{3+} , Ni^{2+} or Cu^{2+} . M is preferably a chromium, cobalt, manganese, tungsten or molybdenum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

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, in particular, 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^- , SbF_6^- , $FeCl_4^-$, $SnCl_6^{2-}$, $SbCl_6^-$ and $BiCl_6^-$. The complex anions which are particularly

preferred are SbF_6^- , BF_4^- , AsF_6^- and PF_6^- .

The compounds of the formula I can be prepared by methods which are in themselves known, for example by reacting a compound of the formula II



with a salt of an anion $[\text{LQ}_m]^{-q}$ wherein a, m, n, q, R^1 , R^2 , M and L have the meanings indicated under the formula I and $[X]^{-q}$ represents an anion other than $[\text{LQ}_m]^{-q}$.

Both the compounds of the formula II and the compounds of the formula III



wherein a and M have the meanings indicated above and $R^{1'}$ represents a π -arene or the anion of a π -arene and R^2 represents an anion of a π -arene can be prepared by reacting identical or different π -arenes in the presence of a Lewis acid with a salt of a metal from group IVb to VIb, VIII or Ib of the periodic system. The compounds of the formulae I, II and III are also suitable for carrying out ligand exchange by reacting these compounds in the presence of a Lewis acid with a π -arene other than R^1 and/or R^2 or $R^{1'}$, respectively. In these cases, n is preferably 2, particularly preferentially 1.

Compounds of the formula I wherein L is a metal can also be prepared by reacting identical or different π -arenes in the presence of a Lewis acid with a suitable salt of a metal from group IVb to VIb, VIII or Ib of the periodic system, for example a titanium, zirconium, chromium, manganese and, especially, iron salt. Finally, it is also possible to convert compounds of the formula I into complexes of the formula I containing a different anion $[\text{LQ}_m]^{-q}$ in a conventional manner by anion exchange.

In a preferred embodiment, uncharged π -complexes of the formula III, for example ferrocene, or bis- $(\eta^5\text{-indenyl})$ -

iron (II) are employed as the starting materials, and these complexes are converted by ligand exchange into a complex of the formula II, which is then reacted with a salt of an anion $[LQ_m]^{-q}$. The complex of the formula II obtained as an intermediate product in this reaction is usually not isolated.

Examples of suitable salts of anions $[LQ_m]^{-q}$ are alkali metal, alkaline earth metal or ammonium salts. It is preferable to use alkali metal salts, particularly preferably sodium and potassium salts.

Examples of suitable Lewis acids for the reaction described above are $AlCl_3$, $AlBr_3$, BF_3 , $SnCl_4$ and $TiCl_4$, $AlCl_3$ being preferred. It can be advantageous to carry out the ligand exchange reactions by adding a reducing agent, for example aluminium or magnesium, to the reaction mixture, or to add a reducing agent, for example Na_2SO_3 or ascorbic acid, to the reaction mixture subsequently. The preferred reducing agent is aluminium. The ligand exchange reactions are expediently carried out in an inert organic solvent.

Examples of suitable solvents are aliphatic or cycloaliphatic hydrocarbons, such as octane, nonane, decane and cyclohexane. If desired, it is also possible to employ an excess of the π -arene as the solvent.

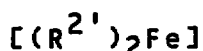
The reaction of the compounds of the formula II with a salt of an anion $[LQ_m]^{-q}$ and the anion replacement conversion of compounds of the formula I are expediently carried out in an aqueous or aqueous-alcoholic medium, for example in mixtures of water and methanol or ethanol. The salts of the anions $[LQ_m]^{-q}$ are employed in at least stoichiometric amounts, but preferably in excess.

The invention also relates to a process for the preparation of compounds of the formula Ia



wherein R^1 , L, Q, m and q have the meaning mentioned above and R^2 represents an anion of a π -arene by reacting an uncharged π -complex of the formula IIIa

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(IIIa)

with a π -arene R^1 in the presence of aluminium and a Lewis acid followed by treatment with a salt of the anion $[LQ_m]^{q-}$, characterized in that the Lewis acid employed is $TiCl_4$.

The new compounds (η^6 -toluene) (η^5 -indenyl)-iron-(II) hexafluorophosphate, (η^6 -pyrene) (η^5 -cyclopentadienyl)-iron-(II) hexafluoroantimonate, (η^6 -naphthalene) (η^5 -cyclopentadienyl)-iron-(II) hexafluoroantimonate, (η^5 -naphthalene) (η^5 -cyclopentadienyl)-iron-(II) hexafluoroarsenate, (η^6 -2-methoxynaphthalene) (η^5 -cyclopentadienyl)-iron-(II) hexafluorophosphate, (η^6 -diphenylene sulfide) (η^5 -cyclopentadienyl)-iron-(II) hexafluorophosphate, (η^6 -perylene) (η^5 -cyclopentadienyl)-iron-(II) hexafluorophosphate and bis-(η^6 -1-methylnaphthalene)-iron-(II) hexafluorophosphate also form a subject of the present invention.

Examples of cationically polymerizable organic materials which are suitable for the curable compositions according to the invention are those of the following types, which can be employed on their own or in the form of mixtures of at least two components:

I. Ethylenically unsaturated compounds which can be polymerized by a cationic mechanism. These include:

1. Monoolefins and diolefins, for example isobutylene, butadiene, isoprene, styrene, α -methylstyrene, divinylbenzenes, N-vinylpyrrolidone, N-vinylcarbazole and acrolein.
2. Vinyl ethers, for example methyl vinyl ether, isobutyl vinyl ether, trimethylolpropane trivinyl ether, ethylene glycol divinyl ether; and cyclic vinyl ethers, for example 3,4-dihydro-2-formyl-2H-pyran (dimeric acrolein) and 2-hydroxymethyl-3,4-dihydro-2H-pyran 3,4-dihydro-2H-pyran-2-carboxylate.
3. Vinyl esters, for example vinyl acetate and vinyl stearate.

II. Cationically polymerizable heterocyclic compounds, for

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example ethylene oxide, propylene oxide, epichlorohydrin and glycidyl ethers of monohydric alcohols or phenols, for example n-butyl glycidyl ether, n-octyl glycidyl ether, phenyl glycidyl ether and cresyl glycidyl ether; glycidyl acrylate, glycidyl methacrylate, styrene oxide and cyclohexene oxide; oxetans, such as 3,3-dimethyloxetan and 3,3-di-(chloromethyl)-oxetan; tetrahydrofuran; dioxolanes, trioxane and 1,3,6-trioxacyclooctane; lactones, such as β -propiolactone, γ -valerolactone and ϵ -caprolactone; thiiranes, such as ethylene sulfide and propylene sulfide; azetidines, such as N-acylazetidines, for example N-benzoylazetidine, and the adducts of azetidine with diisocyanates, for example 2,4-toluylene and 2,6-toluylene diisocyanate and 4,4'-diaminodiphenylmethane diisocyanate; epoxy resins; and linear and branched polymers having glycidyl groups in their side chains, for example homopolymers and copolymers of glycidyl polyacrylates and polymethacrylates.

Compounds which are particularly important amongst these polymerizable compounds mentioned above are the epoxy resins and especially the diepoxides and polyepoxides and epoxide resin prepolymers of the type used for the preparation of crosslinked epoxy resins. The diepoxides and polyepoxides can be 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 or 1,4-dimethylolcyclohexane or of 2,2-bis-(4-hydroxycyclohexyl)-propane and N,N-bis-(2-hydroxyethyl)-aniline; 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. Further examples are N-glycidyl compounds, for example the diglycidyl compounds of ethyleneurea, 1,3-propyleneurea or 5-dimethylhydantoin or of 4,4'-methylene-5,5'-tetramethyldihydantoin, or

compounds such as triglycidyl isocyanurate.

Further 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 acid, isophthalic acid or trimellitic acid or of demerized (sic) fatty acids.

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, 3',4'-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, butadiene diepoxide or isoprene diepoxide, epoxidized linoleic acid derivatives or epoxidized polybutadiene.

Preferred epoxy resins are optionally advanced diglycidyl ethers of dihydric phenols or dihydric aliphatic alcohols having 2 to 4 carbon atoms. The optionally advanced diglycidyl ethers of 2,2-bis-(4-hydroxyphenyl)-propane and of bis-(4-hydroxyphenyl)-methane are particularly preferred.

The following are also suitable as cationically polymerizable compounds:

III. Methylol compounds:

1. Aminoplasts, such as the N-hydroxymethyl, N-methoxymethyl, N-n-butoxymethyl and N-acetoxymethyl derivatives of amides or amide-like compounds, for example cyclic ureas such as ethyleneurea (imidazolidin-2-one), hydantoin, uron (tetrahydro-oxadiazin-4-one), 1,2-propyleneurea (4-methylimidazolidin-2-one), 1,3-propyleneurea (hexahydro-2H-pyrimid-2-one), hydroxypropyleneurea (5-hydroxyhexahydro-2H-pyrimid-2-one), 1,3,5-melamine and further polytriazines, such as acetoguanamine, benzoguanamine and adipoguanamine.

If desired it is possible to employ aminoplasts containing both N-hydroxymethyl and N-alkoxymethyl groups or both N-hydroxymethyl and N-acetoxymethyl groups (for example a hexamethylolmelamine in which 1 to 3 of the hydroxyl groups have been etherified with methyl groups).

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Preferred aminoplasts are the condensation products of urea, uron, hydantoin or melamine with formaldehyde and also partly or completely etherified products of such condensation products with an aliphatic, monohydric alcohol having 1 to 4 carbon atoms.

2. Phenoplasts.

Preferred phenoplasts are resols which have been prepared from a phenol and an aldehyde. Suitable phenols include phenol itself, resorcinol, 2,2-bis-(p-hydroxyphenyl)-propane, p-chlorophenol, a phenol which is substituted by one or two alkyl groups each having 1 to 9 carbon atoms, such as o-, m- and p-cresol, the xlenols, p-tert.-butylphenol and p-nonylphenol and also phenyl-substituted phenols, in particular p-phenylphenol. The aldehyde condensed with the phenol is preferably formaldehyde, but other aldehydes, such as acetaldehyde and furfural, are also suitable. If desired, a mixture of such curable phenol/aldehyde resins can be used.

The preferred resols are condensation products of phenol, p-chlorophenol, resorcinol or o-, m- or p-cresol with formaldehyde.

The curable compositions according to the invention can be obtained in any desired form, for example as homogeneous, liquid mixtures or in a homogeneous or inhomogeneous glassy form. Homogeneous glassy products can be obtained in a manner which is in itself known, for example by liquefying solid polymerizable organic materials, if appropriate with the addition of suitable solvents, in the dark or under red light, heating the materials to temperatures above their glass transition point, adding the initiator of the formula I and cooling the resulting mixtures. If desired, the glassy products thus obtained can then be comminuted. Inhomogeneous glassy products can be obtained, for example, by mixing glassy polymerizable materials in powder form with initiators according to the invention.

The curable compositions according to the invention are stable for a considerable time on storage at room temperature in a relative degree of darkness, for example in red

light. Depending on their composition and their end use, for example for the production of coatings or films, they can be cured by the direct application of heat. The temperatures for direct heat curing are preferably near to the melting point of the initiator employed. Curing by heat is normally complete after about 3 to 10 minutes.

A particularly preferred process is two-stage polymerization (curing) by first activating the initiator of the formula I by irradiating the curable compositions and then subjecting the activated precursors thus obtained to heat-curing, the irradiation temperature being below the temperature employed for the subsequent heat-curing. These activated precursors can normally be cured at temperatures which are appreciably lower than those required in the case of direct heat-curing, being advantageously within the range from 50° to 110°C. This two-stage curing also makes it possible to control the polymerization in a particularly simple and advantageous manner. In addition the activated precursors obtainable from the glassy, curable compositions according to the invention are stable on storage at room temperature for a considerable time, even when exposed to light, in contrast with known cationically polymerizable compositions of the state of the art, for example those containing sulfonium or iodonium salts as initiators. This characteristic constitutes a further essential advantage of the two-stage curing and of these activated precursors. Activated precursors obtainable from liquid, curable compositions according to the invention generally have only a limited stability on storage when exposed to light, and are expediently used further immediately.

The irradiation of the curable mixtures for the preparation of the activated precursors is expediently effected by means of electron beams or actinic light, preferably of a wavelength of 200 to 600 nm and an intensity of 150 to 5,000 watts. Examples of suitable light sources are xenon lamps, argon lamps, tungsten lamps, carbon arcs and metal halide and metal arc lamps, such as low-pressure, medium-pressure and

high-pressure mercury vapour lamps. It is preferable to carry out the irradiation with metal halide or high-pressure mercury vapour lamps. The irradiation time depends on various factors, including, for example, the polymerizable organic material, the nature of the light source and the distance of the latter from the irradiated material. The irradiation time is preferably 10 to 60 seconds.

After exposure, the compositions can be heated in conventional convection ovens. If short heating or reaction times are necessary, heating can be effected by exposure to, for example, IR irradiation, IR lasers or microwave equipment.

Accordingly, the invention also relates to activated curable compositions which can be obtained by irradiating, at a temperature below that used for the subsequent heat-curing, curable compositions containing a cationically polymerizable organic material A) and at least one compound of the formula I. What has been said above in regard to the preferred cationically polymerizable materials and compounds of the formula I also applies here.

The curable compositions and the activated precursors obtainable therefrom can also contain further additives which are known and are customarily employed in the techniques relating to photopolymerizable materials. Examples of such additives are pigments, colorants, fillers and reinforcing agents, glass fibres and other fibres, flame-retardant substances, antistatic agents, flow control agents, antioxidants and light stabilizers.

In order to increase their stability to storage in the dark, the curable compositions and activated precursors can contain weak organic bases, such as nitriles, amides, lactones or urea derivatives. Small amounts of UV absorbers and/or organic dyestuffs can be added in order to avoid premature reaction caused by unintentional exposure to light.

Additionally, the curable composition and the activated precursors can contain monofunctional or polyfunctional compounds or resins which cure by a free radical mechanism. Examples of these are acrylate and/or methacrylate esters of

aliphatic polyols. The curing reaction of these substances is initiated by (photo)initiators or electron beams which form free radicals. Examples of initiators which can be activated by heat are peroxides or azo compounds. Examples of initiators which are activated by exposure to light are acetophenones, acylphosphine oxides or aromatic ketones. Polyfunctional hydroxyl compounds, for example those described in German Offenlegungsschrift 2,639,395, can be incorporated in order to improve the end properties of epoxide resins.

An essential advantage of the curable compositions according to the invention and of the activated precursors obtainable from them consists in the fact that it is possible to dispense with the use of conventional photosensitizers, even for short curing times.

The curable compositions according to the invention and the activated precursors obtainable therefrom are suitable, for example, for the production of surface coatings on various substrates. They are preferably employed in a liquid form for this application. Examples of suitable substrates are metals, such as steel, aluminium, copper, cadmium and zinc, ceramics, glass, plastics, paper or wood.

If, in the two-stage polymerization described above, only part of the coating is initially irradiated through a mask, it is possible to remove the unexposed areas by means of a suitable solvent, after a subsequent brief curing by heat. The curable compositions according to the invention are thus suitable for the reproduction of images or for the production of printing plates and, in particular, printed circuits (photoresists) by methods which are in themselves known (see, for example, British Patent Specification 1,495,746).

The compositions according to the invention and the activated precursors obtainable therefrom can also be used as adhesives or for the preparation of cements, fillers or fibre-reinforced composite materials and laminates. It is also possible to cure in two stages curable compositions

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according to the invention which contain, as the polymerizable material, an epoxy resin or a phenoplast.

The procedure adopted for this is first to convert the mixture of initiator of the formula I and epoxy resin or phenoplast into the partly cured B-stage by irradiation in the presence of a latent crosslinking agent, capable of being activated by heat, for the epoxy resin or phenoplast. The partly cured composition thus obtained is then heated in a second stage to achieve complete curing. It is preferable to use a polycarboxylic anhydride as the latent crosslinking agent capable of being activated by heat. The curable compositions according to the invention, containing epoxy resins or phenoplasts, are particularly suitable for the production of printed circuits, filament winding products, moulding compositions or adhesive films (see, for example, published European Patent Application 44,274, in which known uses of this kind are described in greater detail).

For the above applications, it is expedient for the curable compositions according to the invention or the activated precursors obtainable therefrom to contain 0.1 to 15% by weight, preferably 0.5 to 5% by weight, relative to the polymerizable organic material A), of at least one compound of the formula I.

Particular interest also attaches to homogeneous, glassy, curable compositions and activated precursors obtainable therefrom containing up to equimolar amounts of an initiator of the formula I and a polymerizable organic material A), in which connection "equimolar" is to be understood as meaning that it relates to the reactive group of the polymerizable organic material. Mixtures of this type can be used as curing agents for cationically polymerizable materials of the type described above, in particular epoxy resins. Non-activated, curable mixtures of this type are advantageously added directly to glassy, cationically polymerizable materials and are cured by heat in the above-mentioned manner. Corresponding activated precursors are suitable, in the liquid or solid (glassy) form, for use as

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curing agents for cationically polymerizable material.

Example 1

A mixture of 2 g of bis-(η^5 -indenyl)-iron(II), 1.8 g of aluminium chloride, 0.18 g of aluminium and 50 ml of toluene is stirred for 14 hours at 100°C. The mixture is cooled to room temperature and poured into 200 g of ice-water, stirred for 30 minutes and then filtered. The aqueous, orange-coloured phase is separated off and mixed with a solution of 1.3 g of KPF_6 in 100 ml of water. The resulting crystals are filtered off, washed twice with 20 ml of water and dried for 14 hours at 40°C/13,000 Pa, which gives 2.1 g (75% of theory) of (η^6 -toluene)(η^5 -indenyl)-iron(II) hexafluorophosphate. Recrystallization from methylene chloride/n-hexane affords 1.85 g (66% of theory) of the abovementioned complex; melting point 168-173°C.

Example 2

A mixture of 8 g of ferrocene, 11.4 g of aluminium chloride, 1.12 g of aluminium, 10.3 g of pyrene, 3 drops of mesitylene and 50 ml of an octane fraction is stirred for 14 hours at 110°C. Working up is carried out as described in Example 1. 5.5 g of the sodium salt of SbF_6 are added to the aqueous phase, and the resulting crystals are isolated by filtration and are dried for 14 hours at 40°C/13,000 Pa, which affords 6.0 g (25% of theory) of (η^6 -pyrene)(η^5 -cyclopentadienyl)-iron(II) hexafluoroantimonate. Recrystallization from methylene chloride/n-hexane affords 5.1 g (21.5% of theory) of the abovementioned complex; melting point 160-170°C.

Example 3

(η^6 -Toluene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate, melting point 150-160°C; prepared as described in Bull. Soc. Chim. France, 2572 (1975).

Example 4

(η^6 -Methoxybenzene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate, melting point 125-136°C; prepared as described in Dokl. Akad. Nauk SSSR, 175, 609 (1967).

Example 5

(η^6 -p-Chlorotoluene) (η^5 -cyclopentadienyl)-iron-(II) hexafluorophosphate, melting point 225-230°C; prepared as described in J. Organomet. Chem. 20, 169 (1969).

Example 6

(η^6 -Naphthalene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate, melting point 160-168°C; prepared as described in J. Organomet. Chem., 101, 221 (1975).

Example 7

(η^6 -Naphthalene) (η^5 -cyclopentadienyl)-iron(II) tetrafluoborate; melting point 126-131°C; prepared as described in Izv. Akad. Nauk SSSR, Ser. Khim., 8, 1472 (1966).

Example 8

(η^6 -Naphthalene) (η^5 -cyclopentadienyl)-iron(II) hexafluoroantimonate: prepared from the compound according to Example 7 by dissolving 2 g of (η^6 -naphthalene) (η^5 -cyclopentadienyl)-iron(II) tetrafluoborate in 100 ml of 2:1 water/methanol and adding 1.5 g of NaSbF₆. The brown crystals are isolated and dried for 16 hours at 40°C/13,000 Pa; melting point 151-157°C.

Example 9

(η^6 -Naphthalene) (η^5 -cyclopentadienyl)-iron(II) hexafluoroarsenate; prepared from the compound according to Example 7 by dissolving 2 g of (η^6 -naphthalene) (η^5 cyclopentadienyl)-iron(II) tetrafluoborate in 100 ml of 2:1 water/methanol and adding 1.4 g of KAsF₆. The brown crystals are isolated and dried for 16 hours at 40°C/13,000 Pa; melting point 149-158°C.

Example 10

(η^6 -Chloronaphthalene) (η^5 -cyclopentadienyl)-iron-(II) hexafluorophosphate, melting point 147-151°C; prepared as described in J. Organomet. Chem., 101, 221 (1975).

Example 11

(η^6 -2-Methoxynaphthalene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate.

A mixture of 4 g of ferrocene, 5.7 g of aluminium chloride, 0.56 g of aluminium and 50 g of 2-methoxynaphtha-

lene is heated at 110°C for 16 hours, then cooled and poured into 200 g of ice-water, which is stirred for half an hour and filtered. 3.9 g of potassium hexafluorophosphate are then added to the filtrate. The orange-coloured crystals are isolated and dried for 16 hours at 40°C/13,000 Pa; melting point 123-130°C.

Example 12

(η^6 -Biphenyl) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate; melting point 135-140°C, prepared as described in C.R. Acad. Sc. Ser. C., 272, 1337 (1971).

Example 13

(η^6 -Diphenylene sulfide) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate is prepared in a manner analogous to that described in Example 11 from 4 g of ferrocene, 5.7 g of aluminium chloride, 0.56 g of aluminium, 50 g of diphenylene sulfide and 3.5 g of ammonium hexafluorophosphate; melting point 166-170°C.

Example 14

(η^6 -Pyrene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate is prepared in a manner analogous to that of Example 11 from 4 g of ferrocene, 5.7 g of aluminium chloride, 0.56 g of aluminium, 50 g of pyrene and 3.5 g of ammonium hexafluorophosphate; melting point 169-175°C.

Example 15

A mixture of 1.3 g of ferrocene, 1.8 g of aluminium chloride, 1.7 g of perylene and 30 ml of an octane fraction is stirred at 100°C for 4 hours. Working up is carried out as described in Example 1. 0.9 g of sodium sulfite and 1.2 g of KPF₆ are added to the aqueous phase, and the resulting crystals are isolated by filtration and dried for 14 hours at 40°C/13,000 Pa, thereby affording 0.4 g (11% of theory) of (η^6 -perylene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate.

Example 16

(η^6 -Mesitylene) (η^5 -acetylcyclopentadienyl)-iron(II) hexafluorophosphate; melting point 150-158°C, prepared by the method described in Dokl. Akad. Nauk SSSR 160, 1327

1965, but using potassium hexafluorophosphate.

Example 17

(η^6 -Indene) (η^5 -indenyl)-iron(II) hexafluorophosphate.

A mixture of 2 g of bis-(η^5 -indenyl)-iron(II), 1.8 g of aluminium chloride, 0.18 g of aluminium and 50 ml of an octane fraction is heated at 80°C for 4 hours. After cooling, it is poured into 100 g of ice-water, which is stirred for 30 minutes and filtered. The filtrate is separated off from the organic phase in a separating funnel. 1.3 g of potassium hexafluorophosphate are added to the aqueous, red solution, and the dark red crystals are isolated and dried for 16 hours at room temperature/13,000 Pa; melting point 120-130°C.

Example 18

Bis-(η^6 -mesitylene)-iron(II) bis-(hexafluorophosphate); melting point >250°C; prepared as described in J. Chem. Soc., Chem. Comm., 930 (1971).

Example 19

Bis-(η^6 -1-methylnaphthalene)-iron(II) bis-hexafluorophosphate).

A mixture of 9.72 g of iron(III) chloride, 16 g of aluminium chloride and 50 ml of 1-methylnaphthalene is heated at 95°C for 3.5 hours. It is then cooled and poured into 200 g of 1:1 ice/methanol, which is stirred for 30 minutes, and the organic phase is separated off in a separating funnel. 22 g of potassium hexafluorophosphate are added to the aqueous methanolic phase, and the red crystals are isolated and dried for 24 hours at room temperature/13,000 Pa; melting point 84-99°C.

Example 20

(η^6 -Benzene) (η^5 -cyclopentadienyl)-cobalt(III) bis-(tetrafluoborate); melting point >250°C, prepared as described in Z. Naturforsch., 16b, 556 (1961).

Example 21

(η^6 -Benzene) (η^5 -cyclopentadienyl)-cobalt(III) bis-(hexafluorophosphate); melting point 163-173°C, prepared

as described in Z. Naturforsch., 16b, 556 (1961).

Example 22

A precondensate formed from 38.56 parts by weight of bisphenol A reacted with epichlorohydrin and 10.82 parts by weight of bisphenol A having a total epoxide content of 2.17-2.44 equivalents/kg is dissolved in 14.81 parts by weight of acetone and 34.57 parts by weight of methyl ethyl ketone. 1.24 parts by weight of (η^6 -naphthalene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate are added to this solution. The homogeneous solution is applied to a copper-lined epoxide plate by means of a 24 μ doctor blade (wet film thickness 24 μ). The film is dried at 75°C for 20 minutes and is then irradiated with a 5,000 watt metal halide lamp for 3 minutes at 20°C. In doing this, a Stouffer 21-step grey wedge is used as a photomask. The plate is then cured at 80°C for 3 minutes and developed in methyl ethyl ketone. Etching in 50% strength FeCl₃ solution gives a No. 7 stepped image.

Examples 23-42

Further copper-lined epoxide plates are coated and irradiated in a manner analogous to that described in Example 22, using various initiators of the formula I. The other reaction conditions and the results are shown in Table 1 below.

(See Table 1, page 21 et seq.)

Example 43

Two Anticorodal-100-B test strips measuring 150 x 25 x 1.5 mm are each roughened at one end, cleaned and degreased. The roughened and degreased ends of the test strips are coated on one side in each case with about 0.3 g of an oligomeric diglycidyl ether derived from bisphenol A (epoxide content 5.1-5.5 equivalents/kg) and containing 2.5% by weight of the complex according to Example 6, so that a film 100-300 μ m thick is obtained. These coatings are then irradiated for 16.8 seconds with a PPG irradiation apparatus having 2 lamps (80 watts/cm). The exposed areas are then placed over one another in such a way that the samples overlap by 12 mm. The two strips are then carefully clamped and are cured at

120°C for 30 minutes. They are then cooled to room temperature in the course of 30 minutes and the clamps are removed. The shear strength is measured by means of a tensile tester at an advance rate of 5 mm/minute until the adhesive bond breaks. The adhesive bond has a shear strength of 13 N/mm².

Example 44

A precondensate obtained from 38.56 parts by weight of bisphenol A reacted with epichlorohydrin and 10.82 parts by weight of bisphenol A having a total epoxide content of 2.17-2.44 equivalents/kg is dissolved in 14.81 parts by weight of acetone and 34.57 parts by weight of methyl ethyl ketone. 1.24 parts by weight of (η^6 -naphthalene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate are added to this solution. The homogeneous solution is applied to a copper-lined epoxide plate by means of a 24 μ m doctor blade (wet film thickness 24 μ m). The film is dried for 20 minutes at 75°C and is then irradiated with a 5,000 watt metal halide lamp for 3 minutes at 20°C. In doing this, a Stouffer 21-step grey wedge is used as a photomask. After being exposed, the plate is stored in complete darkness for 4 months at room temperature. It is then cured for 3 hours at 100°C and developed in methyl ethyl ketone. Etching in 50% strength FeCl₃ solution gives a No. 7 stepped image.

Example 45

Two Anticorodal-100-B test strips measuring 150 x 25 x 1.5 mm are each roughened and degreased at one end. The roughened and degreased ends of the test strips are each coated on one side with a homogeneous mixture of a precondensate consisting of 38.56 parts by weight of bisphenol A reacted with epichlorohydrin and 10.82 parts by weight of bisphenol A having a total epoxide content of 2.41 equivalents/kg, and with 14.81 parts by weight of acetone, 34.57 parts by weight of methyl ethyl ketone and 1.24 parts by weight of (η^6 -naphthalene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate as initiator. The treated test strips are then dried at 75°C for 120 minutes with the formation of a non-tacky film on the coated ends. The coated strips

Table 1

Ex- am- ple	Initiator			Curing time, minutes	Curing temperature °C	Last wedge step on a Stouffer 21-step grey wedge forming an image		
	accord- ing to Example	% by weight	mol % (relative to 100 g of resin)			Irradiation time		
						1 minute	3 minutes	12 minutes
23	3	2,6	$7,26 \times 10^{-3}$	3	80	4	6	-
24	4	2,6	$6,94 \times 10^{-3}$	3	80	5	8	-
25	5	2,5	$6,37 \times 10^{-3}$	3	100	-	5	-
26	6	2,5	$6,34 \times 10^{-3}$	3	100	-	8	-
27	9	2,5	$5,69 \times 10^{-3}$	3	100	-	10	-
28	8	2,5	$5,14 \times 10^{-3}$	3	80	-	8	-
29	7	2,5	$7,44 \times 10^{-3}$	3	70	-	3	-
30	7	2,5	$7,44 \times 10^{-3}$	3	100	-	8	-
31	10	2,5	$5,83 \times 10^{-3}$	3	120	-	11	-
32	11	2,6	$5,92 \times 10^{-3}$	3	80	8	11	-
33	12	2,6	$6,18 \times 10^{-3}$	3	80	5	8	-
34	13	2,6	$5,77 \times 10^{-3}$	3	80	8	12	-
35	14	2,6	$5,55 \times 10^{-3}$	3	80	10	16	-
36	15	2,5	$4,82 \times 10^{-3}$	3	100	16	-	-
37	2	2,5	$3,78 \times 10^{-3}$	3	100	-	13	-
38	16	2,5	$5,83 \times 10^{-3}$	3	100	-	1	5
39	1	2,6	$6,37 \times 10^{-3}$	3	100	0	3	-

Table 1 (Continuation)

Ex- ample	Initiator			Curing time, minutes	Curing tempera- ture °C	Last wedge step on a Stouffer 21-step grey wedge forming an image		
	accord- ing to Example	% by weight	mol %			Irradiation time		
		(relative to 100 g of resin)				1 minute	3 minutes	12 minutes
40	17	2,5	$5,77 \times 10^{-3}$	3	100	-	0	2
41	18	2,5	$4,26 \times 10^{-3}$	3	100	1	-	5
42	19	2,5	$3,68 \times 10^{-3}$	3	75	0	5	9

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are then irradiated with a 5,000 watt metal halide lamp for 3 minutes. The exposed areas are then laid on top of one another in such a way that the samples overlap by 12 mm. The two strips are then carefully clamped and are cured for 40 minutes at 100°C. They are then cooled to room temperature and the clamps are removed. The shear strength is measured by means of a tensile tester at an advance rate of 5 mm/minute until the adhesive bond is broken. The adhesive bond has a shear strength of 11.8 N/mm².

Example 46

Two Anticorodal-100-B test strips measuring 150 x 25 x 1.5 mm are each roughened and degreased at one end. The roughened and degreased ends of the test strips are each coated on one side with a homogeneous mixture of a precondensate consisting of 38.56 parts by weight of bisphenol A reacted with epichlorohydrin and 10.82 parts by weight of bisphenol A having a total epoxide content of 2.41 equivalents/kg, and with 14.81 parts by weight of acetone, 34.57 parts by weight of methyl ethyl ketone and 1.24 parts by weight of (η^6 -naphthalene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate as initiator. The treated test strips are then dried at 75°C for 120 minutes with the formation of a non-tacky film on the coated ends. The coated areas are then laid on top of one another in such a way that the samples overlap by 12 mm. The two strips are then carefully clamped and are cured at 160°C for 40 minutes. They are then cooled to room temperature and the clamps are removed. The shear strength is measured by means of a tensile tester at an advance rate of 5 mm/minute until the adhesive bond is broken. The adhesive bond has a shear strength of 10.9 N/mm².

Example 47

Two Anticorodal-100-B test strips measuring 150 x 25 x 1.5 mm are each roughened and degreased at one end. The roughened and degreased ends of the test strips are each coated on one side with a pulverulent mixture of a precondensate consisting of 38.56 parts by weight of bisphenol A

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reacted with epichlorohydrin and 10.82 parts by weight of bisphenol A having a total epoxide content of 2.41 equivalents/kg, and with 1.24 parts by weight of (η^6 -naphthalene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate as initiator. The coated strips are then irradiated with a 5,000 watt metal halide lamp for 3 minutes. The coated areas are then laid on top of one another in such a way that the samples overlap by 12 mm. The two strips are then carefully clamped and are cured at 100°C for 40 minutes. They are then cooled to room temperature and the clamps are removed. The shear strength is measured by means of a tensile tester at an advance rate of 5 mm/minute until the adhesive bond is broken. The adhesive bond has a shear strength of 8.32 N/mm².

Examples 48-51

The following compositions are obtained by mixing the components together and dissolving the additives in the epoxide resin:

Example 48:

100 g of liquid bisphenol A/epoxide resin (epoxide content 5.5-7.5 equivalents/kg, viscosity 9,000-12,000 mPa.s at 25°C)

X g of (η^6 -naphthalene) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate (A)

Example 49:

100 g of liquid epoxide resin obtained from epoxidized cycloolefins (epoxide content 7.0-7.5 equivalents/kg, viscosity 4,500-5,200 mPa.s at 25°C) (B)

X g of A

Example 50:

65 g of liquid epoxide resin B

35 g of hexanediol diacrylate

X g of A

1 g of methyl ethyl ketone peroxide

Example 51:

65 g of liquid epoxide resin B

35 g of hexanediol diacrylate

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X g of A

2 g of (2,4,6-trimethylbenzoyl)-diphenylphosphine
oxide

The compositions are cast onto sheets of glass. The thickness of the films is about 60 μm . The coated sheets are irradiated at a light intensity of 80 watts/cm for 4.2 seconds at 20°C, using a mercury vapour lamp. Immediately after this procedure, the coatings are irradiated with infra-red light (quartz lamp, Heraeus type MMS 2000) in such a way that the temperature of the films is 96°C after 60 seconds and 103°C after 75 seconds. The samples are stored at room temperature for 0.5 hour and 24 hours. The hardness of the films is then determined as specified in DIN 53 157. The results are listed in Table 2.

Table 2

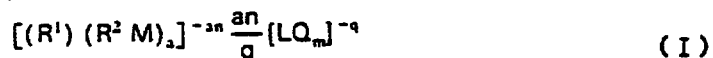
Ex-ample	Compound A (% by weight)	Hardness (DIN 53 157) in seconds after			
		60 seconds		75 seconds	
		0.5 hr.	24 hrs.	0.5 hr.	24 hrs.
48	0	wet	wet	wet	wet
	1.0	38	55	40	55
	2.0	140	155	168	186
	5.0	196	205	210	220
49	0	wet	wet	wet	wet
	1.0	~5	~5	14	14
	2.5	~5	~5	20	20
	5.0	18	21	34	34
50	0	wet	wet	wet	wet
	0.5	wet	wet	wet	wet
	1.0	39	80	62	81
	2.0	14	19	24	28
51	2.0	adhering	10	adhering	25

(54)

Patent Claims

1. Curable compositions containing

- A) a cationically polymerizable organic material and
B) at least one 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 represents the cation of a monovalent to trivalent metal from group IVb to VIIB, VIII or Ib of the periodic system, m is an integer corresponding to the valency of L + q and Q denotes a halogen atom, L denotes a divalent to heptavalent metal or non-metal, R¹ denotes a π -arene and R² denotes a π -arene or the anion of a π -arene.

2. Compositions according to claim 1, characterized in that R¹ and/or R² represent aromatic groups having 6 to 24 carbon atoms or heteroaromatic groups having 3 to 20 carbon atoms, these groups being optionally monosubstituted or polysubstituted by identical or different halogen atoms or C₁-8-alkyl, C₁-8-alkoxy, cyano, C₁-8-alkylthio, C₂-6-monocarboxylic acid ester, phenyl, C₂-5-alkanoyl or benzoyl groups.

3. Compositions according to claim 1, characterized in that R² represents the anion of an aromatic π -arene having 6 to 24 carbon atoms or of a heteroaromatic π -arene having 3 to 20 carbon atoms, each of which is optionally monosubstituted or polysubstituted by identical or different C₁-8-alkyl, C₂-6-monocarboxylic acid ester, cyano, C₂-5-alkanoyl or benzoyl groups.

4. Compositions according to claim 1, characterized in that a is 2 and each R² denotes the anion of a π -arene and each M denotes the same metal atom.

5. Compositions according to claim 1, characterized in that a is 1 and R¹ represents benzene, toluene, xylene, methoxybenzene, chlorobenzene, p-chlorotoluene, naphthalene, methylnaphthalene, chloronaphthalene, methoxynaphthalene,



* C L M S *

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biphenyl, indene, pyrene or diphenylene sulfide and R^2 represents the anion of cyclopentadiene, acetylcyclopentadiene or indene or represents benzene, toluene, xylene, trimethylbenzene, naphthalene or methylnaphthalene.

6. Compositions according to claim 1, characterized in that a is 1, R^1 represents η^6 -pyrene or η^6 -naphthalene and R^2 represents the anion of η^5 -cyclopentadiene and n is 1 or 2 and q is 1.

7. Compositions according to claim 1, characterized in that a chromium, cobalt, manganese, tungsten, molybdenum or iron cation is present as M and SbF_6^- , BF_4^- , AsF_6^- or PF_6^- is present as $[LQ_m]^{-q}$.

8. Compositions according to claim 1, characterized in that an epoxy resin is present as the cationically polymerizable organic material.

9. Compositions according to claim 1, characterized in that an optionally advanced diglycidyl ether of a dihydric phenol or of a dihydric aliphatic alcohol having 2 to 4 carbon atoms is present as the cationically polymerizable organic material.

10. Activated curable compositions obtainable by irradiating a curable composition according to claim 1 at a temperature below that used for the subsequent curing by heat.

11. Compositions according to claim 1 or 10, characterized in that they contain 0.1 to 15% by weight, preferably 0.5 to 5% by weight, relative to the polymerizable organic material A), of at least one compound of the formula I.

12. Compositions according to claim 1 or 10, characterized in that they contain up to equimolar amounts of an initiator of the formula I and of a polymerizable organic material A), equimolar relating to the reactive group of this polymerizable organic material.

13. Compounds selected from the group consisting of (η^6 -toluene) (η^5 -indenyl)-iron-(II) hexafluorophosphate, (η^6 -pyrene) (η^5 -cyclopentadienyl)-iron-(II) hexafluoroantimonate, (η^6 -naphthalene) (η^5 -cyclopentadienyl)-iron-(II) hexafluoroantimonate, (η^6 -naphthalene) (η^5 -cyclo-



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pentadienyl)-iron)-(II) hexafluoroarsenate, (η^6 -2-methoxynaphthalene) (η^5 -cyclopentadienyl)-iron-(II) hexafluorophosphate, (η^6 -diphenylene sulfide) (η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate, (η^6 -perylene) (η^5 -cyclopentadienyl)-iron-(II) hexafluorophosphate and bis- η^6 -1-methylnaphthalene)-iron-(II) hexafluorophosphate.

14. Process for the preparation of compounds of the formula Ia



wherein R^1 , L, Q, m and q have the meaning defined in claim 1 and R^2 represents an anion of a π -arene, by reacting an uncharged π -complex of the formula IIIa



with a π -arene R^1 in the presence of aluminium and a Lewis acid and subsequently treating the product with a salt of the anion $[LQ_m]^{q-}$, characterized in that the Lewis acid employed is $TiCl_4$.

15. Coated material characterized in that it contains, on a substrate, a coating consisting of compositions according to claim 1 or 10.

16. The use of curable compositions according to claim 1 or 10 for the preparation of cured products, characterized in that these compositions are subjected to direct curing by heat.

17. The use of curable compositions according to claim 1 for the preparation of cured products, characterized in that the initiator of the formula I is first activated by irradiation, and the activated precursor thus obtained is then cured by heat, in such a way that the irradiation temperature is below the temperature used for the subsequent curing by heat.

18. The use of curable compositions according to claim 12 as curing agents for cationically polymerizable organic materials.



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Claims (as printed)

1. A curable composition which comprises
 - A) a cationically polymerisable organic material and
 - B) at least one compound of the formula I



wherein a is 1 or 2, each of n and q independently of the other is an integer from 1 to 3, M is the cation of a monovalent to trivalent metal of groups IVb to VIIb, VIII or Ib of the Periodic Table, m is an integer corresponding to the valency of L + 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 or the anion of a π -arene.

2. A composition as claimed in claim 1, wherein R¹ and/or R² are aromatic groups having 6 to 24 carbon atoms or heteroaromatic groups having 3 to 20 carbon atoms, which groups are unsubstituted or mono- or polysubstituted by identical or different halogen atoms, C₁₋₆alkyl, C₁₋₆alkoxy, cyano, C₂₋₆alkylthio, C₂₋₆monocarboxylic acid ester, phenyl, C₂₋₆alkanoyl or benzoyl groups.

3. A composition as claimed in claim 1, wherein R² is the anion of an aromatic π -arene containing 6 to 24 carbon atoms or a heteroaromatic π -arene having 3 to 20 carbon atoms, each of which is unsubstituted or mono- or polysubstituted by identical or different C₁₋₆alkyl, C₂₋₆monocarboxylic acid ester, cyano, C₂₋₆alkanoyl or benzoyl groups.

4. A composition as claimed in claim 1, wherein a is 2, each R² is an anion of a π -arene and each M is an identical metal atom.

5. A composition as claimed in claim 1, wherein a is 1, R¹ is benzene, toluene, xylene, methoxybenzene, chlorobenzene, p-chlorotoluene, naphthalene, methylnaphthalene, chloronaphthalene, methoxynaphthalene, biphenyl, indene, pyrene or diphenylene sulfide, and R² is the anion of cyclopentadiene, acetylcyclopentadiene or indene, or is benzene, toluene, xylene, trimethylbenzene, naphthalene or methylnaphthalene.

6. A composition as claimed in claim 1, wherein a is 1, R¹ is η^6 -pyrene or η^6 -naphthalene, and R² is the anion of η^5 -cyclopentadiene, n is 1 or 2, and q is 1.

7. A composition as claimed in claim 1, wherein M is a chromium, cobalt, manganese, tungsten, molybdenum or an iron cation, and [LQ_m]^{-q} is SbF₆⁻, BF₄⁻, AsF₆⁻ or PF₆⁻.

8. A composition as claimed 1, wherein the cationically polymerisable organic material is an epoxy resin.

9. A composition as claimed in claim 1, wherein the cationically polymerisable organic material is a diglycidyl ether, which may have been advanced, of a divalent phenol or of a divalent aliphatic alcohol containing 2 to 4 carbon atoms.

10. An activated curable composition which is obtainable by irradiating a curable composition as claimed in claim 1 at a temperature which is below that employed for the subsequent heat-curing.

11. A composition as claimed in either claim 1 or claim 10, which comprises 0.1 to 15 % by weight, preferably 0.5 to 5 % by weight, based on the polymerisable organic material A), of at least one compound of the formula I.

12. A composition as claimed in either claim 1 or claim 10, which contains up to equimolar amounts of an initiator of the formula I and a polymerisable organic material A), equimolar referring to the reactive group of said polymerisable organic material.

13. A compound selected from the group consisting of (η^6 -toluene) (η^5 -indenyl) iron(II) hexafluorophosphate, (η^6 -pyrene) (η^5 -cyclopentadienyl) iron(II) hexafluoroantimonate, (η^6 -naphthalene) (η^5 -cyclopentadienyl) iron(II) hexafluoroantimonate, (η^6 -naphthalene) (η^5 -cyclopentadienyl) iron(II) hexafluoroarsenate, (η^5 -2-methoxynaphthalene) (η^5 -cyclopentadienyl) iron(II) hexafluorophosphate, (η^6 -diphenylene sulfide) (η^5 -cyclopentadienyl) iron(II) hexafluorophosphate, (η^6 -perylene) (η^5 -cyclopentadienyl) iron(II) hexafluorophosphate and bis(η^6 -1-methylnaphthalene) iron(II) hexafluorophosphate.

14. A process for the preparation of a compound of the formula Ia



wherein R¹, L, Q, m and q are as claimed in claim 1 and R² is an anion of a π -arene, by reacting an uncharged π -complex of the formula IIIa



with a π -arene R¹ in the presence of aluminium and a Lewis acid and subsequently treating the reaction





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product with a salt of the anion $[LQ_m]^{n-}$, which process comprises the use of $TiCl_4$ as Lewis acid.

15. A coated material which comprises on a substrate a coating of the compositions as claimed in either claim 1 or claim 10.

16. Use of a curable composition as claimed in either claim 1 or claim 10 for the production of cured products, which comprises heat-curing said composition direct.

17. Use of a curable composition as claimed in claim 1 for the production of cured products, which comprises first activating the initiator of the formula I by irradiation and then heat-curing the resultant activated precursor, such that the irradiation temperature is below the temperature employed for the subsequent heat-curing.

18. Use of a curable composition as claimed in claim 12 as hardener for cationically polymerisable organic materials.

Revendications (as printed)

1. Compositions durcissables contenant :

- A) une matière organique polymérisable par voie cationique, et
- B) au moins un composé de formule I



dans laquelle a vaut 1 ou 2 et n et q sont chacun, indépendamment l'un de l'autre, un nombre entier valant 1 à 3, M représente le cation d'un métal monovalent à trivalent du groupe IVb à VIIb, VIII ou Ib du système périodique, m est un nombre entier correspondant à la valeur de $L + q$ et Q représente un atome d'halogène, L est un métal ou non-métal divalent à heptavalent, R^1 est un arène- π et R^2 est un arène- π ou l'anion d'un arène- π .

2. Compositions selon la revendication 1, caractérisées en ce que R^1 et/ou R^2 représentent des groupes aromatiques ayant 6 à 24 atomes de carbone ou des groupes hétéroaromatiques ayant 3 à 20 atomes de carbone, ces groupes étant éventuellement substitués, de façon identique ou différente, une ou plusieurs fois, par des atomes d'halogène, des groupes alkyle en C_1-C_8 , alcoxy en C_1-C_8 , cyano, alkylthio en C_1-C_8 , ester d'acide monocarboxylique en C_2-C_8 , phényle, alcanoyle en C_2-C_8 ou benzoyle.

3. Compositions selon la revendication 1, caractérisées en ce que R^2 représente l'anion d'un arène- π aromatique ayant 6 à 24 atomes de carbone ou d'un arène- π hétéroaromatique ayant 3 à 20 atomes de carbone, qui est éventuellement substitué, une ou plusieurs fois, par des groupes alkyle en C_1-C_8 , ester d'acide monocarboxylique en C_2-C_8 , cyano, alcanoyle en C_2-C_8 ou benzoyle identiques ou différents.

4. Compositions selon la revendication 1, caractérisées en ce que a vaut 2 et R^2 représente chaque fois l'anion d'un arène- π et chaque M représente le même atome de métal.

5. Compositions selon la revendication 1, caractérisées en ce que a vaut 1 et R^1 représente un groupe benzène, toluène, xylène, méthoxybenzène, chlorobenzène, p-chlorotoluène, naphtalène, méthyl-naphtalène, chloronaphtalène, méthoxynaphtalène, biphenyle, indène, pyrène ou sulfure de diphenyle, et R^2 représente l'anion du cyclopentadiène, de l'acétilylcyclopentadiène ou de l'indène, ou un groupe benzène, toluène, xylène, triméthylbenzène, naphtalène ou méthyl-naphtalène.

6. Compositions selon la revendication 1, caractérisées en ce que vaut 1, R^1 représente le pyrène- η^6 ou le naphtalène- η^5 et R^2 représente l'anion du cyclopentadiène- η^5 , et n vaut 1 ou 2 et q vaut 1.

7. Compositions selon la revendication 1, caractérisées en ce que M représente un cation chrome, cobalt, manganèse, tungstène, molybdène ou fer, et $[LQ_m]^{-q}$ représente SbF_6^- , SbF_4^- , AsF_6^- ou PF_6^- .

8. Compositions selon la revendication 1, caractérisées en ce qu'une résine époxyde est présente comme matière organique polymérisable par voie cationique.

9. Compositions selon la revendication 1, caractérisées en ce qu'un éther-oxyde diglycidylque d'un phénol divalent à chaîne éventuellement allongée, ou d'un dialcool aliphatique comportant 2 à 4 atomes de carbone est présent comme matière organique polymérisable par voie cationique.

10. Compositions durcissables activées, que l'on peut obtenir en exposant à un éclairage une composition durcissable selon la revendication 1, à une température inférieure à celle appliquée pour le durcissement subséquent à chaud.

11. Compositions selon la revendication 1 ou 10, caractérisées en ce qu'elles contiennent 0.1 à 15 % en poids, avantageusement 0.5 à 5 % en poids, par rapport à la matière A) organique polymérisable, d'au moins un composé de formule I.

12. Compositions selon la revendication 1 ou 10, caractérisées en ce qu'elles contiennent jusqu'à des quantités équimolaires d'un amorceur de formule I et d'une matière A) organique polymérisable, le terme équimolaire se fondant sur le groupe réactif de cette matière organique polymérisable.

13. Composés choisis dans l'ensemble constitué par le (η^6 -toluène) (η^5 -indényle)-fer(II)-hexafluorantimoniato, le (η^6 -pyrène) (η^5 -cyclopentadiényle)-fer(II)-hexafluorantimoniato, le (η^6 -naphtalène) (η^5 -cyclopentadiényle)-fer(II)-hexafluorantimoniato, le (η^6 -naphtalène) (η^5 -cyclopentadiényle)-fer(II)-hexafluoroarséniate, le

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(η^6 -2-méthoxynaphtalène) (η^5 -cyclopentadiényl)-fer(II)-hexafluorophosphate, le (sulfure d' η^6 -diphénylène) (η^5 -cyclopentadiényl)-fer(II)-hexafluorophosphate, le (η^5 -pérylène) (η^5 -cyclopentadiényl)-fer(II)-hexafluorophosphate et le bis(η^6 -méthyl-1-naphtalène) fer(II)-hexafluorophosphate.

14. Procédé pour préparer des composés de formule Ia :



dans laquelle R^1 , L, Q, m et q ont les sens indiqués à la revendication 1 et R^2 représente un anion d'un arène- π , par réaction d'un complexe- π non chargé de formule IIIa :



avec un arène- π R^1 en présence d'aluminium et d'un acide de Lewis, puis traitement avec un sel de l'anion $[LQ_m]^{q-}$, procédé caractérisé en ce qu'on utilise comme acide de Lewis $TiCl_4$.

15. Matière enduite, caractérisée en ce qu'elle contient, sur un substrat, un enduit de compositions selon la revendication 1 ou 10.

16. Utilisation de compositions durcissables selon la revendication 1 ou 10 pour préparer des produits durcis, caractérisée en ce qu'on fait durcir directement à chaud ces compositions.

17. Utilisation de compositions durcissables selon la revendication 1 pour préparer des produits durcis, caractérisée en ce qu'on active tout d'abord, par exposition à un éclairage, l'amorceur de formule I et l'on fait ensuite durcir à chaud le précurseur activé obtenu, de manière que la température d'exposition à l'éclairage se situe au-dessous de la température utilisée pour le durcissement subséquent par chauffage.

18. Utilisation de compositions durcissables selon la revendication 12, comme durcisseurs pour des matières organiques polymérisables par voie cationique.



* C L M S *