

Description

The present invention relates to compositions comprising 1,2-epoxides and certain types of organometallic salts, and optionally certain types of photoaccelerators. It also relates to the polymerisation of such compositions by means of actinic radiation, to the further crosslinking of polymerised products so obtained by means of heat in the presence of heat-curing agents, and to the use of the compositions as surface coatings, in printing plates, in printed circuits, and in reinforced composites, and as adhesives.

For a number of reasons it has become desirable to induce polymerisation by means of actinic radiation. Employing photopolymerisation procedures may, for example, avoid the use of organic solvents with their attendant risks of toxicity, flammability and environmental pollution, and the cost of recovering the solvent. Photopolymerisation enables insolubilisation of a composition to be restricted to defined areas, i.e., those which have been irradiated, and so permits the production of printed circuits and printing plates or allows the bonding to substrates to be confined to required zones. Further, in production processes, irradiation procedures are often more rapid than those involving heating and a subsequent cooling step.

In US-A-3,709,861 there are described curable compositions comprising (a) an epoxide resin, (b) a polycarboxylic acid anhydride or polymercaptan as curing agent, and (c) a cyclopentadienylmanganese tricarbonyl as a light-activated accelerator. When curing is desired, the compositions are exposed to actinic radiation for 10 minutes to 8 hours (irradiation times from 15 minutes to 3 hours are used in the Examples). Exposure at room temperature produces a cure that is dry to the touch, but the composition can be heated, simultaneously with or subsequent to the exposure, at 50 to 250°C for 1 hour to 3 days to accelerate and complete the cure.

It has now been found that 1,2-epoxides can be photopolymerised by means of certain salts of complexes of transition metals with arenes and

cyclic dienes. These salts are in general soluble in liquid 1,2-epoxides and thus can be readily incorporated to form a photopolymerisable composition without the need to use toxic or inflammable solvents or complex dispersion means.

The salts used in the compositions of this invention have little or no effect on 1,2-epoxides on heating in the absence of actinic radiation. Thus, a composition comprising 2 parts by weight of tricarbonyl-(cyclohexa-2,4-dienylium)iron tetrafluoroborate and 100 parts by weight of a commercially available epoxide resin, the diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane, did not gel on heating at 150°C for 40 hours. It follows that, protected from actinic radiation, the compositions of the present invention have desirably long pot lives.

The invention accordingly relates to polymerisable compositions containing

- (a) a compound, or a mixture of such compounds, containing at least one 1,2-epoxide group and
- (b) an effective amount of a salt of the formula



I

where

- Y represents an arene group or a cyclic dienylium group
- Q represents an atom of a d-block transition metal chosen from titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper; niobium, molybdenum, ruthenium, rhodium, palladium, silver; tantalum, tungsten, rhenium, osmium, iridium, platinum, and gold,
- a is a positive integer such that the atom Q has a closed electron shell configuration,
- M represents an atom of a metal or metalloid,
- n is 4, 5, or 6, and is one more than the valency of M, and
- X represents a fluorine or chlorine atom, with the proviso that if M represents antimony, n is 6, and five of the symbols X represent fluorine, and one may also represent a hydroxo group.

This invention also relates to a process for the transformation into

higher-molecular weight material of a compound containing at least one 1,2-epoxide group, or a mixture of such compounds, comprising subjecting a said composition of this invention to actinic radiation.

When Y denotes an arene group i.e., is itself a 6-electron ligand, this may be a mononuclear or polynuclear group, including a condensed ring group. Preferably it is a hydrocarbon group which is optionally substituted by one or more alkoxy groups, and preferably it contains from 6 to 18 carbon atoms, such as benzene, toluene, mesitylene, naphthalene, biphenyl, phenanthrene, fluorene, and anthracene.

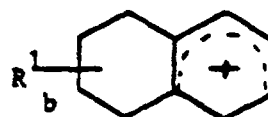
When Y denotes a cyclic dienylium group it is preferably a group of one of the following formulae



II



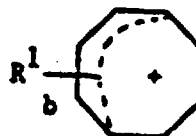
III



V



V



VI,

where

R^1 denotes an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, or an alkyl group interrupted by one or more oxycarbonyl groups and containing up to 12 carbon atoms, and

b is zero, 1, 2, or 3.

Q preferably represents chromium, cobalt, nickel, and particularly iron or manganese.

The atom M may represent, for example, iron, tin, bismuth, aluminium, gallium, indium, titanium, zirconium, scandium, vanadium, chromium, or manganese, but preferably it represents antimony, arsenic, boron, or phosphorus. The cation MX_n^+ may thus denote tetrachloroaluminate or

hexachloroferrate, for example, but it preferably denotes tetrafluoroborate, hexafluoroarsenate, hydroxopentafluoroantimonate, hexafluoroantimonate, or hexafluorophosphate.

Salts of formula I where Y denotes an arene group may be prepared by heating, for example, pentacarbonylmanganese bromide with an arene in the presence of aluminium chloride and treating the product in aqueous solution with, for example, potassium hexafluorophosphate, to precipitate the arenetricarbonylmanganese hexafluorophosphate (T.H. Coffield, V. Sandel, and R.D. Closson, J. Amer. Chem. Soc., 1957, 79, 5826).

Individual salts of formula I, where Y denotes an arene group, which are particularly preferred include the hexafluorophosphates of π -toluenetricarbonylmanganese, π -benzenetricarbonylmanganese, π -mesitylenetricarbonylmanganese, π -1-methyl-5,6,7,8-tetrahydronaphthalenetricarbonylmanganese, π -hexylbenzenetricarbonylmanganese, π -methoxybenzene tricarbonylmanganese, and π -hexyloxybenzenetricarbonylmanganese.

These salts satisfy the requirement that the central atom (manganese) has a closed electron shell configuration, i.e., 18 electrons in its valency shell, univalent manganese with its unipositive cation contributing 6 electrons, the arene group contributing 6 electrons, and the three carbonyl groups contributing 2 electrons each.

Salts of formula I where Y denotes a cyclic dienylium group are likewise generally known.

For example, a diene is heated with a metal carbonyl such as iron pentacarbonyl to form a neutral complex, e.g., tricarbonyl(cyclohexa-1,3-diene)iron, and abstraction of a hydride ion from the complex by means of triphenylmethyl tetrafluoroborate yields the corresponding tricarbonyl(cyclohexadienylium)iron tetrafluoroborate (E.O. Fischer and R.D. Fischer, Angew. Chem., 1960, 72, 919; A.J. Birch, K.B. Chamberlain, M.A. Haas, and D.J. Thompson, J. Chem. Soc., Perkin 1, 1973, 1882). The hexafluorophosphate or another desired salt of formula I may be made

similarly, using triphenylmethyl hexafluorophosphate and corresponding salts.

Reaction of cyclopentadienyliron dicarbonyl bromide with carbon monoxide in an inert solvent in the presence of aluminium tribromide as catalyst followed by hydrolysis and then treatment with ammonium hexafluorophosphate affords tricarbonyl(cyclopentadienyl)iron hexafluorophosphate (E.O. Fischer and K. Fichtel, Chem. Ber., 1961, 94, 1200).

Reaction of a cyclopentadienyliron dicarbonyl halide with carbon monoxide in acetone solution with sodium tetraphenylborate yields tricarbonyl(cyclopentadienyl)iron tetraphenylborate (A. Davison, M.L.H. Green and G. Wilkinson, J. Chem. Soc., 1961, 3172), from which salts such as the tetrafluoroborate may be prepared.

Such a cyclopentadienyliron dicarbonyl halide may also be carbonylated in the presence of a mixture of hexafluorophosphoric acid and propionic anhydride to afford tricarbonyl(cyclopentadienyl)iron, tricarbonyl(cycloheptatrienyl)iron, and tricarbonyl(cyclo-octa-tetraenyl)iron hexafluorophosphates (R.B. King, Inorg. Chem., 1962, 1, 964).

Tetracarbonyl(cyclopentadienyl)molybdenum hexafluorophosphate and tetracarbonyl(cyclopentadienyl)tungsten hexafluorophosphate can be prepared by reaction of cyclopentadienylmolybdenumtricarbonyl chloride and the corresponding tungsten compound with carbon monoxide in the presence of aluminium chloride followed by treatment of the tetracarbonyl(cyclopentadienyl) tetrachloroaluminate with ammonium hexafluorophosphate (E.O. Fischer, K. Fichtel, and K. Öfele, Chem. Ber., 1962, 95, 249-252).

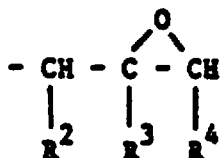
Tetracarbonyl(cyclopentadienyl)chromium tetrafluoroborate can be obtained by reaction of hydridotricarbonyl(cyclopentadienyl)chromium with boron trifluoride dimethyl etherate in benzene under an atmosphere of carbon monoxide (E.O. Fischer and K. Ulm, Z. Naturforsch., 1961, 16 B, 757).

Individual salts of formula I, where Y denotes a cyclic dienylium group, which are particularly preferred include tricarbonyl(cyclohexa-1,3-dienylium)iron tetrafluoroborate, tricarbonyl(1-methylcyclohexa-2,4-dienylium)iron hexafluorophosphate, tricarbonyl(1-methyl-4-methoxycyclohexa-2,4-dienylium)iron hexafluorophosphate, tricarbonyl(2-methoxybicyclo[4.4.0]deca-2,4-dienylium)iron hexafluorophosphate, tricarbonyl(1-(acetoxymethyl)-2-(methoxycarbonylacetoxy)ethylcyclohexa-2,4-dienylium)-iron hexafluorophosphate, tricarbonyl(1-ethyl-4-isopropoxycyclohexa-2,4-dienylium)iron hexafluorophosphate, and tricarbonyl(1-(methoxycarbonyl)-4-methoxycyclohexa-2,4-dienylium)iron tetrafluoroborate.

These salts likewise satisfy the requirement that the central atom (iron) has a closed electron shell configuration, the iron contributing 7 electrons, the dienylium group contributing 5, and the carbonyl groups also contributing 2 electrons each (i.e., 18 in all).

The compositions of this invention preferably contain from 0.5 to 7.5, and particularly 1 to 5.0, parts by weight of (b) per 100 parts by weight of (a).

Suitable mono-1,2-epoxides include epichlorohydrin, propylene oxide, glycidyl ethers of monohydric alcohols or phenols, such as n-butyl glycidyl ether or phenyl glycidyl ether, and glycidyl esters of monocarboxylic acids, such as glycidyl acrylate or glycidyl methacrylate. Preferably (a) is an epoxide resin, i.e., a compound containing on average more than one 1,2-epoxide group per molecule, such as a resin containing more than one terminal group of formula



VII

directly attached to an atom of oxygen, where either R^2 and R^4 each represent a hydrogen atom, in which case R^3 denotes a hydrogen atom or a methyl group, or R^2 and R^4 together represent $-\text{CH}_2\text{CH}_2-$, in which case R^3 denotes a hydrogen atom.

As examples of such resins may be mentioned polyglycidyl and poly(β -methylglycidyl) esters obtainable by reaction of a compound containing two or more carboxylic acid groups per molecule with epichlorohydrin, glycerol dichlorohydrin, or β -methylepichlorohydrin in the presence of an alkali. Such polyglycidyl esters may be derived from aliphatic polycarboxylic acids, e.g., succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, or dimerised or trimerised linoleic acid; from cycloaliphatic polycarboxylic acids such as tetrahydrophthalic acid, 4-methyltetrahydrophthalic acid, hexahydrophthalic acid, and 4-methylhexahydrophthalic acid; and from aromatic polycarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid. Other suitable polyglycidyl esters are obtainable by polymerisation of glycidyl esters of vinylic acids, especially glycidyl acrylate and glycidyl methacrylate.

Further examples are polyglycidyl and poly(β -methylglycidyl) ethers obtainable by reaction of a compound containing at least two free alcoholic and/or phenolic hydroxyl groups per molecule with the appropriate epichlorohydrin under alkaline conditions or, alternatively, in the presence of an acidic catalyst and subsequent treatment with alkali. These ethers may be prepared from acyclic alcohols such as ethylene glycol, diethylene glycol, and higher poly(oxyethylene) glycols, propane-1,2-diol and poly(oxypropylene) glycols, propane-1,3-diol, poly(oxytetramethylene) glycols, pentane-1,5-diol, hexane-2,4,6-triol, glycerol, 1,1,1-trimethylolpropane, pentaerythritol, sorbitol, and poly(epichlorohydrin), from cycloaliphatic alcohols such as resorcitol, quinitol, bis(4-hydroxycyclohexyl)methane, 2,2-bis(4-hydroxycyclohexyl)propane, and 1,1-bis(hydroxymethyl)cyclohex-3-ene; and from alcohols having aromatic nuclei, such as N,N-bis(2-hydroxyethyl)-aniline and p,p'-bis(2-hydroxyethylamino)diphenylmethane. They may also be prepared from mononuclear phenols, such as resorcinol and hydroquinone, and from polynuclear phenols, such as bis(4-hydroxyphenyl)methane (otherwise known as bisphenol F), 4,4'-dihydroxydiphenyl, bis(4-hydroxyphenyl) sulphone, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane (otherwise known as bisphenol A), 2,2-

bis(3,5-dibromo-4-hydroxyphenyl)propane, and novolaks formed from aldehydes such as formaldehyde, acetaldehyde, chloral, and furfuraldehyde, with phenol itself, or phenol substituted in the ring by chlorine atoms or by alkyl groups each containing up to 9 carbon atoms, such as 4-chlorophenol, 2-methylphenol, and 4-tert.butylphenol.

Poly(N-glycidyl) compounds may also be used, e.g., the N-glycidyl derivatives of amines such as aniline, n-butylamine, bis(4aminophenyl)-methane, and bis(4-methylaminophenyl)methane; triglycidyl isocyanurate; and N,N'-diglycidyl derivatives of cyclic alkylene ureas, such as ethyleneurea and 1,3-propyleneurea, and of hydantoins (sic) such as 5,5-dimethylhydantoin. In general, however, they are not preferred.

Poly(S-glycidyl) compounds may also be used, e.g., di(S-glycidyl) derivatives of dithiols such as ethane-1,2-dithiol and bis(4-mercapto-methylphenyl) ether, but they also are not preferred.

Examples of epoxide resins having groups of formula VII where R_2 and R_4 conjointly denote a $-CH_2CH_2-$ group are bis(2,3-epoxycyclopentyl) ether, 2,3-epoxycyclopentyl glycidyl ether, and 1,2-bis(2,3-epoxycyclopentyloxy)ethane.

Epoxide resins having 1,2-epoxide groups attached to different kinds of heteroatoms may also be employed, e.g., the glycidyl ether-glycidyl ester of salicylic acid.

Epoxide resins in which some or all of the epoxide groups are not terminal may also be employed, such as vinylcyclohexene dioxide, limonene dioxide, dicyclopentadiene dioxide, 4-oxatetracyclo[6.2.1.0^{2,7}.0^{3,5}]undec-9-yl glycidyl ether, 1,2-bis(4-oxatetracyclo (sic) [6.2.1.0^{2,7}.0^{3,5}]undec-9-yloxy)ethane, 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate and its 6,6'-dimethyl derivative, ethylene glycol bis(3,4-epoxycyclohexane carboxylate), 3-(3,4-epoxycyclohexyl)-8,9-epoxy-2,4-dioxaspiro[5,5]undecane, and epoxidised butadienes or copolymers of butadienes with ethylene compounds such as styrene and vinyl acetate.

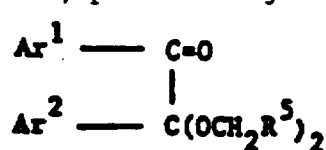
If desired, a mixture of epoxide resins may be used.

Especially preferred epoxide resins used in this invention are diglycidyl ethers, which may have been advanced, of dihydric phenols such as 2,2-bis(4-hydroxyphenyl)propane and bis(4-hydroxyphenyl)methane and of dihydric aliphatic alcohols such as butane-1,4-diol.

When Y denotes an arene group it will normally be necessary to apply heat as well as actinic radiation to bring about curing if the epoxide groups in (a) are of formula VII: with such salts the use of epoxide resins where the 1,2-epoxide groups are directly attached to cycloaliphatic carbon atoms is preferred.

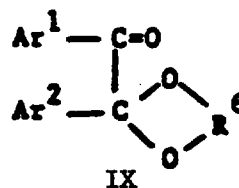
Preferably the compositions of this invention also contain a photoaccelerator. It has been found that, by incorporation of suitable photoaccelerators, the speed of curing is further increased, thereby permitting the use of shorter exposure times and/or of less powerful sources of irradiation.

Substances suitable as the photoaccelerator include ketals of aromatic diketones, particularly compounds of formula



VIII

or



IX

where

R^5 represents a hydrogen atom, an alkyl group of 1 to 5 carbon atoms, an alkenyl group of 2 or 3 atoms, an aralkyl group of 7 to 9 carbon atoms, an aralkenyl group of 8 or 9 carbon atoms, or a group of formula $-(\text{CH}_2)_m\text{R}^7$

wherein

R^7 denotes a halogen atom or a group of formula $-\text{OR}^8$, $-\text{SR}^8$, OAr^3 , SAr^3 , OCOR^8 , or $-\text{COOR}^8$,

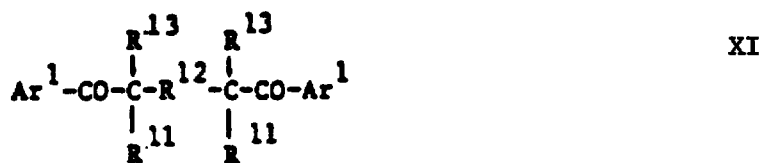
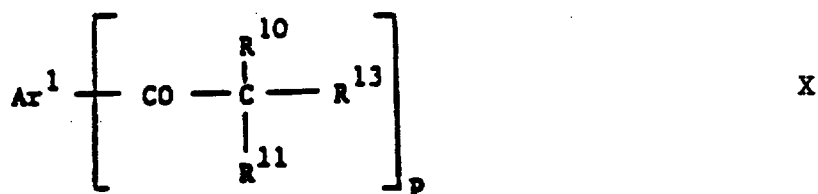
m is 1, 2, or 3,

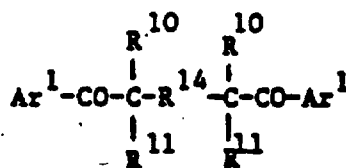
R^6 represents a group of formula $-\text{CH}_2\text{CH}(R^9)-$ or $-\text{CH}_2\text{CH}(R^9)\text{CH}_2-$,
 R^8 denotes an alkyl group of 1 to 4 carbon atoms,
 R^9 denotes a hydrogen atom or an alkyl group of 1 to 18 carbon atoms,
 and
 Ar^1 , Ar^2 , and Ar^3 independently of one another each represent a phenyl group which is unsubstituted or is substituted by up to 3 substituents chosen from halogen atoms, alkyl or alkoxy groups of 1 to 4 carbon atoms, and phenyl groups.

Examples of compounds of formula VIII are benzil dimethyl ketal, benzil diethyl acetal, benzil di(2-methoxyethyl) ketal, and benzil di(2-chloroethyl) ketal. Examples of compounds of formula IX are 2-phenyl-2-benzoyl-4-methyl-1,3-dioxolane and 2-phenyl-2-benzoyl-1,3-dioxane. The particularly preferred photosensitiser is benzil dimethyl ketal.

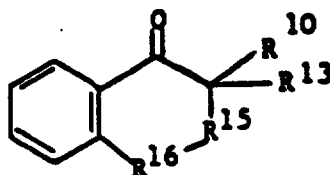
Compounds of formula VIII or IX are described in GB-A-1,390,006, where they are employed for the photopolymerisation and photocrosslinking of ethylenically-unsaturated compounds such as methyl acrylate, styrene-containing polyesters based on maleic acid, and diallyl phthalate prepolymers.

Other substances suitable as the photoaccelerator include aromatic-aliphatic ketones of one of the formulae





XII



XIII

where

Ar^1 has the meaning given above,

R^{10} and R^{11} each denote a monovalent aliphatic, cycloaliphatic, or araliphatic group, or together with the attached carbon atom denote a cycloalkylene group,

R^{12} is a carbon-carbon bond or a divalent organic radical,

R^{13} represents a hydroxyl group or an amino group, or a monovalent etherified or silylated such group,

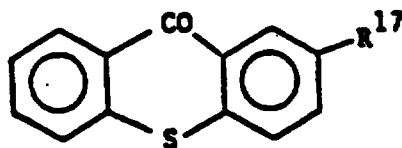
R^{14} represents a divalent amino, ether, or siloxy group,

R^{15} represents a direct chemical formation (sic) or $-\text{CH}_2-$, and

R^{16} represents $-\text{O}-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{CH}_2-$, or $-\text{C}(\text{CH}_3)_2-$.

These compounds, preferred members of which include 2-allyloxy-2-methylpropiofenone, 2-benzyloxy-2-methylpropiofenone, 2-hydroxy-2-methyl-p-phenoxypropiofenone, 1-benzoylcyclohexanol, 1-benzoylcyclopentanol, and bis(4-(α -hydroxyisoburyl)phenyl) (sic) ether, are likewise described as photopolymerisation catalysts for ethylenically-unsaturated compounds and as photocrosslinkers for polyolefins in European Patent Application No. 0 003 002.

Other compounds which may be used to enhance the photopolymerisation rate of 1,2-epoxides by the salts of formula I are 2-substituted thioxanthenes of formula



XIV

where R^{17} denotes either a chlorine atom or an alkyl group of 1 to 6

carbon atoms such as an isopropyl or tert.butyl group. Compounds of formula XIV, especially the 2-chloro compound, are used commercially as photopolymerisation catalysts for ethylenically-unsaturated compounds and as photocrosslinkers for polyolefins.

That compounds of formulae VIII to XIV accelerate the photoinduced polymerisation of 1,2-epoxides by means of organometallic salts is therefore unexpected.

It is preferred to incorporate from 0.5 to 7.5% by weight, and especially from 1 to 5% by weight of the photoaccelerator, calculated on the weight of (a).

In the photopolymerisation step actinic radiation of wavelength from 200 to 600 nm is preferably used. Suitable sources of actinic radiation include carbon arcs, mercury vapour arcs, fluorescent lamps with phosphors emitting ultraviolet light, argon and xenon glow lamps, tungsten lamps, and photographic flood lamps. Of these, mercury vapour arcs, particularly sun lamps, fluorescent sun lamps, and metal halide lamps are most suitable. The time required for the exposure will depend upon a variety of factors which include, for example, the individual polymerisable substance used, the type of light source, and its distance from the irradiated material. Suitable times may be readily determined by those familiar with photopolymerisation techniques. If, as in a process described below, it is necessary that the product so photopolymerised must still be curable on heating with a heat-curing agent mixed therewith, then, of course, irradiation is to be carried out at a temperature below that at which substantial heat-curing of the photopolymerised product by means of the heat-curing agent would occur.

The compositions of this invention may be used as surface coatings. They may be applied here to substrates such as steel, aluminium, copper, cadmium, zinc, paper, or wood, preferably as a liquid, and irradiated. By polymerising part of the coating, such as by irradiation through a mask, those sections which have not been exposed may be washed with a solvent to remove the unpolymerised portions while leaving the

photopolymerised, insoluble portions in place. Thus the compositions of this invention may be used in the production of printing plates and printed circuits. Methods of producing printing plates and printed circuits from photopolymerisable compositions are well known (see, e.g., GB-A-1,495,746).

The compositions may also be used as adhesives. A layer of the composition may be sandwiched between two surfaces of objects, at least one of which is transparent to the actinic radiation, e.g., of glass, and the assembly is then irradiated and, if desired, heated to complete the polymerisation.

The compositions are also useful in the production of fibre-reinforced composites, including sheet moulding compounds.

They may be applied directly, in liquid form, to reinforcing fibres (including strands, filaments, and whiskers), which may be in the form of woven or nonwoven cloth, unidirectional fibres, or chopped strands.

The fibre-reinforced composite may be made by a batch process, the fibrous reinforcing material being laid on a film of the photopolymerised composition, which is advantageously held under slight tension, when a second such film may, if desired, be laid on top, and the assembly is pressed while being heated. It may also be made continuously, such as by contacting the fibrous reinforcing material with a film of the photopolymerised composition, then, if desired, placing a second such film on the reverse face of the fibrous reinforcing material and applying heat and pressure. More conveniently, two such films, preferably supported on the reverse side by belts or strippable sheets, are applied simultaneously to the fibrous reinforcing material so as to contact each exposed face. When two such films are applied, they may be the same or different.

Multilayer composites may be made by heating under pressure interleaved films and layers of one or more fibrous reinforcing materials. When unidirectional fibres are used as the reinforcing material, layers of

them may be oriented to form cross-ply structures.

With the fibrous reinforcing material there may be used additional types of reinforcement such as a foil of metal or plastic or rubber sheets.

In the production of sheet moulding compounds, a composition of this invention, together with the chopped strand reinforcing material and any other components, are exposed to radiation in layers through supporting sheets.

The polymerisable composition is preferably applied so that the composite contains a total of from 20 to 80% by weight of the said composition and, correspondingly, 80 to 20% by weight of the reinforcement. Particularly preferably, a total of 30 to 50% by weight of the composition is employed.

The compositions of this invention are useful in the production of putties and fillers. They may be used as dip-coatings, an article to be coated being dipped in the liquid composition, withdrawn, and the adhering coating being irradiated to photopolymerise, and hence solidify it, and subsequently, if desired, being heated.

It has been found that it is possible, using the compositions of this invention, to cure epoxide resins in two stages; the resin is first converted into the partially cured B-stage by exposing it to actinic radiation in the presence of an organometallic salt of formula I and a latent, heat-activated crosslinking agent for the epoxide resin and, in a second stage, the partially cured composition is heated so that curing is completed by means of the heat-activated crosslinking agent. Thus, a liquid or semiliquid composition may be prepared, which may then be shaped or used to impregnate a substrate while being irradiated to solidify it; then the solidified body is heated when desired, to complete the cure of the resin.

This invention accordingly also relates to a process for the polymerisation of an epoxide resin, wherein a) an epoxide resin is

irradiated, in the presence of an amount of an organometallic salt of formula I effective for the polymerisation of the epoxide resin and of a curing amount of a latent heat-curing agent for the epoxide resin, to form a B-stage product and, if desired, b) curing of the composition is completed by heating.

A further subject is a composition containing an epoxide resin, an amount of an organometallic salt of formula I effective for polymerisation of the said epoxide resin on exposure of the composition to actinic radiation, and a curing amount of a latent heat-curing agent for the epoxide resin.

Suitable heat-activated crosslinking agents for the epoxide resin compositions include polycarboxylic acid anhydrides, complexes of amines, especially primary or tertiary aliphatic amines such as ethylamine, trimethylamine, and n-octyldimethylamine, with boron trifluoride or boron trichloride, and latent boron difluoride chelates. Aromatic polyamines and imidazoles are usually not preferred, because indifferent results are obtained, possibly due to a reaction between the acid catalyst liberated and the amine. Dicyandiamide can be used successfully, providing it is relatively coarse particles.

The temperatures and duration of heating required for the heat-curing and the proportions of heat-activated curing agent are readily found by routine experimentation and easily derivable from what is already well known concerning the heat-curing of epoxide resins.

By virtue of the compositions having groups through which they can be heat-cured after photopolymerisation, they are particularly useful in the production of multilayer printed circuits.

Conventionally, a multilayer printed circuit is prepared from several double-sided printed circuit boards of copper, stacked one on top of another and separated from each other by insulating sheets, usually of glass fibres impregnated with an epoxide resin in the B-stage. If a heat-curing agent is not admixed with the layer of photopolymerisable

epoxide resin in the circuit board, it can be incorporated in the insulating layers which alternate with the plates, these layers conveniently being of an epoxide resin prepreg; sufficient of the heat-curing agent contained in the prepreg, providing the latter is not too thick, migrates to include crosslinking of the photopolymerised epoxide resin. The stack is heated and compressed to bond the layers together. Conventional photopolymerisable materials, however, do not form strong bonds either with copper or with resin-impregnated glass fibre sheets. A stack which is bonded with the photopolymer and still covering the copper is therefore inherently weak and in use can become delaminated. It is therefore normal practice to remove the residual photopolymer after the etching stage, either by means of powerful solvents or by a mechanical method, e.g., by means of brushing. Such a stripping process can damage the copper of the printed circuit or the surface of the laminate on which the circuit rests, and so there is a need for a method which would avoid the necessity of removing the photopolymerised material prior to bonding the boards together. The presence of residual 1,2-epoxide groups means that crosslinking can occur when the boards are bonded, resulting in good adhesion to the copper and to the resin-impregnated glass fibre substrate, so avoiding the necessity just referred to.

Another application involving heat-curing after photopolymerisation of the compositions of this invention is filament winding. Thus, a continuous tow of fibrous reinforcement is impregnated with a composition containing a latent heat-curing agent for epoxide resins and then wound around a mandrel while exposing the winding to actinic radiation. Such filament windings still have a certain degree of flexibility, permitting the mandrel to be removed more readily than when a rigid winding is formed in one step. When required, the winding is heated to crosslink the composition.

In a further such application, a layer of the composition in liquid form is irradiated until it solidifies, producing a film adhesive which is then placed between, and in contact with, two surfaces which are to be bonded, and the assembly is heated to complete crosslinking of the

composition. The film may be provided on one face with a strippable backing sheet. Manipulation of the assembly is often easier if the film has a tacky surface. This may be produced by coating the film with a substance which is tacky at room temperature but which crosslinks to a hard, insoluble, infusible resin under the conditions of heat employed to complete crosslinking of the composition. However, an adequate degree of tackiness often exists without additional treatment, especially if polymerisation of the composition has not proceeded too far. Suitable bonding substrates include metals such as iron, zinc, cadmium, copper, nickel, and aluminium, ceramics, glass, and types of rubber.

The following Examples serve to illustrate the invention. Unless otherwise indicated, parts are by weight.

Epoxide Resin I denotes a diglycidyl ether of 2,2-bis(4-hydroxyphenyl)-propane, of epoxide content 5.2 equiv./kg.

Epoxide Resin II denotes 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate.

Epoxide Resin III denotes an advanced epoxide resin of epoxide content 2.30 equiv./kg, prepared by reaction in a conventional manner of bisphenol A diglycidyl ether (38.56 parts) and bisphenol A (10.82 parts).

Epoxide Resin IV denotes a diglycidyl ether of 1,4-butanediol, of epoxide content 9.35 equiv./kg.

Epoxide Resin V denotes an epoxidised bisphenol A novolak having a softening point of 72°C and an epoxide content of 4.9 equiv./kg.

The organoiron salts employed in these Examples are prepared as described by A.J. Birch et al., loc. cit.

π -1-Methyl-5,6,7,8-tetrahydronaphthalene-tricarbonylmanganese hexafluorophosphate

This is prepared following the method of T.H. Coffield, V. Sandel and R.D. Closson, loc. cit.

A mixture of pentacarbonylmanganese bromide (2.5 g), aluminium chloride (2 g), and 1-methylnaphthalene is stirred for 6 hours under nitrogen at 100°C. The mixture is cooled and hydrolysed with 100 g of ice water, and to the separated aqueous solution is added potassium hexafluorophosphate (1.7 g) dissolved in 30 ml of water. The yellow precipitate is filtered off, washed with ice water, and dried for 16 hours at 40°C/13000 N/m. The product has a melting point of 175°C (decomp.)

(Found: C, 39.55; H, 3.25; F, 26.6; Mn, 12.6; P, 7.2.

Calculated for $C_{14}H_{14}F_6MnO_3P$ - C, 39.09; H, 3.28; F, 26.50; Mn, 12.77; P, 7.20%).

π -Toluene-tricarbonylmanganese hexafluorophosphate

This is prepared in a similar manner by the method of T.H. Coffield et al. (loc. cit.). The product melts at above 250°C.

(Found: C, 31.9; H, 2.2; F, 31.7; Mn, 14.8.

Calculated for $C_{10}H_8F_6MnO_3P$; C, 31.94; H, 2.14; F, 30.31; Mn, 14.61; O, 12.76; P, 8.24%).

π -Methoxybenzene-tricarbonylmanganese hexafluorophosphate

A mixture of pentacarbonylmanganese bromide (2.5 g), aluminium chloride (2 g) and methoxybenzene (30 ml) is heated to 110°C for 3.5 hours with stirring under nitrogen. The mixture is cooled and hydrolysed with 100 g ice-water and to the separated aqueous solution is added potassium hexafluorophosphate (1.7 g) dissolved in 30 ml of water. The yellow precipitate is filtered off, washed with ice-water and dried for 16 hours at 40°C/13000 N/m². The product melts at above 290°C.

(Found: C, 30.5; H, 2.2; F, 29.6; Mn, 13.4.

Calculated for $C_{10}H_8F_6MnO_4P$; C, 30.64; H, 2.06; F, 29.07; Mn, 14.01).

π -Hexyloxybenzene-tricarbonylmanganese hexafluorophosphate

This is prepared in a similar way as the corresponding methoxybenzene compound, hexyloxybenzene (30 ml) being used in place of the methoxybenzene. The product melts at 146-151°C.

π -Hexylbenzene-tricarbonylmanganese hexafluorophosphate

This is prepared in a similar way as the corresponding methoxybenzene compound, hexylbenzene (10 ml.) being used together with octane (20 ml) in place of the methoxybenzene. The product melts at 148-151°C.

(Found: C, 39.9; H, 4.1; F, 25.8; Mn, 12.0.

Calculated for $C_{15}H_{18}F_6MnO_3P$; C, 40.38; H, 4.07; F, 25.55; Mn, 12.31).

EXAMPLES 1-6

Epoxide Resin I and tricarbonyl(cyclohexadienylum)iron salts are mixed as listed in the following Table, the compositions are drawn as films 6 μ m thick on tinfoil and then subjected at a distance of 20 cm to radiation from a medium pressure mercury arc lamp (80 W per cm) for the indicated time. The results obtained are also shown in Table I.

TABLE I

Example No.	Complex Name	Amount by weight on Resin	Irradiation time	Result
1	Tricarbonyl(cyclohexa-1,3-dienylium) iron tetrafluoroborate	2%	2 minutes	Film slightly tacky, becomes tack-free on standing
2	Tricarbonyl(1-methylcyclohexa-2,4-dienylium)iron hexafluorophosphate	3%	2 minutes	Film tack-free
3	Tricarbonyl(1-methyl-4-methoxycyclohexa-2,4-dienylium)iron hexafluorophosphate	2%	2 minutes	Film tack-free
4	Tricarbonyl(2-methoxybicyclo[4.4.0]deca-2,4-dienylium)iron hexafluorophosphate	3%	40 seconds	Film tack-free
5	Tricarbonyl(1-(acetoxymethyl)-2-(methoxycarbonylacetoxymethyl)cyclohexa-2,4-dienylium)iron hexafluorophosphate	4%	2 minutes	Film slightly tacky, becomes tack-free on standing
6	Tricarbonyl(1-methoxycarbonyl)-4-methoxycyclohexa-2,4-dienylium)iron tetrafluoroborate	3%	2 minutes	Film slightly tacky, becomes tack-free on standing
-	None	-	20 minutes	No effect

EXAMPLES 7-8

The procedure of Examples 1 to 6 is repeated, with Epoxide Resin II. The results obtained are shown in Table II.

TABLE II

Example No.	Complex Name	Amount by weight on Resin	Irradiation time	Result
7	Tricarbonyl(1-methyl-cyclohexa-2,4-dienylium)iron hexafluorophosphate	3%	2 minutes	Film slightly tacky, becomes tack-free on standing
8	Tricarbonyl(2-methoxy-bicyclo[4.4.0]deca-2,4-dienylium)iron hexafluorophosphate	3%	2 minutes	Film tack-free

EXAMPLE 9

A mixture comprising 5 grams of Epoxide Resin II, 0.2 g of π -1-methyl-5,6,7,8-tetrahydronaphthalenetricarbonyliron hexafluorophosphate, and 1 drop of a commercially available flow control agent (a fluorocarbon) is applied to tinplate as in Examples 1 to 6. The film becomes tack-free after irradiation for 12 seconds. After the film has been heated to 100°C for 10 minutes it withstands 12-13 rubs in the standard acetone rub test for solvent resistance, in which a cotton wool swab soaked in acetone is rubbed across the surface.

EXAMPLE 10

Epoxide Resin III (49.38 parts) is dissolved in a mixture of acetone (14.81 parts) and ethyl methyl ketone (34.57 parts). To this solution is added π -toluenetricarbonylmanganese hexafluorophosphate (1.5 parts), and the homogeneous solution is spread on a copper-coated plate of epoxide resin / glass laminate by means of a 24 μ m roller coater (i.e., the wet film is 24 μ m thick). The coating, after being dried at 75°C for 20 minutes, is irradiated with a 5000 W metal halide lamp for 3 minutes through a Stouffer 21 step sensitivity guide. The plate is heated for 3 minutes at 80°C and then developed with ethyl methyl ketone. Etching in 50% ferric chloride solution yields a No. 2 step image.

EXAMPLES 11-13

These examples, set out in Table III, illustrate the use of photoinitiators in conjunction with a complex of formula I to photopolymerise an epoxide resin. The procedure of Examples 1-6 is followed here. In Example 11 Epoxide Resin II is used, in Examples 12 and 13 Epoxide Resin I is used.

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TABLE III

Example No.	Complex Name	Amount by weight on Epoxide Resin	Name	Photoinitiator	Amount by weight on Epoxide Resin	Irradiation time to form a tack-free film
11	Tricarbonyl-(2-methoxy-bicyclo[4.4.0]deca-2,4-dienyl)iron hexafluorophosphate	3%	-	-	-	5 secs.
	Tricarbonyl-2-methoxy-bicyclo[4.4.0]deca-2,4-dienyl)iron hexafluorophosphate	3%	Benzil dimethyl ketal	3%	1-2 secs.	
12	Tricarbonyl-(1-methyl-4-methoxycyclohexa-2,4-dienyl)iron hexafluorophosphate	3%	-	-	-	3 mins.
	Tricarbonyl-(1-methyl-4-methoxycyclohexa-2,4-dienyl)iron hexafluorophosphate	3%	Benzil dimethyl ketal	3%	1 min	
13	Tricarbonyl-(1-ethyl-4-isopropoxycyclohexa-2,4-dienyl)iron hexafluorophosphate	4%	-	-	-	40 secs
	Tricarbonyl-(1-ethyl-4-isopropoxycyclohexa-2,4-dienyl)iron hexafluorophosphate	4%	2-Chlorothioxanthone	4%	25 secs	

In Examples 14 to 23 an epoxide resin is photopolymerised and subsequently heat-cured.

EXAMPLE 14

A mixture comprising 5 parts of Epoxide Resin I, 0.2 part of tri-carbonyl(1-ethyl-4-isopropoxycyclohexa-2,4-dienylium)iron hexafluorophosphate, and 0.2 part of boron trichloridetrимethylamine complex is applied as a coating 6 μ m thick onto tinplate and irradiated with a lamp (80 W per cm) at a distance of 20 cm for 50 seconds. The film is tack-free. On rubbing the coating with a cotton wool swab soaked in acetone it is attacked after two rubs. Next, the plate is heated at 150°C for 1 hour, after which the coating has appreciably greater resistance to the solvent, withstanding 13 such rubs.

EXAMPLE 15

A mixture comprising Epoxide Resin I (100 parts), π -methoxybenzenetricarbonylmanganese hexafluorophosphate (3 parts), and acetone (3 parts) is applied as a coating 8 μ m thick on tinplate. The coating is irradiated using a medium pressure mercury arc lamp (80 W per cm) at a distance of 20 cm and then heated in an oven at 120°C. Irradiation for 30 seconds followed by heating for 10 minutes produces a hard, tack-free film.

EXAMPLE 16

The procedure of Example 15 is repeated, replacing the hexafluorophosphate with π -hexyloxybenzenetricarbonylmanganese hexafluorophosphate (3 parts). Irradiation of the coating for 30 seconds followed by heating for 3 minutes produces a tack-free film.

EXAMPLE 17

The procedure of Example 15 is repeated, replacing the hexafluorophosphate with π -hexylbenzenetricarbonylmanganese hexafluorophosphate (3 parts). Irradiation of the coating for 20 seconds followed by heating for 1 minute gives a tack-free film.

EXAMPLE 18

The procedure of Example 15 is repeated using a mixture of Epoxide Resin I (50 parts), Epoxide Resin II (30 parts), Epoxide Resin IV (20 parts), π -hexylbenzenetricarbonylmanganese hexafluorophosphate (3 parts) and acetone (3 parts) in place of the mixture used in Example 15. Irradiation of the coating for 10 seconds followed by heating for 1 minute gives a hard tack-free film.

EXAMPLE 19

The procedure of Example 18 is repeated, replacing the hexafluorophosphate with an equal weight of π -hexyloxybenzenetricarbonylmanganese hexafluorophosphate. Irradiation for 10 seconds followed by heating for 2 minutes produces a hard, tack-free film.

EXAMPLE 20

The procedure of Example 18 is repeated, replacing the hexafluorophosphate with an equal amount of π -methoxybenzenetricarbonylmanganese hexafluorophosphate. Irradiation for 10 seconds followed by heating for 2 minutes produces a tack-free film.

EXAMPLE 21

A mixture of Epoxide Resin V (60 parts), Epoxide Resin II (40 parts), π -methoxybenzenetricarbonylmanganese hexafluorophosphate (3 parts) and acetone (5 parts) is applied as a coating 8 μ m thick on tinplate. The coating is irradiated using a medium pressure mercury lamp (80 W per cm) at a distance of 20 cm and then heated in an oven at 100°C. Irradiation for 20 seconds followed by heating for 3 minutes results in a tack-free film.

EXAMPLE 22

Example 21 is repeated, replacing the hexafluorophosphate with an equal weight of π -hexyloxybenzenetricarbonylmanganese hexafluorophosphate. Irradiation for 20 seconds followed by heating for 35 seconds results in a tack-free film.

EXAMPLE 23

The procedure of Example 21 is repeated, replacing the hexafluorophosphate with an equal weight of π -hexylbenzenetricarbonylmanganese hexafluorophosphate. Irradiation for 20 seconds followed by heating for 1 minute produces a hard, tack-free film.

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CLAIMS

1. A polymerisable composition containing
- (a) a compound, or a mixture of such compounds containing at least one 1,2-epoxide group, and
- (b) an effective amount of a salt of the formula



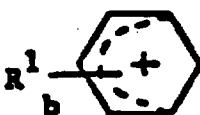
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where

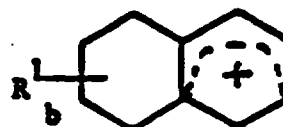
- Y represents an arene group or a cyclic dienylium group
- Q represents an atom of a d-block transition metal chosen from titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, niobium, molybdenum, ruthenium, rhodium, palladium, silver, tantalum, tungsten, rhenium, osmium, iridium, platinum, and gold,
- a is a positive integer such that the atom Q has a closed electron shell configuration,
- M represents an atom of a metal or metalloid,
- n is 4, 5, or 6, and is one more than the valency of M, and
- X represents a fluorine or chlorine atom, with the proviso that if M represents antimony, n is 6, and five of the symbols X represent fluorine, and one may also represent a hydroxo group.
2. A composition according to claim 1, wherein Y represents an arene hydrogen group which is optionally substituted by one or more alkoxy groups.
3. A composition according to claim 1, wherein Y denotes a cyclic dienylium group of one of the following formulae



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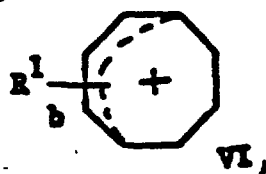
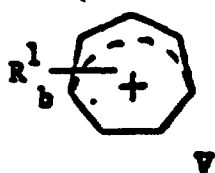
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where

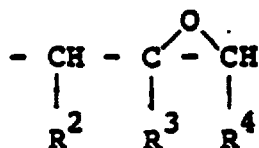
R^1 denotes an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, or an alkyl group interrupted by one or more oxycarbonyl groups and containing up to 12 carbon atoms, and

b is zero, 1, 2, or 3.

4. A composition according to claim 1, in which Q represents chromium, cobalt, nickel, iron, or manganese.

5. A composition according to claim 1, in which M represents antimony, arsenic, boron, or phosphorus.

6. A composition according to claim 1, wherein (a) is an epoxide resin containing more than one terminal group of formula



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directly attached to an atom of oxygen, where either R^2 and R^4 each represent a hydrogen atom, in which case R^3 denotes a hydrogen atom or a methyl group, or R^2 and R^4 together represent $-\text{CH}_2\text{CH}_2-$, in which case R^3 denotes a hydrogen atom.

7. A composition according to claim 6, wherein Y in formula I denotes an arene group and (a) is an epoxide resin wherein the 1,2-epoxide group is directly attached to cycloaliphatic carbon atoms.

8. A composition according to claim 6 or 7, which also contains a latent heat-curing agent for the epoxide resin.

9. A composition according to claim 1, containing from 0.5 to 7.5 parts by weight of (b) per 100 parts by weight of (a).

10. A composition according to claim 1, which also contains a photoaccelerator.

11. A composition according to claim 1, which contains the diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane (epoxide content 5.2 equiv./kg) and tricarbonyl (2-methoxy-bicyclo[4.4.0]deca-2,4-dienylium)iron hexafluorophosphate.

12. A process for the transformation into higher-molecular weight material of a compound containing at least one 1,2-epoxide resin group, or a mixture of such compounds, comprising subjecting a composition

according to claim 1 to actinic radiation.

13. A process according to claim 12, wherein a) an epoxide resin is irradiated, in the presence of an amount of a compound of formula I effective for the polymerisation of an epoxide resin and of a curing amount of a latent heat-curing agent for the epoxide resin, to form a partially cured B-stage product and, if desired, b) curing of the composition is completed by heating.

14. The use of the composition according to claim 1, as surface coatings, in printing plates, in printed circuits, in reinforced composites and as adhesives.

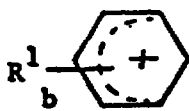


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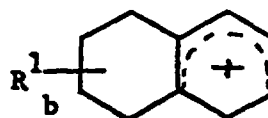
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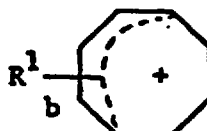
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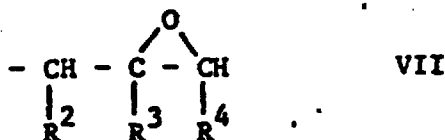
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where
 R¹ denotes an alkyl group of 1 to 4 carbon atoms, an alkoxy group of 1 to 4 carbon atoms, or an alkyl group interrupted by one or more oxycarbonyl groups and containing up to 12 carbon atoms, and
 b is zero, 1, 2; or 3.

4. A composition according to claim 1, wherein Q represents chromium, cobalt, nickel, iron, or manganese.

5. A composition according to claim 1, wherein M represents antimony, arsenic, boron, or phosphorus.

6. A composition according to claim 1, wherein (a) is an epoxide resin containing more than one group of formula



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directly attached to an atom of oxygen, where either R² and R⁴ each represent a hydrogen atom, in which case R³ denotes a hydrogen atom or a methyl group, or R² and R⁴ together represent -CH₂CH₂-, in which case R₃ denotes a hydrogen atom.

7. A composition according to claim 1, wherein Y in formula 1 denotes an arene group and (a) is an epoxide resin having 1,2-epoxide groups directly linked to cycloaliphatic carbon atoms.

8. A composition according to either of claims 6 or 7, which also contains a latent heat-curing agent for the epoxide resin.

9. A composition according to claim 1, containing from 0.5 to 7.5 parts by weight of (b) per 100 parts by weight of (a).

10. A composition according to claim 1, which also contains a photoaccelerator.

11. A composition according to claim 1, which contains the diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane (epoxide content 5.2 val/kg) and tricarbonyl-(2-methoxybicyclo[4.4.0]deca-2,4-dienylium)iron hexafluorophosphate.

12. A Process for converting a compound containing at least one 1,2-epoxide resin group, or a mixture of such compounds, into high molecular material, which comprises exposing a composition as claimed in claim 1 to actinic radiation.

13. A process according to claim 12, which comprises

a) irradiating an epoxide resin in the presence of a compound of formula 1 in an amount sufficient to polymeric the epoxide resin, and of a latent heat curing agent for the epoxide resin in an amount sufficient to form a partially cured β-stage product, and, if desired,

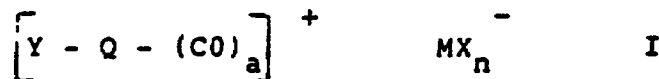
b) curing the composition by heating.

14. Use of a composition as claimed in claim 1 as surface coating, in printing plates, in printed circuits, in reinforced composites, and as adhesive.



Revendications

1. Compositions polymérisables contenant a) un composé contenant au moins un groupe époxyde-1,2 ou un mélange de tels composés et b) une quantité efficace d'un sel de formule



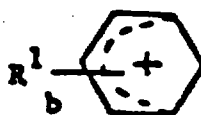
dans laquelle Y représente un groupe arène ou un groupe diénylium cyclique, Q représente un atome d'un métal de transition d choisi parmi le titane, le vanadium, le chrome, le manganèse, le fer, le cobalt, le nickel, le cuivre; le niobium, le molybdène, le ruthénium, le rhodium, le palladium, l'argent; le tantale, le tungstène, le rhénium, l'osmium, l'iridium, le platine et l'or, a est un nombre entier positif tel que l'atome Q présente une configuration de la couche électronique complète, M représente un atome de métal ou de métalloïde, n est 4, 5 ou 6 et est supérieur de 1 à la valence de M et X est un atome de fluor ou de chlore, sous réserve que, lorsque M représente de l'antimoine, n est 6, cinq des symboles X sont du fluor et l'un peut également représenter un groupe hydroxo.

2. Compositions selon la revendication 1, dans lesquelles Y représente un groupe hydrocarboné arène, éventuellement substitué par un ou plusieurs groupes alcoxy.

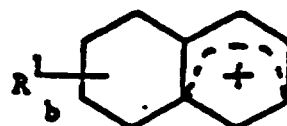
3. Compositions selon la revendication 1, dans lesquelles Y représente un groupe diénylium cyclique répondant à l'une des formules suivantes:



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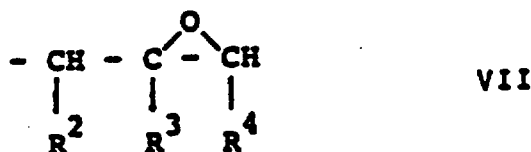
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ou R¹ représente un groupe alkyle avec 1 à 4 atomes de carbone, un groupe alcoxy avec 1 à 4 atomes de carbone ou un groupe alkyle possédant jusqu'à 12 atomes de carbone interrompu par un ou plusieurs groupes oxycarbonyles et b est 0, 1, 2 ou 3.

4. Compositions selon la revendication 1, dans lesquelles Q représente le chrome, le cobalt, le nickel, le fer ou le manganèse.

5. Compositions selon la revendication 1, dans lesquelles M est l'antimoine, l'arsenic, le bore ou le phosphore.

6. Compositions selon la revendication 1, dans lesquelles (a) est une résine époxyde comportant plus d'un groupe terminal directement lié à un atome d'oxygène, de formule



dans laquelle R² et R⁴ sont chacun un atome d'hydrogène, auquel cas R³ représente alors un atome d'hydrogène ou un groupe méthyle, ou R² et R⁴ représentent ensemble -CH₂CH₂-, auquel cas R³ représente alors un atome d'hydrogène.

7. Compositions selon la revendication 6, dans lesquelles Y dans la formule I représente un groupe arène et est présent sous forme (a) d'une résine époxyde comportant un groupe époxy-1,2 directement lié à des atomes de carbone cycloaliphatiques.

8. Compositions selon la revendication 6 ou 7, renfermant en outre un durcisseur thermique latent pour la résine époxyde.

9. Compositions selon la revendication 1, contenant 0,5 à 7,5 parties en poids de (b) pour 100 parties en poids de (a).

10. Compositions selon la revendication 1, contenant en outre un photo-accélérateur.

11. Compositions selon la revendication 1, contenant l'éther diglycidique du bis-(hydroxy-4 phényl)-2,2 propane (teneur en époxy 5,2 val/kg) et de l'hexafluorophosphate de tri-carbonyl-(méthoxy-2 bicyclo[4,4,0]décadiène-2,4 ylium)fer.

12. Procédé de conversion d'un composé renfermant au moins un groupe époxy-1,2 ou d'un mélange de tel composés en un matière de poids moléculaire supérieur, caractérisé en ce qu'on expose une composition selon la revendication 1 à un rayonnement actinique.

13. Procédé selon la revendication 12, caractérisé en ce que

a) on irradie une résine époxyde en présence d'une quantité d'un composé de formule I efficace pour la polymérisation de la résine époxyde et d'une quantité durcissante d'un durcisseur thermique latent pour la résine époxyde en vue de la formation d'un produit partiellement durci correspondant au stade B et

b) on durcit éventuellement la composition par chauffage.

14. Utilisation des compositions selon la revendication 1 comme revêtement de surface, dans des plaques d'impression, des circuits imprimés, des composites renforcés et comme adhésifs.

