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Description

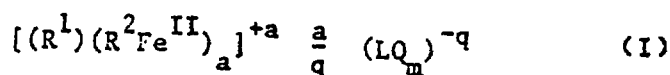
The present invention relates to a hardenable composition consisting of a) a material polymerizable by cationic or free radical polymerization, b) an iron(II)- η^6 -benzene- η^5 -cyclopentadienyl complex salt, c) a sensitizer for the compounds b), and d) an electron acceptor as an oxidizing agent for the material polymerizable by free radical polymerization, to a process for the polymerization of this material by the action of radiation, and to a material coated with the composition and its use.

Patent document EP-A-0,094,915 describes a hardenable composition consisting of a material polymerizable by cationic polymerization, which contains a (π -arene)-metal complex salt as the initiator. The composition can be hardened directly by the action of heat or first irradiated to activate the initiator and then hardened by the action of heat. For complete hardening, however, the period of exposure must be relatively long, which is uneconomic. It is therefore desirable to increase the photosensitivity. It is also desirable to avoid thermal hardening after irradiation and to effect the hardening by means of radiation alone. It has now been found that the photosensitivity can be substantially increased by the simultaneous use of a sensitizer in conjunction with selected (π -arene)-metal complex salts. It has furthermore been found that thermal hardening can be extensively avoided by the concomitant use of an oxidizing agent as well.

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The present invention relates to a composition containing:

- a) a material polymerizable by free radical or cationic polymerization,
- 5 b) at least one iron compound of the formula I



wherein

- a is 1 or 2 and q is 1, 2 or 3,
- L is a divalent to heptavalent metal or non-metal,
- 10 Q is a halogen atom,
- m is an integer corresponding to the sum of the values of L and q,
- R^I is an unsubstituted or substituted η^6 -benzene and
- R² is an unsubstituted or substituted cyclopentadienyl anion,
- 15 and
- c) at least one sensitizer for the compound of the formula I,
- and, in the case of materials polymerizable by free radical polymerization, also d) an electron acceptor as an oxidizing
- 20 agent.

Advantageously, the composition including a material hardenable by cationic polymerization also contains an electron acceptor as an oxidizing agent, especially when used for hardening by irradiation.

- 25 The iron compound of the formula I, or the iron compound of the formula I and the oxidizing agent d), are preferably present in a quantity of 0.1-15% by weight, particularly 0.1-10% by weight and very particularly 0.1-5% by weight. The weight ratio of the iron compound of the formula
- 30 I to the oxidizing agent d) is preferably 1:10 to 5:1, particularly 1:1 to 5:1. The sensitizer c) is preferably incorporated in a quantity of 0.1-10% by weight, particularly 0.1-5% by weight and especially 0.1-2.5% by weight.

As a mononuclear π -arene derived from benzene, R^I

35 in the formula I can be monosubstituted or polysubstituted

by identical or different halogen atoms or C₁-C₁₂-alkyl, C₂-C₁₂-alkenyl, C₂-C₁₂-alkynyl, C₁-C₈-alkoxy, cyano, C₁-C₁₂-alkylthio, C₂-C₆-monocarboxylic acid ester, phenyl, C₂-C₅-alkanoyl or benzoyl groups.

- 5 The cyclopentadienyl anion R² can be monosubstituted or polysubstituted by identical or different C₁-C₈-alkyl, C₂-C₈-alkenyl, C₂-C₈-alkynyl, C₂-C₆-monocarboxylic acid ester, cyano, C₂-C₅-alkanoyl or benzoyl groups.

- The abovementioned alkyl, alkoxy, alkylthio, mono-
10 carboxylic 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,
15 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
20 valeroyl. 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. When R¹ is a substituted π -arene derived
25 from benzene, it preferably contains one or two of the abovementioned substituents, especially chlorine or bromine atoms, methyl, ethyl, propyl, isopropyl, methoxy, ethoxy, cyano or carboxylic acid methyl or ethyl ester groups and acetyl groups.

- 30 Examples of suitable π -arenes derived from benzene are benzene, toluene, xylenes, ethylbenzene, methoxybenzene, ethoxybenzene, dimethoxybenzene, p-chlorotoluene, chlorobenzene, bromobenzene, dichlorobenzene, acetylbenzene, trimethylbenzene, trimethoxybenzene, 1,2-dihydronaphthalene,
35 1,2,3,4-tetrahydronaphthalene, mesitylene, cumene, biphenyl, anisole and dodecylbenzene. Preference is given to benzene, toluene, xylene, cumene, mesitylene, chlorobenzene, chloro-

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toluene, anisole, dimethoxybenzene, biphenyl, dodecylbenzene or tetralin.

R^2 is preferably the cyclopentadienyl anion or a C_1 - C_4 -alkylated cyclopentadienyl anion, particularly the
5 methylcyclopentadienyl anion.

In the formula I, a 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,
10 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. The halogen atom Q is preferably Cl and particularly F.

In the formula I, q is preferably 1, m is preferably
15 6, Q is preferably F and L is preferably B, P, As or Sb.

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 particularly preferred complex anions are SbF_6^- , BF_4^- , AsF_6^- and PF_6^- .

20 The compounds of the formula I are known or can be prepared by analogous processes.

The electron acceptors as oxidizing agent d) are preferably an organic hydroperoxide, an organic peracid or a quinone.

25 Examples are: tertiary butyl hydroperoxide, cumene hydroperoxide, triphenylmethyl hydroperoxide, tetralin hydroperoxide, α -methyltetralin hydroperoxide, decalin hydroperoxide, perbenzoic acid, m-chloroperbenzoic acid or benzoquinone.

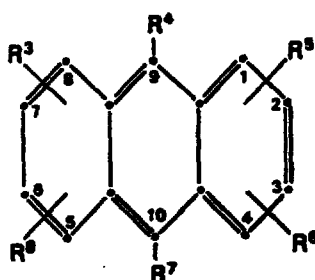
30 Examples of suitable sensitizers c) are those having a triplet energy of at least 125.6 (30) and preferably of at least 146.5 (35) KJ/mol^1 (kcal/mol). They can be selected, for example, from the group consisting of the monocyclic or polycyclic hydrocarbon aromatics or heteroaromatics, the
35 phenones, particularly the acetophenones and the benzophenones, the benzils, the stilbenes, the polyacetylenes, the xanthenes and thioxanthenes, the anthracenes, the phthalimides, particularly the phthalimide thioethers, and the diones

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with adjacent CO groups. Other suitable sensitizers and examples are mentioned in S.L. Murov, Handbook of Photochemistry, M. Dekker Inc., New York, pages 27 et seq. (1973).

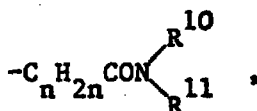
Preferred sensitizers are thioxanthenes, phthalimides, particularly phthalimide thioethers, coumarins and anthracenes. Suitable phthalimide thioethers are described in patent documents DE-A-31 17 589 and EP-A-0,062,615. Suitable thioxanthenes are described, for example, in patent documents DE-A-30 18 891 and EP 0,033,720.

10 Particularly preferred sensitizers are unsubstituted or substituted anthracenes or mixtures of such anthracenes. They can correspond to the formula II



(II)

wherein R^3 to R^8 independently of one another are a hydrogen atom, halogen, cyano, linear or branched C_1 - C_{18} -alkyl, C_1 - C_{18} -alkoxy or C_1 - C_{18} -alkylthio, C_5 - C_{12} -cycloalkyl which is unsubstituted or substituted by C_1 - C_6 -alkyl, linear or branched C_3 - C_{18} -alkenyl, C_7 - C_{16} -aralkyl, $-C_nH_{2n}OZ$, $-C_nH_{2n}CN$, $-C_nH_{2n}COOR^9$ or



20 wherein n is a number from 1 to 18, R^9 is linear or branched C_1 - C_{18} -alkyl, C_5 - C_{12} -cycloalkyl which is unsubstituted or substituted by C_1 - C_6 -alkyl, C_6 - C_{12} -aryl, C_7 - C_{16} -alkaryl, C_7 - C_{16} -aralkyl, C_8 - C_{16} -alkaralkyl or a metal

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cation, R^{10} and R^{11} independently of one another are a hydrogen atom, C_1 - C_{18} -alkyl or C_5 - C_{12} -cycloalkyl, or R^{10} and R^{11} together are tetramethylene, pentamethylene or 3-oxapentylene, and Z is a hydrogen atom or C_1 - C_{18} -alkyl.

In a preferred embodiment, at least one of the radicals R^3 to R^8 is one of the substituents defined previously. In another embodiment, R^3 , R^5 , R^6 and R^8 are a hydrogen atom and R^4 and/or R^5 are C_1 - C_{18} -alkyl or C_1 - C_{18} -alkoxy. In another preferred embodiment, R^4 and R^6 to R^8 are a hydrogen atom and R^3 and R^5 are one of the substituents defined previously, R^3 being bonded especially in the 6-position or 7-position and R^5 in the 2-position.

Halogen R^3 to R^8 are preferably chlorine, ethyl, alkoxy and alkylthio R^3 to R^8 preferably contain 1 to 12 and particularly 1-6 C atoms and cycloalkyl R^3 to R^8 contain 5 or 6 ring carbon atoms. Alkenyl R^3 to R^8 preferably contain 3 to 8 C atoms. Aralkyl R^3 to R^8 are preferably phenylalkyl having especially 7 to 12 C atoms.

The number n is preferably 1 to 12 and particularly 1 to 6. Alkyl R^9 preferably contains 1 to 12 and particularly 1 to 6 C atoms and cycloalkyl R^9 preferably contains 5 or 6 ring carbon atoms. Aryl R^9 is preferably phenyl, alkaryl R^9 is preferably C_7 - C_{12} -alkylphenyl, aralkyl R^9 is preferably C_7 - to C_{12} -phenylalkyl and alkaralkyl R^9 is preferably C_8 - C_{12} -alkylphenylalkyl. Metal cation R^9 is preferably selected from the alkali metal and alkaline earth metal group, for example Mg, Ca, K and particularly Na.

Alkyl R^{10} and R^{11} preferably contain 1 to 12 and particularly 1 to 6 C atoms. Cycloalkyl R^{10} and R^{11} preferably contain 5 or 6 ring carbon atoms. Alkyl Z preferably contains 1 to 12 and particularly 1 to 6 C atoms.

Examples of alkyl, alkoxy and alkylthio are: methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, 1-, 2- or 3-pentyl, 1-, 2- or 3-hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl or octadecyl and

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corresponding alkoxy and alkylthio radicals.

Examples of cycloalkyl are: cyclopentyl, methylcyclopentyl, cyclohexyl and methylcyclohexyl.

Examples of alkenyl are: allyl and prop-1-enyl.

- 5 Examples of aryl, aralkyl, alkaryl and alkaralkyl are: phenyl, benzyl, 2-phenylethyl, methylphenyl, ethylphenyl and methylbenzyl.

- Some of the compounds of the formula II are known. Novel compounds of the formula II can be obtained by known
10 processes, for example by Friedel-Crafts alkylation reactions carried out on anthracene or substituted anthracenes.

- Examples are: perylene, 3,4-benzopyrene, 1,12-benzperylene, pyrene, pentaphene, 1,2-benzopyrene, fluoroanthrene, 1,2-benzochrysene, 1-aminonaphthalene, coronene,
15 1-nitronaphthalene, 3,4-benzofluorene, 2,2'-binaphthyl, 1-naphthaldehyde, 5,6-benzochrysene, 1-acetylnaphthalene, 3,4,5,6-dibenzophenanthrene, chrysene, 1,2- and 2,3-benzofluorene, 1-benzoylnaphthalene, 1-naphthonitrile, naphthalene-1-carboxylic acid, 1,2,6,7-dibenzopyrene, 9-acetylphenanthrene,
20 1-naphthol, 1-iodonaphthalene, 2-phenylnaphthalene, 3,4-benzophenanthrene, 3-acetylphenanthrene, 1-bromonaphthalene, 1-chloronaphthalene, 2-naphthonitrile, acenaphthene, 2-naphthaldehyde, naphthalene-2-carboxylic acid, 2-acetylnaphthalene, 2-benzoylnaphthalene, 1-methylnaphthalene,
25 1-methoxynaphthalene, 1-fluoronaphthalene, 2-iodonaphthalene, 2-bromonaphthalene, 2-chloronaphthalene, 2-naphthol, 2-methylnaphthalene, naphthalene, phenanthrene, anthraquinone, triphenylene, 4-benzoylpyridine, 2-benzoylpyridine, fluorene, 3-benzoylpyridine, carbazole, 4-acetylpyridine, 4-methoxy-
30 benzaldehyde, 4-methylbenzaldehyde, benzaldehyde, anthrone, 1-tetralone, 4-phenylacetophenone, 3,4-methylenedioxyacetophenone, 4-cyanoacetophenone, α -chloroacetophenone, 3,4,5-trimethylacetophenone, 3,5-dimethylacetophenone, 4-bromoacetophenone, 4-methoxyacetophenone, 3,4-dimethylacetophenone,
35 triphenylmethylacetophenone, 4-chloroacetophenone, 4-trifluoromethylacetophenone, 2,4,6-trimethylacetophenone, 3-methoxyacetophenone, 3-methylacetophenone, 3-bromoacetophenone,

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- 4-methylacetophenone, 3-cyanoacetophenone, 3-trifluoro-
methylacetophenone, acetophenone, allylacetophenone, benzo-
phenone, 4-phenylbenzophenone, 4,4'-bisdimethylaminobenzo-
phenone, 4-cyanobenzophenone, 4,4'-dichlorobenzophenone, 4-
5 trifluoromethylbenzophenone, 3-methoxybenzophenone, 4-chloro-
benzophenone, 3-chlorobenzophenone, 4,4'-dibromobenzophenone,
4-methoxybenzophenone, 3,4-dimethylbenzophenone, 4-methyl-
benzophenone, 2-methylbenzophenone, 4,4'-dimethylbenzo-
phenone, 2,5-dimethylbenzophenone, 2,4-dimethylbenzophenone,
10 4-fluorobenzophenone, orthobenzylbenzophenone, 4,4'-dimethoxy-
benzophenone, 2-phenylbutyrophenone, β -phenylpropiophenone,
propiophenone, valerophenone, butyrophenone, benzil,
trans-stilbene, cis-stilbene, diphenyltetraacetylene, tetra-
acetylene glycol, diethyltetraacetylene, diphenylacetylene,
15 xanthone, thioxanthone, 2-isopropylthioxanthone, 2-chloro-
thioxanthone, 2-dodecylthioxanthone, 1-methoxycarbonyl-
thioxanthone, 2-ethoxycarbonylthioxanthone, 3-(n-methoxy-
ethoxycarbonyl)thioxanthone, 4-butoxycarbonylthioxanthone,
1-cyano-3-chlorothioxanthone, 2-ethoxycarbonyl-3-nitrothio-
20 xanthone, anthracene, 1-chloroanthracene, 2-methylantracene,
9-methylantracene, 2-tert.-butylantracene, 9-methoxy-
anthracene, 9,10-dimethoxyanthracene, 2,6- or 2,7-dimethyl-
anthracene, 2-t-butylantracene, 2,6- or 2,7-di-t-butyl-
anthracene, 2-(methoxycarbonylmethyl)anthracene, 2-(5-
25 methoxycarbonyl-2-methylpent-2-yl)anthracene, 2,6- or 2,7-
di(5-methoxycarbonyl-2-methylpent-2-yl)anthracene, 1,2-
benzanthracene, 1,2,3,4-dibenzanthracene, 1,2,5,6-dibenzo-
anthracene, 1,2,7,8-dibenzoanthracene, 3-thiophenyl-
phthalimide, N-methyl-4-thiophenylphthalimide, 2,3-butane
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Examples of organic materials polymerizable by
cationic polymerization and suitable for the hardenable
compositions according to the invention are of the following
types, it being possible for these to be used by themselves
35 or as mixtures of at least two components:

I. Ethylenically unsaturated compounds polymerizable by a
cationic mechanism. These include:

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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 and ethylene glycol divinyl ether; and cyclic vinyl ethers, for example 3,4-dihydro-2-formyl-2H-pyran (acrolein dimer) and the 3,4-dihydro-2H-pyran-2-carboxylic acid ester of 2-hydroxymethyl-3,4-dihydro-2H-pyran.
 3. Vinyl esters, for example vinyl acetate and vinyl stearate.
- II. Heterocyclic compounds polymerizable by cationic polymerization, for example ethylene oxide, propylene oxide, epichlorohydrin, 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; oxetanes such as 3,3-dimethyloxetane and 3,3-di(chloromethyl)oxetane; 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, as well as the adducts of azetidine with diisocyanates, for example toluylene-2,4-diisocyanate and toluylene-2,6-diisocyanate and 4,4'-diaminodiphenylmethane diisocyanate; epoxy resins; and linear and branched polymers with glycidyl groups in the side-chains, for example homopolymers and copolymers of polyacrylate and polymethacrylate glycidyl esters.
- Of particular importance among these abovementioned polymerizable compounds are the epoxy resins and especially the diepoxides and polyepoxides and epoxy resin prepolymers of the type used to prepare 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

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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; 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. Further 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, especially 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.

Preferred epoxy resins are diglycidyl ethers (which may or may not have been lengthened beforehand) of dihydric phenols or dihydric aliphatic alcohols having 2 to 4 carbon atoms. Particular preference is given to the diglycidyl ethers (which may or may not have been lengthened beforehand) of 2,2-bis(4-hydroxyphenyl)propane and bis(4-hydroxyphenyl)methane.

The following are also suitable as compounds polymerizable by cationic polymerization:

III. Methylol compounds:

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1. Aminoplasts such as the N-hydroxymethyl, N-methoxymethyl, N-n-butoxymethyl and N-acetoxymethyl derivatives of amides or related compounds, for example cyclic ureas such as ethyleneurea (imidazolidin-2-one), hydantoin, urone (tetra-
5 hydrooxadiazin-4-one), 1,2-propyleneurea (4-methylimidazol-
idin-2-one), 1,3-propyleneurea (hexahydro-2H-pyrimidin-2-one),
hydroxypropyleneurea (5-hydroxyhexahydro-2H-pyrimidin-2-one),
1,3,5-melamine and other polytriazines such as acetoguanamine,
benzoguanamine and adipoguanamine.

10 If desired, it is also possible to use aminoplasts which contain 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 are etherified with methyl groups).

15 Preferred aminoplasts are the condensation products of urea, urone, hydantoin or melamine with formaldehyde, and partially or completely etherified products of these condensation products with an aliphatic monohydric alcohol having 1 to 4 carbon atoms.

20 2. Phenoplasts.

Preferred phenoplasts are resols prepared from a phenol and an aldehyde. Suitable phenols include phenol itself, resorcinol, 2,2-bis(p-hydroxyphenyl)propane, p-chlorophenol, a phenol substituted by one or two alkyl
25 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, especially p-phenylphenol. The aldehyde condensed with the phenol is preferably formaldehyde, but other aldehydes, such as
30 acetaldehyde and furfural, are also possible. If desired, a mixture of hardenable phenol/aldehyde resins of these types can be used.

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

Suitable organic materials polymerizable by free radical polymerization are, in particular, monoethylenically

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or polyethylenically unsaturated compounds. Examples are: styrene, vinylpyridine, vinyl acetate, divinylbenzene, vinyl ether, acrylamide, methacrylamide, bisacrylamide, bismethacrylamide and unsaturated polyesters, especially those based on maleic acid. Preferred materials are the esters or amides of acrylic acid and/or methacrylic acid with linear or branched alcohols or polyols or, respectively, with monoamines or polyamines. Partial esters may also be used in the case of the polyols and polyamines.

10 Examples of polyamines are ethylenediamine, propylenediamine, butylenediamine, hexylenediamine, phenylenediamine, benzylenediamine, naphthylenediamine, diethylenetriamine, triethylenetetramine and diaminoethyl ether. Examples of polyols are linear and branched alkylenediols such as ethylenediol, propylenediol, butylenediol, pentylenediol, hexylenediol and octylenediol, polyoxaalkylenediols such as diethylene glycol and triethylene glycol and polyethylene glycols with a molecular weight of 200 to 500, 1,4-dihydroxycyclohexane, 1,4-di(hydroxymethyl)cyclohexane, dihydroxybenzenes, hydroxymethylphenols, triols such as 1,2,3-trihydroxypropane, 1,2,4-trihydroxybutane and trimethylolpropane, pentaerythritol, dipentaerythritol and low-molecular polyesters with terminal hydroxyl groups.

25 Examples of suitable alcohols and monoamines are methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, 2-ethylhexanol, cyclohexanol, phenol, glycidol, methylamine, dimethylamine and ethylamine.

30 Preferred organic materials polymerizable by free radical polymerization are partial esters of epoxy resins and acrylic acid, methacrylic acid or a mixture of these acids, and acrylic acid esters and/or methacrylic acid esters of polyols.

35 The hardenable compositions according to the invention can be obtained, for example, as homogeneous liquid mixtures or in the form of homogeneous or inhomogeneous glasses. Homogeneous glass-like products can be obtained in a manner known per se, for example by the liquefaction of

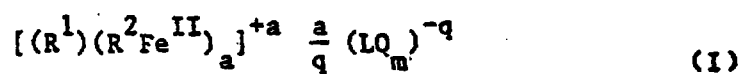
solid polymerizable organic materials, if appropriate with the addition of suitable solvents, in the dark or under red light, heating to temperatures above their glass transition temperature, the addition of components b) and c) and if
5 appropriate d), and cooling of the mixtures formed. If desired, the resulting glass-like products can then be comminuted. Inhomogeneous glass-like products can be obtained, for example, by mixing glass-like polymerizable materials in powder form with components b) and c) and if
10 appropriate d).

The compositions according to the invention are stable, and thus capable of being stored, at room temperature and under yellow light conditions. They can be hardened directly by the action of heat, advantageously at temperatures
15 near the melting point or decomposition point of components b) and c) and if appropriate d). They have a high photo-sensitivity and at the same time are stable to yellow light in the case of sensitizers which absorb light in the region below 400 nm.

20 An essential advantage of the composition according to the invention which contains component d) is that it can be hardened by the action of radiation, complete hardening generally being effected by the heat of reaction produced, and external heating being superfluous. However, it can
25 sometimes be advantageous also to apply external heat after exposure, for example if shorter reaction times are desired.

The present invention thus relates also to a process for the polymerization of an organic material polymerizable by free radical or cationic polymerization, under the action
30 of radiation, in the presence of a photoinitiator and, if appropriate, with heating, wherein the photoinitiator is a mixture of

a) at least one iron compound of the formula I



wherein

a is 1 or 2 and q is 1, 2 or 3,

L is a divalent to heptavalent metal or non-metal,

Q is a halogen atom,

5 m is an integer corresponding to the sum of the values of L and q,

R¹ is an unsubstituted or substituted η^6 -benzene and

R² is an unsubstituted or substituted cyclopentadienyl anion,

10 b) at least one sensitizer for the compound of the formula I and

c) at least one electron acceptor as an oxidizing agent, and, if appropriate, the polymerization reaction is then completed by the application of heat.

15 These 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 5000 Watts. Examples of suitable light sources are xenon lamps, argon lamps, tungsten lamps, carbon arcs, metal
20 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 including,
25 for example, the polymerizable organic material, the type of light source and its distance from the material irradiated. The irradiation time is preferably 10 to 60 seconds.

The exposed compositions can be heated in conventional convection ovens. If short heating or reaction times are
30 required, the heating can be effected by exposure with, for example, IR radiation, IR lasers or microwave devices. The polymerization temperatures are in the range from room temperature to about 80°C.

The compositions according to the invention can also
35 contain other known additives normally used in the technology of photopolymerizable materials. Examples of these additives are pigments, dyes, fillers and reinforcements,

glass fibres and other fibres, flame retardants, antistatic agents, flow control agents, antioxidants and light stabilizers, as well as conventional photoinitiators such as acetophenones, acylphosphine oxides or aromatic ketones. To
5 improve the final properties of epoxy resins, it is possible to incorporate polyfunctional hydroxyl compounds, for example those described in German Offenlegungsschrift 26 39 395.

To increase the storage stability in the dark, the hardenable compositions can contain weak organic bases such
10 as nitriles, amides, lactones or urea derivatives. To prevent premature reaction through unintentional exposure, small quantities of UV absorbers and/or organic dyes can be added.

The composition according to the invention can be applied by usual methods to at least one surface of a sub-
15 strate. The coated material also forms a subject of the invention. Examples of suitable substrates are metals and metalloids, such as steel, aluminium, copper, cadmium, zinc and silicon, as well as ceramic, glass, plastics, paper and wood. The coated material can be used to prepare protective
20 layers and passivating layers by exposure, and this forms a further subject of the invention.

If, on exposure, only part of the coating is irradiated through a photomask, the unexposed areas can subsequently be removed with a suitable solvent. Thus, the coated
25 material is also suitable as a photographic recording material, for the production of printing plates and particularly printed circuits, and as a solder resist. The use as a photographic recording material also forms a subject of the present invention.

30 The compositions according to the invention which contain a material polymerizable by cationic polymerization and which do not contain any oxidizing agents d) can be hardened by processes described in patent document EP-A-0, 094,915. These compositions can be hardened directly by the
35 action of heat. A two-step polymerization process is preferable, the iron complex of the formula I initially being activated by irradiation and the resulting activated

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precursors then being hardened by the action of heat, for example at temperatures from about 50 to 120°C. If irradiation is carried out through a photomask, photographic images can be produced. The irradiation time is approximately between 5 and 60 seconds and the thermal hardening time is approximately between 30 seconds and 5 minutes. These compositions according to the invention are characterized by a high photosensitivity.

The compositions according to the invention can also be used as adhesives or for the manufacture of putties, fillers or fibre-reinforced composites and laminates.

The compositions according to the invention have a high photosensitivity, which also means short exposure times for the hardening process. Initiators having a cationic action and a free radical action are produced simultaneously on exposure, which broadens the range of applications in respect of the polymerizable materials. It is surprising here that the oxidizing agent only becomes active after exposure and permits hardening by irradiation. It is a great advantage that the hardening is generally effected by the action of radiation, without the external application of heat.

The examples which follow illustrate the invention in greater detail.

Example a: (η^6 -Toluene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate is prepared according to Bull. Soc. Chim. France, 2572 (1975).

Example b: (η^6 -Anisole)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate is prepared according to Dokl. Akad. Nauk SSSR, 175, 609 (1967).

Example c: (η^6 -p-Dimethoxybenzene)(η^5 -cyclopentadienyl)iron(II) tetrafluoroborate is prepared according to J. Chem. Soc. C, 116 (1969).

Example d: (η^6 -p-Chlorotoluene)(η^5 -cyclopentadienyl)-iron(II) hexafluorophosphate is prepared according to J. Organomet. Chem. 20, 169 (1969).

Example e: (η^6 -Isopropylbenzene)(η^5 -cyclopentadienyl)-

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iron(II) hexafluorophosphate is prepared according to C.R. Acad. Sc. Paris, Ser. C, 272, 1337 (1971).

Example f: (η^6 -Isopropylbenzene)(η^5 -cyclopentadienyl)-iron(II) hexafluoroantimonate is prepared according to

5 Example e, but using potassium hexafluoroantimonate.

Example g: (η^6 -Isopropylbenzene)(η^5 -cyclopentadienyl)-iron(II) hexafluoroarsenate is prepared according to Example e, but using potassium hexafluoroarsenate.

Example h: (η^6 -Biphenyl)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate is prepared according to J. Chem. Soc. Chem. Comm. 907 (1972).

Example i: (η^6 -Tetralin)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate is prepared according to J. Organomet. Chem. 101, 221 (1975).

15 Application Examples

Example 1: A solution consisting of 10 g of an industrial epoxycresol novolak (epoxy content 4.5 eq/kg), 0.25 g (7×10^{-4} mol) of (η^6 -toluene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate (prepared according to Example a), 0.25 g
20 (1.3×10^{-3} mol) of 9-methylanthracene and 4 g of 1-acetoxy-2-ethoxyethane is applied to a copper-coated epoxy board with a 25 nm wire doctor. The initially wet film is dried at 80°C (dry film thickness approx. 15 nm). The photo-polymeric board prepared in this way is exposed with a
25 5000 Watt high-pressure mercury discharge lamp located 50 cm from the sample bench, a 21 step Stouffer sensitivity guide being used as the pattern (cf. W.S. DeForest, Photoresist, McGraw-Hill Book Comp., N.Y., page 109 et seq.). The exposure time is 30 seconds and the exposed board is then
30 hardened for 2 minutes at 110°C. It is developed in 1-acetoxy-2-ethoxyethane, the unexposed parts being dissolved. This results in a relief image, no. 5 being the last step of which an image is formed.

Examples 2 to 14: The procedure of Example 1 is followed
35 using different initiators and sensitizers.

The results are collated in Table 1. The content of initiator (arene-ferrocenium complex) is always 2.5 per cent

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by weight based on the epoxycresol novolak, and the corresponding sensitizer concentration is always 1.3 mmol based on the epoxycresol novolak. Exposure is carried out for 10, 20 and 30 seconds in each case.

Table 1

Example No.	Initiator (according to Example No.)	Sensitizer	Last step of which an image is formed after an exposure time of		
			10	20	30 sec.
1	a	9-methylanthracene	2	4	5
2	a	2-methylanthracene	3	4	6
3	b	9-methylanthracene	3	4	6
4	c	9-methylanthracene	3	4	6
5	d	9,10-diethoxyanthracene	3	5	6
6	e	2-methylanthracene	2	4	6
7	f	2-methylanthracene	12	14	16
8	g	2-methylanthracene	9	11	14
9	h	9,10-diethoxyanthracene	3	5	6
10	i	9-methylanthracene	2	4	5
11	a	2,6-di-t-butylanthracene	2	4	5
12	a	2,7-di-t-butylanthracene	2	3	5
13	a	2,6-di(5-methoxycarbonyl-2-methylpent-2-yl)-anthracene	3	4	6
14	a	2,7-di(5-methoxycarbonyl-2-methylpent-2-yl)-anthracene	3	4	6

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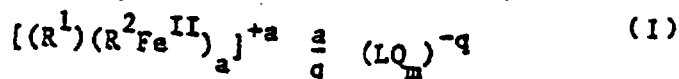
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What is claimed is:

1. A composition containing:

- a) a material polymerizable by free radical or cationic polymerization,
- b) at least one iron compound of the formula I



wherein

a is 1 or 2 and q is 1, 2 or 3,

L is a divalent to heptavalent metal or non-metal,

Q is a halogen atom,

m is an integer corresponding to the sum of the values of L and q,

R¹ is an unsubstituted or substituted η⁶-benzene and

R² is an unsubstituted or substituted cyclopentadienyl anion, and

c) at least one sensitizer for the compound of the formula I,

and, in the case of materials polymerizable by free radical polymerization, also d) an electron acceptor as an oxidizing agent.

2. A composition according to Claim 1, wherein an electron acceptor is also present as an oxidizing agent for the material polymerizable by cationic polymerization.

3. A composition according to Claim 1 or 2, wherein the iron compound b), or the iron compound b) and the oxidizing agent d), are present in a quantity of 0.1 to 15% by weight based on component a).

4. A composition according to Claim 3, wherein the weight ratio of the iron compound b) to the oxidizing agent d) is from 1:10 to 5:1.

5. A composition according to Claim 1, wherein the sensitizer c) is present in a quantity of 0.1 to 10% by weight based on component a).

6. A composition according to Claim 1, wherein R¹ is mono-



substituted or polysubstituted by identical or different halogen atoms or C_1 - C_{12} -alkyl, C_2 - C_{12} -alkenyl, C_2 - C_{12} -alkynyl, C_1 - C_8 -alkoxy, cyano, C_1 - C_8 -alkylthio, C_2 - C_6 -monocarboxylic acid ester, phenyl, C_2 - C_5 -alkanoyl or benzoyl groups.

7. A composition according to Claim 1, wherein R^2 is mono-substituted or polysubstituted by identical or different C_1 - C_8 -alkyl, C_2 - C_8 -alkenyl, C_2 - C_8 -alkynyl, C_2 - C_6 -monocarboxylic acid ester, cyano, C_2 - C_5 -alkanoyl or benzoyl groups.

8. A composition according to Claim 1, wherein a is 1 in the formula I.

9. A composition according to Claim 1, wherein m is 6, L is B, P, As or Sb, Q is F and q is 1 in the formula I.

10. A composition according to Claim 1, wherein R^1 is benzene, toluene, xylene, cumene, mesitylene, chlorobenzene, chlorotoluene, anisole, dimethoxybenzene, biphenyl, dodecylbenzene or tetralin in the formula I.

11. A composition according to Claim 1, wherein R^2 is the cyclopentadienyl or methylcyclopentadienyl anion in the formula I.

12. A composition according to Claim 1, wherein the oxidizing agent d) is an organic hydroperoxide, an organic peracid or a quinone.

13. A composition according to Claim 12, wherein the oxidizing agent is tertiary butyl hydroperoxide, cumene hydroperoxide, triphenylmethyl hydroperoxide, tetralin hydroperoxide, α -methyltetralin hydroperoxide, decalin hydroperoxide, perbenzoic acid, m-chloroperbenzoic acid or benzoquinone.

14. A composition according to Claim 1, wherein the sensitizer c) is selected from the group consisting of the monocyclic or polycyclic hydrocarbon aromatics or heteroaromatics, the phenones, particularly the acetophenones and the benzophenones, the benzils, the stilbenes, the polyacetylenes, the xanthenes and thioxanthenes, the anthracenes, the phthalimides, particularly the phthalimide thioethers, and



cc

the diones with adjacent CO groups.

15. A composition according to Claim 14, wherein the sensitizer c) is a thioxanthone, a phthalimide, a coumarin and particularly an anthracene.

16. A composition according to Claim 1, wherein the organic material polymerizable by cationic polymerization is an epoxy resin.

17. A composition according to Claim 1, wherein the material polymerizable by free radical polymerization is a mono-ethylenically or polyethylenically unsaturated compound.

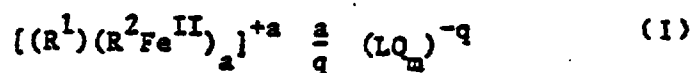
18. A composition according to Claim 17, wherein the material polymerizable by free radical polymerization is a partial ester of an epoxy resin and acrylic acid, methacrylic acid or a mixture of the acids, or an acrylic acid ester or methacrylic acid ester of a polyol.

19. A coated material, wherein a layer of the composition according to Claim 1 is applied to at least one surface of a substrate.

20. Use of the material according to Claim 19 for the production of protective coatings and as a photographic recording material.

21. A process for the polymerization of a material polymerizable by free radical or cationic polymerization, under the action of radiation, in the presence of a photoinitiator and, if appropriate, with heating, wherein the photoinitiator is a mixture of

a) at least one iron compound of the formula I



wherein

a is 1 or 2 and q is 1, 2 or 3,

L is a divalent to heptavalent metal or non-metal,

Q is a halogen atom,

m is an integer corresponding to the sum of the values of L and q,

R¹ is an unsubstituted or substituted η⁶-benzene and



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- R^2 is an unsubstituted or substituted cyclopentadienyl anion,
- b) at least one sensitizer for the compounds of the formula I, and
 - c) at least one electron acceptor as an oxidizing agent for the material polymerizable by free radical polymerization.

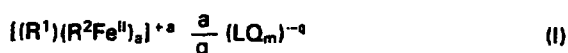
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Claims

1. A composition containing:
 a) a material polymerizable by free radical or cationic polymerization,
 b) at least one iron compound of the formula I



wherein

- a is 1 or 2 and q is 1, 2 or 3,
 L is a divalent to heptavalent metal or non-metal,
 Q is a halogen atom,
 m is an integer corresponding to the sum of the values of L and q,
 R¹ is an unsubstituted or substituted η⁶-benzene and
 R² is an unsubstituted or substituted cyclopentadienyl anion, and
 c) at least one sensitizer for the compound of the formula I, and, in the case of materials polymerizable by free radical polymerization, also d) an electron acceptor as an oxidizing agent.
2. A composition according to claim 1, wherein an electron acceptor is also present as an oxidizing agent for the material polymerizable by cationic polymerization.
3. A composition according to claim 1 or 2, wherein the iron compound b), or the iron compound b) and the oxidizing agent d), are present in a quantity of 0.1 to 15% by weight based on component a).
4. A composition according to claim 3, wherein the weight ratio of the iron compound b) to the oxidizing agent d) is from 1 : 10 to 5 : 1.
5. A composition according to claim 1, wherein the sensitizer c) is present in a quantity of 0.1 to 10% by weight based on component a).
6. A composition according to claim 1, wherein R¹ is monosubstituted or polysubstituted by identical or different halogen atoms or C₁-C₁₂-alkyl, C₂-C₁₂-alkenyl, C₂-C₁₂-alkynyl, C₁-C₈-alkoxy, cyano, C₁-C₈-alkylthio, C₂-C₈-monocarboxylic acid ester, phenyl, C₂-C₈-alkanoyl or benzoyl groups.
7. A composition according to claim 1, wherein R² is monosubstituted or polysubstituted by identical or different C₁-C₈-alkyl, C₂-C₈-alkenyl, C₂-C₈-alkynyl, C₂-C₈-monocarboxylic acid ester, cyano, C₂-C₈-alkanoyl or benzoyl groups.
8. A composition according to claim 1, wherein a is 1 in the formula I.
9. A composition according to claim 1, wherein m is 6, L is B, P, As or Sb, Q is F and q is 1 in the formula I.

10. A composition according to claim 1, wherein R¹ is benzene, toluene, xylene, cumene, mesitylene, chlorobenzene, chlorotoluene, anisole, dimethoxybenzene, biphenyl, dodecylbenzene or tetralin in the formula I.

11. A composition according to claim 1, wherein R² is the cyclopentadienyl or methylcyclopentadienyl anion in the formula I.

12. A composition according to claim 1, wherein the oxidizing agent d) is an organic hydroperoxide, an organic peracid or a quinone.

13. A composition according to claim 12, wherein the oxidizing agent is tertiary butyl hydroperoxide, cumene hydroperoxide, triphenylmethyl hydroperoxide, tetralin hydroperoxide, α-methyltetralin hydroperoxide, decalin hydroperoxide, perbenzoic acid, m-chloroperbenzoic acid or benzoquinone.

14. A composition according to claim 1, wherein the sensitizer c) is selected from the group consisting of the monocyclic or polycyclic hydrocarbon aromatics or heteroaromatics, the phenones, particularly the acetophenones and the benzophenones, the benzils, the stilbenes, the polyacetylenes, the xanthenes and thioxanthenes, the anthracenes, the phthalimides, particularly the phthalimide thioethers, and the diones with adjacent CO groups.

15. A composition according to claim 14, wherein the sensitizer c) is a thioxanthone, a phthalimide, a coumarin and particularly an anthracene.

16. A composition according to claim 1, wherein the organic material polymerizable by cationic polymerization is an epoxy resin.

17. A composition according to claim 1, wherein the material polymerizable by free radical polymerization is a monoethylenically or polyethylenically unsaturated compound.

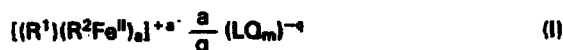
18. A composition according to claim 1, wherein the material polymerizable by free radical polymerization is a partial ester of an epoxy resin and acrylic acid, methacrylic acid or a mixture of the acids, or an acrylic acid ester or methacrylic acid ester of a polyol.

19. A coated material, wherein a layer of the composition according to claim 1 is applied to at least one surface of a substrate.

20. Use of the material according to claim 19 for the production of protective coatings and as a photographic recording material.

21. A process for the polymerization of a material polymerizable by free radical or cationic polymerization, under the action of radiation, in the presence of a photoinitiator and, if appropriate, with heating, wherein the photoinitiator is a mixture of

- a) at least one iron compound of the formula I



wherein

- a is 1 or 2 and q is 1, 2 or 3,
 L is a divalent to heptavalent metal or non-metal,
 Q is a halogen atom,
 m is an integer corresponding to the sum of the values of L and q,



R¹ is an unsubstituted or substituted η^6 -benzene and

R² is an unsubstituted or substituted cyclopentadienyl anion,

b) at least one sensitizer for the compounds of the formula I, and

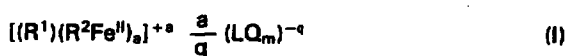
c) at least one electron acceptor as an oxidizing agent for the material polymerizable by free radical polymerization.

Revendications

1. Composition qui contient:

a) une matière polymérisable par voie radicalaire ou cationique.

b) au moins un composé du fer répondant à la formule I:



dans laquelle:

a est égal à 1 ou à 2,

q est égal à 1, à 2 ou à 3,

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

Q représente un atome d'halogène,

m représente un nombre entier qui est égal à la somme de la valence de L et de q,

R¹ représente un η^6 -benzène substitué ou non, et R² représente un anion cyclopentadiényle substitué ou non,

c) au moins un sensibilisateur pour le composé de formule I, et, dans le cas de matières polymérisables par voie radicalaire,

d) un accepteur d'électrons en tant qu'oxydant.

2. Composition selon la revendication 1, caractérisée en ce qu'elle contient également, pour la matière polymérisable par voie cationique, un accepteur d'électrons comme oxydant.

3. Composition selon l'une des revendications 1 et 2, caractérisée en ce que le composé du fer (b) ou le composé du fer (b) et l'oxydant (d) sont présents en une quantité de 0,1 à 15% en poids par rapport à la composante (a).

4. Composition selon la revendication 3, caractérisée en ce que le rapport pondéral du composé du fer (b) à l'oxydant (d) est compris entre 1 : 10 et 5 : 1.

5. Composition selon la revendication 1, caractérisée en ce que le sensibilisateur (c) est présent en une quantité de 0,1 à 10% en poids par rapport à la composante (a).

6. Composition selon la revendication 1, caractérisée en ce que R¹ porte un substituant ou plusieurs substituants, identiques ou différents, pris dans l'ensemble constitué par les atomes d'halogènes, les alkyles en C₁-C₁₂, les alcényles en C₂-C₁₂, les alcynyles en C₂-C₁₂, les alcoxy en C₁-C₈, le cyano, les alkylthio en C₁-C₈, les radicaux d'esters d'acides monocarboxyliques en C₂-C₈, le phényle, les alcanoyles en C₂-C₈ et le benzoyle.

7. Composition selon la revendication 1, caractérisée en ce que R² porte un substituant ou plusieurs substituants, identiques ou différents, pris dans l'ensemble constitué par les alkyles en C₁-C₈, les

alcényles en C₂-C₈, les alcynyles en C₂-C₈, les radicaux d'esters d'acides monocarboxyliques en C₂-C₈, le cyano, les alcanoyles en C₂-C₈ et le benzoyle.

8. Composition selon la revendication 1, caractérisée en ce que l'indice a, dans la formule I, représente le nombre 1.

9. Composition selon la revendication 1, caractérisée en ce que, dans la formule I, m est égal à 6, L représente B, P, As ou Sb, Q représente F, et q est égal à 1.

10. Composition selon la revendication 1, caractérisée en ce que, dans la formule I, R¹ représente le benzène, le toluène, le xylène, le cumène, le mésitylène, le chlorobenzène, le chlorotoluène, l'anisole, le diméthoxybenzène, le biphenyle, le dodécylbenzène ou la tétraline.

11. Composition selon la revendication 1, caractérisée en ce que, dans la formule I, R² représente l'anion cyclopentadiényle ou l'anion-cyclopentadiényle.

12. Composition selon la revendication 1, caractérisée en ce que l'oxydant (d) est un hydroperoxyde organique, un peracide organique ou une quinone.

13. Composition selon la revendication 12, caractérisée en ce que l'oxydant est l'hydroperoxyde de tert-butyle, l'hydroperoxyde de cumène, l'hydroperoxyde de triphénylméthyle, l'hydroperoxyde de tétraline, l'hydroperoxyde d' α -méthyltétraline, l'hydroperoxyde de décaline, l'acide perbenzoïque, l'acide m-chloro-perbenzoïque ou la benzoquinone.

14. Composition selon la revendication 1, caractérisée en ce que le sensibilisateur (c) est choisi dans l'ensemble constitué par les hydrocarbures aromatiques et les composés aromatiques hétérocycliques comportant un ou plusieurs cycles, les phénones, en particulier les acétophénones et les benzophénones, les benziles, les stilbènes, les polyacétylènes, les xanthones et thioxanthones, les anthracènes, les phthalimides, en particulier les thioéthers phthalimidiques, et les diones à radicaux -CO- voisins.

15. Composition selon la revendication 14, caractérisée en ce que le sensibilisateur (c) est une thioxanthone, une phthalimide, une coumarine ou, mieux, un anthracène.

16. Composition selon la revendication 1, caractérisée en ce que la matière organique polymérisable par voie cationique est une résine époxydique.

17. Composition selon la revendication 1, caractérisée en ce que la matière polymérisable par voie radicalaire est un composé monoéthylénique ou polyéthylénique.

18. Composition selon la revendication 17, caractérisée en ce que la matière polymérisable par voie radicalaire est un ester partiel formé par une résine époxydique et l'acide acrylique, l'acide méthacrylique ou un mélange de ces acides, ou est un ester acrylique ou méthacrylique d'un polyol.

19. Matière revêtue caractérisée en ce qu'une couche de la composition selon la revendication 1 est appliquée sur au moins une surface d'un support.

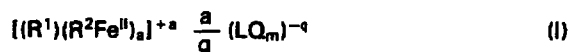
20. Application de la matière selon la revendication 19 pour la réalisation de revêtements protecteurs et comme matières d'enregistrement photographique.



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21. Procédé pour polymériser une matière polymérisable par voie radicalaire ou cationique, sous l'action d'un rayonnement, en présence d'un photo-amorceur et, éventuellement, avec chauffage, procédé caractérisé en ce que le photo-amorceur est un mélange constitué:

a) d'au moins un composé du fer répondant à la formule I:



dans laquelle:

a représente un nombre égal à 1 ou à 2,

q représente un nombre égal à 1, à 2 ou à 3,

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

Q représente un atome d'halogène,

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

R¹ représente un η⁶-benzène substitué ou non, et

R² représente un anion cyclopentadiényle substitué ou non,

b) d'au moins un sensibilisateur pour les composés de formule I, et

c) d'au moins un accepteur d'électrons comme oxydant pour la matière polymérisable par voie radicalaire.