



G00002

03 OCT 2002

- 1 -



166166

Heavy metal-free coating formulations

The present invention relates to heavy metal-free UV-curable, cationically polymerisable compositions and to their use.

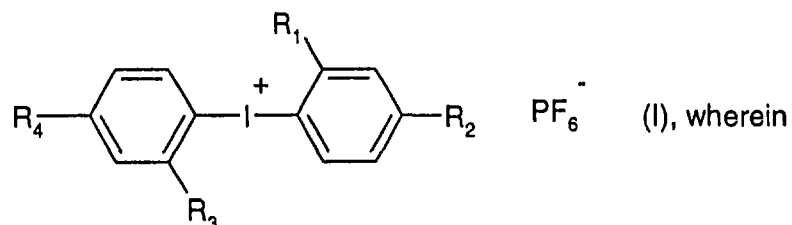
In J. of Photopolym. Sci. and Techn., Vol. 5 (1992), p. 247-254, F. Hamazu et al. published investigations regarding the reactivity of sulfonium salts containing different anions. A curing process for cationically curable pigmented formulations is known from WO 98/02493. JP-A Sho 61-175921 describes back coatings for magnetic recording materials based on glycidyl ether formulations. US 4378277 discloses unpigmented photocurable formulations comprising glycidyl ether and a mixture of initiator compounds. US 4287228 describes glycidyl ether-containing compositions pigmented with titanium dioxide. WO 96/13538 discloses cationically polymerisable formulations using aryl iodonium salts as initiators and dicarbonyl compounds as sensitisers.

The technology has a demand for formulations which are radiation-curable, reactive, cationically curable, inexpensive, white and hardly yellowing, especially for use as coatings.

It has been found that the above requirements are fully met by a composition, which comprises

- (a) mono-, bis- or higher aliphatic or aromatic glycidyl ethers,
- (b) titanium dioxide,
- (c) at least one iodonium hexafluorophosphate salt as photoinitiator, and
- (d) a sensitizer compound.

The photoinitiator (c) is, for example, a compound of formula I



R₁, R₂, R₃ and R₄ are each independently of one another hydrogen, C₁-C₂₀alkyl or unsubstituted or hydroxyl-substituted C₁-C₂₀alkoxy, with the proviso that at least one of R₁, R₂, R₃ or R₄ is not hydrogen.

- 2 -

C₁-C₂₀Alkyl is linear or branched and is, for example, C₁-C₁₂-, C₁-C₈-, C₁-C₆- or C₁-C₄alkyl. Examples are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, hexyl, heptyl, 2,4,4-trimethylpentyl, 2-ethylhexyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl or eicosyl. Branched alkyl is preferred, in particular C₃-C₈-, C₃-C₆- and C₃-C₄alkyl. R₂ and R₄ are, for example, C₁-C₁₂alkyl, C₁-C₈alkyl or C₁-C₆alkyl, preferably C₁-C₄alkyl, such as isobutyl, or C₁-C₁₂alkyl, such as dodecyl.

C₁-C₂₀Alkoxy is a linear or branched radical and is, for example, C₁-C₁₂-, C₁-C₈-, C₁-C₆- or C₁-C₄alkoxy. Examples are methoxy, ethoxy, propoxy, isopropoxy, n-butyloxy, sec-butyloxy, isobutyloxy, tert-butyloxy, pentyloxy, hexyloxy, heptyloxy, 2,4,4-trimethylpentyloxy, 2-ethylhexyloxy, octyloxy, nonyloxy, decyloxy, dodecyloxy, hexadecyloxy or octadecyloxy, preferably methoxy, ethoxy, propoxy, isopropoxy, n-butyloxy, sec-butyloxy, isobutyloxy, tert-butyloxy, more preferably methoxy. Preferred compounds are, for example, n-C₄-C₆-, n-C₁-C₆-, n-C₂-C₆-, n-C₁-C₄- n-C₂-C₄alkoxy. n-C₁₂-C₂₀Alkoxy is also interesting.

Compounds of formula I to be highlighted are those, wherein R₁, R₂, R₃ and R₄ are C₁-C₂₀alkyl, preferably C₁-C₁₂alkyl.

Other interesting compounds are those of formula I, wherein R₁, R₂, R₃ and R₄ are branched C₁-C₂₀alkyl, preferably branched C₁-C₁₂alkyl or branched C₁-C₄alkyl.

Preferred compounds of formula I are those, wherein R₂ and R₄ are C₁-C₂₀alkyl, and R₁ and R₃ are hydrogen.

Other interesting compounds of formula I are those, wherein R₂ and R₄ are identical.

Those compounds of formula I merit particular mention, wherein R₂ is C₁-C₁₂alkyl, preferably isobutyl or dodecyl, and R₁, R₃ and R₄ are hydrogen.

Other particularly preferred compounds of formula I are those, wherein R₂ and R₄ are C₁-C₁₂alkyl, such as isobutyl or dodecyl.

Preferred compounds of formula I are those, wherein R₂ is C₁-C₄alkyl if R₁, R₃ and R₄ are hydrogen.

Other preferred compounds of formula I are those wherein R_2 is C_1 - C_4 alkoxy if R_1 , R_2 and R_3 are hydrogen. Those compounds of formula I are also preferred wherein R_2 is C_{10} - C_{20} alkoxy if R_1 , R_2 and R_3 are hydrogen.

Examples of compounds of formula I are

bis(4-hexylphenyl)iodonium hexafluorophosphate; (4-hexylphenyl)phenyl iodonium hexafluorophosphate; bis(4-octylphenyl)iodonium hexafluorophosphate; (4-octylphenyl)phenyl iodonium hexafluorophosphate; bis(4-decylphenyl)iodonium hexafluorophosphate; (4-isobutylphenyl)phenyl iodonium hexafluorophosphate; bis(4-isobutylphenyl)iodonium hexafluorophosphate; (4-dodecylphenyl)phenyl iodonium hexafluorophosphate; (2-hydroxydodecyloxyphenyl)phenyl iodonium hexafluorophosphate; (2-hydroxytetradecyloxyphenyl)phenyl iodonium hexafluorophosphate.

This invention also relates to (4-isobutylphenyl)phenyl iodonium hexafluorophosphate, in particular dissolved in propylene carbonate.

In certain cases it may be advantageous to use mixtures of two or more of such iodonium salt photoinitiators in the compositions of this invention.

The preparation of the photoinitiator compounds of formula I is familiar to the skilled person and is described in the literature. Thus, compounds of formula I can be prepared, for example, by the process described in US patents 4399071 and 4329300 and in DE 2754853. The hexafluorophosphate salts can be prepared, for example, by exchanging the anions of the simple salts of the corresponding iodonium compounds (e.g. those of the bisulfates). These methods have been published, inter alia, by Beringer et al. in J. Am. Chem. Soc. 81, 342 (1959). This literature also describes different methods for the preparation of the above-mentioned simple salts, for example the reaction of two aromatic compounds with iodyl sulfate in sulfuric acid; the reaction of two aromatic compounds with iodate in acetic acid, acetic anhydride, sulfuric acid; the reaction of two aromatic compounds with iodine acylate in the presence of an acid, or the condensation of a iodosyl compound, of a iodosyl diacetate or of a iodoxy compound with another aromatic compound in the presence of an acid.

In some cases it is also possible to oxidise an aryl iodide *in situ* and to then condense it with another aromatic compound. This variant of the condensation proceeds, for example, in dilute sulfuric acid (EP 119 068).

In the compositions of this invention, the photoinitiator (c) is conveniently used in an amount from 0.05% to 15%, for example from 0.5% to 10%, preferably from 0.1% to 5%, based on the composition.

The glycidyl ether components (a) used in the novel formulations are typically glycidyl ethers of polyvalent phenols obtained by reacting polyvalent phenols with an excess of chlorohydrin, such as epichlorohydrin (e.g. glycidyl ether of 2,2-bis(2,3-epoxypropoxyphenol)propane. Other examples of glycidyl ether epoxides which can be used in connection with this invention are described, inter alia, in US 3018262 and in "Handbook of Epoxy Resins" by Lee and Neville, McGraw-Hill Book Co., New York (1967).

There are also numerous commercially available glycidyl ether epoxides which can be used as component (a), for example glycidyl methacrylate, diglycidyl ether of bisphenol A, e.g. those obtainable under the tradenames EPON 828, EPON 825, EPON 1004 and EPON 1010, of Shell; DER-331, DER-332 and DER-334, of Dow Chemical; 1,4-butanediol diglycidyl ether of phenolformaldehyde novolak, e.g. DEN-431, DEN-438, of Dow Chemical; and resorcinol diglycidyl ether; alkyl glycidyl ether, such as C₈-C₁₀glycidyl ether, e.g. HELOXY modifier 7, C₁₂-C₁₄glycidyl ether, e.g. HELOXY modifier 8, butyl glycidyl ether, e.g. HELOXY modifier 61, cresyl glycidyl ether, e.g. HELOXY modifier 62, p-tert-butylphenyl glycidyl ether, e.g. HELOXY modifier 65, polyfunctional glycidyl ethers, for example diglycidyl ether of 1,4-butanediol, e.g. HELOXY modifier 67, diglycidyl ether of neopentyl glycol, e.g. HELOXY modifier 68, diglycidyl ether of cyclohexanedimethanol, e.g. HELOXY modifier 107, trimethylol-ethane triglycidyl ether, e.g. HELOXY modifier 44, trimethylolpropane triglycidyl ether, e.g. HELOXY modifier 48, polyglycidyl ether of aliphatic polyols, e.g. HELOXY modifier 84 (all HELOXY glycidyl ethers are available from Shell).

Other suitable glycidyl ethers are those containing copolymers of acrylates, for example styrene glycidyl methacrylate or methyl methacrylate glycidyl acrylate. Examples are 1:1 styrene/glycidyl methacrylate, 1:1 methyl methacrylate/glycidyl acrylate, 62.5:24:13.5 methyl methacrylate/ethyl acrylate/glycidyl methacrylate.

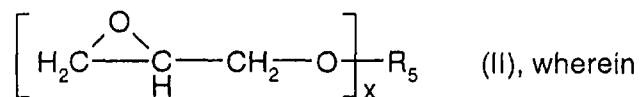
The polymers of the glycidyl ether compounds can, for example, also contain other functionalities, provided they do not impair the cationic cure.

Other glycidyl ether compounds suitable as component (a) and commercially available from Ciba Spezialitätenchemie are polyfunctional liquid and solid novolak glycidyl ether resins, for example PY 307, EPN 1179, EPN 1180, EPN 1182 and ECN 9699.

- 5 -

It is, of course, also possible to use mixtures of different glycidyl ether compounds as component (a).

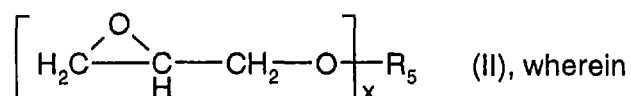
The glycidyl ethers (a) are, for example, compounds of formula II



x is a number from 1 to 6; and

R₅ is a monovalent to hexavalent alkyl or aryl radical.

The glycidyl ethers (a) are preferably e.g. compounds of formula II

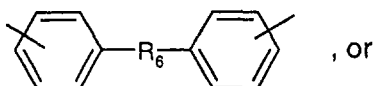


x is a number from 1, 2 or 3; and

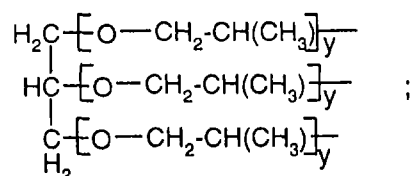
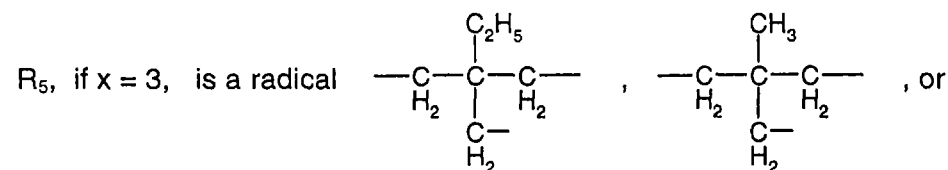
R₅, if x = 1, is unsubstituted or C₁-C₁₂alkyl-substituted phenyl, naphthyl, anthracyl, biphenyl-, C₁-C₂₀alkyl, or C₂-C₂₀alkyl which is interrupted by one or more than one oxygen atom, or

R₅, if x = 2, is 1,3-phenylene, 1,4-phenylene, C₆-C₁₀cycloalkylene, unsubstituted or halogen-substituted C₁-C₄₀alkylene; C₂-C₄₀alkylene which is interrupted by one or more than one

oxygen atom, or a group

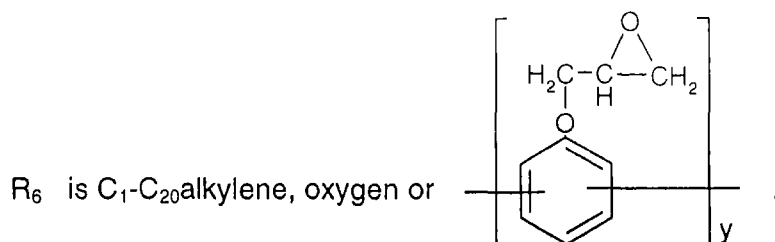


, or

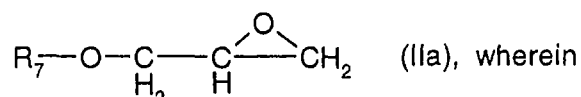


y is a number from 1 to 10; and

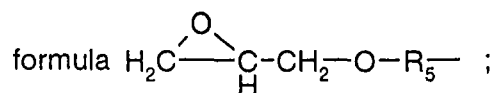
- 6 -



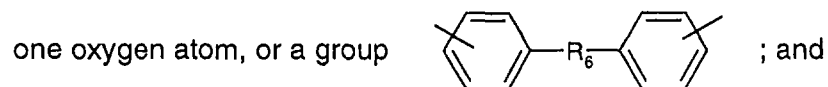
The glycidyl ethers (a) are, for example, compounds of formula IIa



R_7 is unsubstituted or C_1 - C_{12} alkyl-substituted phenyl; naphthyl; anthracyl; biphenyl; C_1 - C_{20} alkyl; C_2 - C_{20} alkyl which is interrupted by one or more than one oxygen atom; or a group of

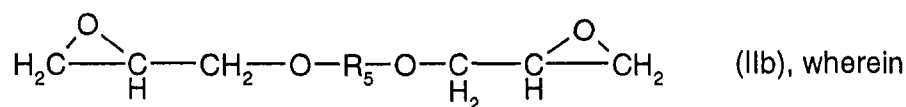


R_5 is phenylene, C_1 - C_{20} alkylene; C_2 - C_{20} alkylene which is interrupted by one or more than

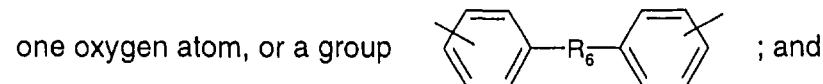


R_6 is C_1 - C_{20} alkylene or oxygen.

Preferred glycidyl ethers are the compounds of formula IIb



R_5 is phenylene, C_1 - C_{20} alkylene; C_2 - C_{20} alkylene which is interrupted by one or more than



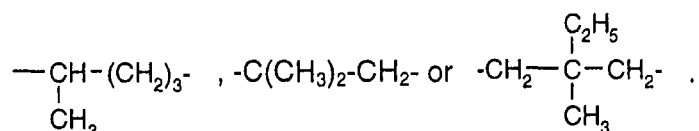
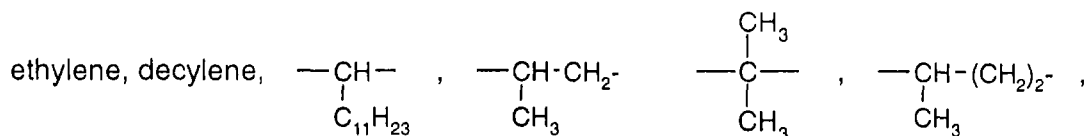
R_6 is C_1 - C_{20} alkylene or oxygen.

Alkyl radicals are, for example, C_1 - C_{20} alkyl, C_1 - C_{18} -, C_1 - C_{12} -, C_1 - C_{10} -, C_1 - C_8 -, C_1 - C_6 - or C_1 - C_4 alkyl. Meanings of these radicals are given above.

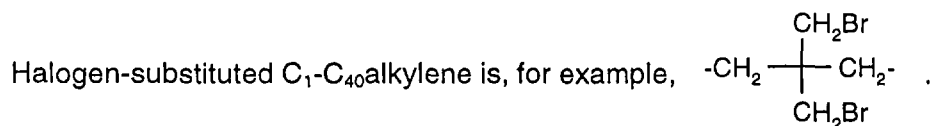
C_1 - C_{20} Alkylene is linear or branched and is, for example, C_1 - C_{18} -, C_1 - C_{16} -, C_1 - C_{14} -, C_1 - C_{12} -, C_1 - C_{10} -, C_1 - C_8 -, C_1 - C_6 -, C_2 - C_{12} -, C_2 - C_8 -, C_4 - C_8 - or C_1 - C_4 alkylene. Examples are methylene, ethylene, propylene, isopropylene, n-butylene, sec-butylene, isobutylene, tert-butylene,

- 7 -

pentylene, hexylene, heptylene, octylene, nonylene, decylene, dodecylene, tetradecylene, heptadecylene or octadecylene. C_1 - C_{20} Alkylene is preferably understood to mean e.g.

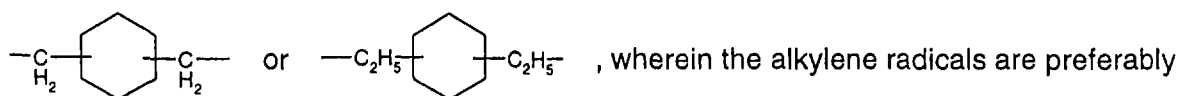


Halogen is fluoro, chloro and bromo, preferably bromo and chloro, most preferably bromo.



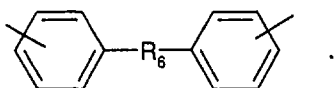
C_2 - C_{20} Alkylene which is interrupted by one or more than one oxygen atom is also linear or branched and is interrupted, for example, one to nine times, one to five times or once or twice by non-consecutive oxygen atoms. This gives structures such as $\text{---CH}_2\text{---O---CH}_2\text{---}$, $\text{---CH}_2\text{CH}_2\text{---O---CH}_2\text{CH}_2\text{---}$, $\text{---[CH}_2\text{CH}_2\text{O]}_y\text{---}$, where $y = 1-9$, $\text{---(CH}_2\text{CH}_2\text{O)}_7\text{CH}_2\text{CH}_2\text{---}$, or $\text{---CH}_2\text{---CH(CH}_3\text{)---O---CH}_2\text{---CH(CH}_3\text{)---}$.

C_6 - C_{10} Cycloalkylene is for example 1,4-, 1,3- or 1,6- cyclohexylene, or also

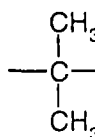


in 1,4-position.

R_5 is preferably a group



R_6 is preferably C_1 - C_{12} alkylene, more preferably



Other examples of component (a) are polyglycidyl ether and poly(β -methylglycidyl)ether which are obtainable by reacting a compound containing at least two free alcoholic and/or phenolic hydroxyl groups per molecule with the corresponding epichlorohydrin under alkaline conditions, or also in the presence of an acid catalyst with subsequent treatment with alkali. It is also possible to use mixtures of different polyols.

These ethers can be prepared with poly(epichlorohydrin) from acyclic alcohols, such as ethylene glycol, diethylene glycol and higher poly(oxyethylene)glycol, propane-1,2-diol and poly(oxypropylene)glycols, propane-1,3-diol, butane-1,4-diol, poly(oxytetramethylene)glycols, pentane-1,5-diol, hexane-1,6-diol, hexane-2,4,6-triol, glycerol, 1,1,1-trimethylolpropane, pentaerythritol and sorbitol, 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 containing aromatic nuclei, such as N,N-bis(2-hydroxyethyl)-aniline and p,p'-bis(2-hydroxyethylamino)diphenylmethane. It is also possible to prepare these ethers from mononuclear phenols, such as resorcinol and hydroquinone, and from polynuclear phenols, such as bis(4-hydroxyphenyl)methane, 4,4-dihydroxydiphenyl, bis(4-hydroxyphenyl)sulfone, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane.

Other suitable hydroxy compounds for the preparation of polyglycidyl ethers and poly(β -methylglycidyl)ethers are the novolaks obtainable by condensing aldehydes, such as formaldehyde, acetaldehyde, chloral and furfural, and phenols, such as phenol, o-cresol, m-cresol, p-cresol, 3,5-dimethylphenol, 4-chlorophenol and 4-tert-butylphenol.

Poly(N-glycidyl) compounds can be obtained, for example, by dehydrochlorinating the reaction products of epichlorohydrin with at least two amines containing active hydrogen bound to amino nitrogen atoms, for example aniline, n-butylamine, bis(4-aminophenyl)methane and bis(4-methylaminophenyl)methane. Other suitable poly(N-glycidyl) compounds are triglycidyl isocyanurate and N,N'-diglycidyl derivatives of cyclic alkylene ureas, such as ethylene urea and 1,3-propylene urea, and hydantoins, for example 5,5-dimethylhydantoin.

Poly(S-glycidyl) compounds are also suitable. Examples are the di-S-glycidyl derivatives of dithiols, such as ethane-1,2-dithiol and bis(4-mercaptomethylphenyl)ether.

Other suitable components (a) are also epoxy resins in which the glycidyl groups or β -methylglycidyl groups are bound to different kinds of heteroatoms, e.g. the N,N,O-triglycidyl de-

rivative of 4-aminophenol, the glycidyl ether/glycidyl ester of salicylic acid or p-hydroxybenzoic acid, N-glycidyl-N'-(2-glycidyloxypropyl)-5,5-dimethylhydantoin and 2-glycidyloxy-1,3-bis-(5,5-dimethyl-1-glycidylhydantoinyl-3)propane.

The diglycidyl ethers of bisphenols are preferred. Examples thereof are diglycidyl ethers of bisphenol A, such as ARALDIT GY 250, of Ciba Spezialitätenchemie, diglycidyl ether of bisphenol F and diglycidyl ether of bisphenol S. Diglycidyl ether of bisphenol A is particularly preferred.

If desired, the composition can also contain a free-radically polymerisable material, including ethylenically unsaturated monomers, oligomers or polymers. Suitable materials contain at least one ethylenically unsaturated double bond, and are capable of undergoing addition polymerisation. Such free-radically polymerisable materials include mono-, di- or polyacrylates and mono-, di- or polymethacrylates such as methylacrylate, methyl methacrylate, ethylacrylate, isopropyl methacrylate, n-hexylacrylate, stearylacrylate, allylacrylate, glycerol diacrylate, glycerol triacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol dimethacrylate, 1,3-propanedioldiacrylate, 1,3-propanediol dimethacrylate, trimethylolpropanetriacrylate, 1,2,4-butanetrioltrimethacrylate, 1,4-cyclohexanedioldiacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyldimethylmethane, and tris-hydroxyethylisocyanurate trimethacrylate; the bisacrylates and bismethacrylates of polyethylene glycols having a molecular weight of 200-500, copolymerisable mixtures of acrylated monomers; and vinyl compounds such as styrene, diallyl phthalate, divinyl succinate, divinyl adipate and divinyl phthalate. Mixtures of two or more of these free-radically polymerisable materials can be used, if desired.

If free-radically polymerisable components are added to the novel formulation, then it is useful to also add one, or a mixture of, corresponding radical photoinitiator(s), for example benzophenone and benzophenone derivatives, acetophenone and acetophenone derivatives, such as α -hydroxycyclohexylphenylketone or 2-hydroxy-2-methyl-1-phenylpropanone, α -hydroxy- or α -aminoacetophenone, such as (4-methylthiobenzoyl)-1-methyl-1-morpholinoethane, (4-morpholinobenzoyl)-1-benzyl-1-dimethylaminopropane, 4-aroxy-1,3-dioxolanes, benzoinalkyl ether and benzilketal, such as benzildimethylketal, phenylglyoxalate and phe-

nylglyoxalate derivatives, mono- or bisacylphosphine oxide, such as (2,4,6-trimethylbenzoyl)-phenylphosphine oxide, bis(2,6-dimethoxybenzoyl)-(2,4,4-trimethylpent-1-yl)phosphine oxide, bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide or bis(2,4,6-trimethylbenzoyl)-(2,4-dipentoxyphenyl)phosphine oxide.

The novel compositions can also contain vinyl ether monomers such as cyclohexanedimethanol divinyl ether or hydroxybutyl vinyl ether.

Other additional components may be, for example, hydroxy-functional components such as alcohols, polyester polyols, polyether polyols, castor oil and the like. Examples are aliphatic and cycloaliphatic polyols such as alkylene diols containing preferably 2 to 12 carbon atoms, e.g. ethylene glycol, 1,2- or 1,3-propanediol, 1,2-, 1,3- or 1,4-butanediol, pentanediol, hexanediol, octanediol, dodecanediol, diethylene glycol, triethylene glycol, polyethylene glycols having molecular weights from preferably 200 to 1500, 1,3-cyclopentanediol, 1,2-, 1,3- or 1,4-cyclohexanediol, 1,4-dihydroxymethylcyclohexane, glycerol, tris(β -hydroxyethyl)amine, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol and sorbitol. The polyols can be partially or completely esterified with one or different unsaturated carboxylic acids, it being possible for the free hydroxyl groups in partial esters to be modified, for example etherified or esterified, with other carboxylic acids. Examples of esters are: trimethylolpropanetriacrylate, trimethylolethanetriacrylate, trimethylolpropanetrimethacrylate, trimethylolethanetrimethacrylate, tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol diacrylate, dipentaerythritol triacrylate, dipentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, tripentaerythritol octaacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, dipentaerythritol dimethacrylate, dipentaerythritol tetramethacrylate, tripentaerythritol octamethacrylate, pentaerythritol diitaconate, dipentaerythritol trisitaconate, dipentaerythritol penta-itaconate, dipentaerythritol hexaitaconate, ethylene glycol diacrylate, 1,3-butanedioldiacrylate, 1,3-butanedioldimethacrylate, 1,4-butanedioldiitaconate, sorbitol triacrylate, sorbitol tetraacrylate, pentaerythritol-modified triacrylate, sorbitol tetramethacrylate, sorbitol pentaacrylate, sorbitol hexaacrylate, oligoester acrylate and oligoester methacrylate, glycerol di- and -triacrylate, 1,4-cyclohexanediacylate, bisacrylates and bismethacrylates of polyethylene glycol having a molecular weight of 200 to 1500, or mixtures thereof.

Components (a) of particular interest are pure glycidyl ether formulations, i.e. mixtures consisting only of one or several different glycidyl ether compounds.

The titanium dioxide pigment (b) can be added to the novel compositions in a very wide range of forms. Thus, it can be incorporated, for example, in the form of fine particles or powders. The particle size is usefully from 100 to 400 nm, but is not restricted to these sizes. The titanium dioxide pigments used are preferably surface-treated, for example with stabilisers, to increase their dispersibility. Such stabiliser components are usually oxides or hydrated oxides of silicon, magnesium or aluminium, or amines or other organic compounds. Examples thereof are cited in US 4054498. Although the titanium dioxide can be present in different crystalline forms, it is preferred to use the rutile form which is also commercially available.

The amount of titanium dioxide component (b) in the polymerisable composition can vary within a wide range, depending on the desired opacity, for example from 5% to 60%, typically from 20 % to 55%, preferably from 40 % to 50%, based on the composition.

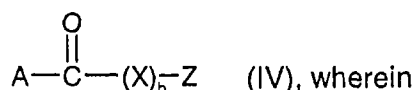
In order to improve the dispersion of the pigment in the formulation to be polymerised, it is possible, for example, to first predisperse the pigment in part of the formulation and then to incorporate this dispersion into the remainder of the formulation.

Suitable sensitizer compounds (d) are, for example, compounds from the class of the aromatic hydrocarbons, such as anthracene and its derivatives, from the group of the xanthenes and their derivatives, benzophenones and their derivatives, for example Michler's ketone, Mannich bases or bis(p-N,N-dimethylaminobenzylidene)acetone. Other suitable compounds are thioxanthone and its derivatives, such as isopropylthioxanthone, or dyes, such as acridines, triarylmethanes, e.g. malachite green, indolines, thiazines, e.g. methylene blue, oxazines, phenazines, e.g. safranin, or rhodamines. Particularly suitable compounds are aromatic carbonyl compounds, such as the benzophenone, thioxanthone, anthraquinone and 3-acylcoumarine derivatives, and also 3-(arylmethylene)thiazolines, as well as eosine, rhodamine and erythrosine dyes.

The sensitizer compound should be soluble in the photopolymerisable composition and should be free of functional groups which crucially influence the cationic crosslinking process. The light absorption of the compounds should furthermore be in the range of about 300 to 1000 nm.

Suitable sensitisers are (as mentioned above to some extent) compounds of the following classes: ketones, coumarines (e.g. ketocoumarine), xanthenes, acridines, thiazole dyes, thiazine dyes, oxazine dyes, azine dyes, aminoketone dyes, porphyrines, aromatic polycyclic hydrogens, p-substituted aminostyryl ketone compounds, aminotriarylmethanes, merocyanines, squarylium dyes and pyridinium dyes. Preferred compounds are ketones (e.g. monoketone or α -diketone), ketocoumarines, aminoarylketones and p-substituted aminostyryl ketone compounds. For applications requiring a deep cure (e.g. curing of highly filled composite materials), it is preferred to use sensitisers having an extinction coefficient of less than about $1000 \text{ l mol}^{-1} \text{ cm}^{-1}$, preferably of less than about $100 \text{ l mol}^{-1} \text{ cm}^{-1}$, at the desired radiation wavelength for the photopolymerisation. The α -diketones are one example of a class of sensitisers possessing these properties.

Suitable ketone sensitisers are, for example, those of formula IV



X is CO or CR_aR_b ,

R_a and R_b are each independently of the other hydrogen, alkyl, alkaryl, or aralkyl;

b is 1 or 2; and

A and Z are each independently of the other aryl, alkyl, alkaryl or aralkyl, which groups are unsubstituted or substituted, or A and Z together form a ring which is substituted or unsubstituted, cycloaliphatic, aromatic or heteroaromatic.

Suitable ketones of this formula are, for example, monoketones ($b=0$) such as 2,2-, 4,4- or 2,4-dihydroxybenzophenone, dipyridylketone, difuranylketone, dithiophenylketone, benzoin, fluorenone, chalcone, Michler's ketone, thioxanthone, isopropylthioxanthone, 2-fluoro-9-fluorenone, 2-chlorothioxanthone, acetophenone, benzophenone, 1- or 2-acetonaphthone, 9-acetylanthracene, 2-, 3- or 9-acetylphenanthrene, 4-acetylbiphenyl, propiophenone, n-butyrophenone, valerophenone, 2-, 3- or 4-acetylpyridine, 3-acetylcoumarine and the like. Suitable diketones include aralkyldiketones such as anthraquinone, phenanthrenequinone, o-, m- and p-diacetylbenzene, 1,3-, 1,4-, 1,5-, 1,6-, 1,7- and 1,8-diacetylnaphthalene, 1,5-, 1,8- and 9,10-diacetylanthracene and the like. Suitable diketones ($b=1$ and $\text{X}=\text{CO}$) include 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, 3,4-hexanedione, 2,3-heptanedione, 3,4-heptanedione, 2,3-octanedione, 4,5-octanedione, benzile, 2,2'-, 3,3'- and 4,4'-dihydroxybenzile, furile, di-3,3'-indolyethanedione, 2,3-bornanedione (camphorquinone), biacetyl, 1,2-cyclohexanedione, 1,2-naphthaquinone, acenaphthaquinone and the like.

Preferred sensitisers are those of the group of the anthracenes, xanthenes, benzophenones and thioxanthenes, also including the derivatives of these compounds. Thioxanthenes are particularly preferred, in particular isopropylthioxanthone.

The sensitizer compound (d) is usefully added to the novel compositions in an amount from 0.1%-3%, e.g. from 0.2%-1.5%, preferably from 0.4%-1.0%.

The novel composition conveniently comprises 40-70% of the glycidyl ether component (a), 20-60% of the titanium dioxide (b), 0.5-10% of the photoinitiator (c) and 0.1-3% of the sensitizer compound (d).

Other additives may be added to the novel compositions besides components (a), (b), (c) and (d). Examples thereof are light stabilisers, for example UV absorbers such as those of the hydroxyphenylbenztriazole, hydroxyphenylbenzophenone, oxalic acid amide or hydroxyphenyl-s-triazine type. These compounds can be used separately or as mixtures, with or without addition of sterically hindered amines (HALS).

The novel compositions can contain as additional additive, inter alia, an electron-donor compound. Examples of such compounds are described in US 5545676. Examples are alkyl-aromatic polyethers or alkyl-aryl-amino compounds, wherein the aryl group is substituted by one or several electron-attracting group(s). Examples thereof are 4-dimethylaminobenzoic acid, ethyl 4-dimethylaminobenzoate, 3-dimethylaminobenzoic acid, 4-dimethylaminobenzoic acid, 4-dimethylaminobenzoin, 4-dimethylaminobenzaldehyde, 4-dimethylaminobenzonitrile and 1,2,4-trimethoxybenzene.

Other customary additives are - depending on the end use requirements - fluorescent whitening agents, fillers, dyes, wetting agents or flow control agents. The novel compositions may contain as further additives dispersants, emulsifiers, antioxidants, light stabilisers, dyes, pigments, fillers, e.g. talcum, gypsum, silicic acid, rutile, carbon black, zinc oxide, iron oxides, reaction accelerators, flow control agents, wetting agents, thickeners, flattening agents, antifoams, antioxidants and other auxiliaries customarily used in the paint system technology. Suitable dispersants are, for example, high molecular weight organic compounds containing polar groups, such as polyvinyl alcohols, polyvinyl pyrrolidone or cellulose ether. Suitable emulsifiers are non-ionic or ionic emulsifiers.

The choice of the additives depends on the respective field of applications and on the properties desired in this field. The additives are standard in the technology and are thus used in amounts known to the skilled person.

The novel compositions can be used in different fields, for example in coating materials, laminating adhesives, in printing inks, white enamel formulations, for example for wood or metal, or in paints used, *inter alia*, for paper, wood, metal or plastic materials.

The compositions of this invention can be used to coat or bond substrates of all kinds, for example wood, textiles, paper, ceramics, glass, plastic materials, such as polyester, polyethylene terephthalate, polyolefins or cellulose acetate, in particular in the form of films, and metals such as Al, Cu, Ni, Fe, Zn, Mg or Co and GaAs, Si or SiO₂ to which a protective coating is to be applied.

The substrates can be coated by applying a liquid composition, a solution or suspension to the substrate. The choice of solvent used and its concentration depends mainly on the type of composition and on the coating process used. The solvent should be inert, i.e. it should not chemically react with the components and should be removable during drying after coating. Suitable solvents are, for example, ketones, ethers and esters, such as methyl ethyl ketone, isobutyl methyl ketone, cyclopentanone, cyclohexanone, N-methylpyrrolidone, dioxane, tetrahydrofuran, 2-methoxyethanol, 2-ethoxyethanol, 1-methoxy-2-propanol, 1,2-dimethoxyethane, ethyl acetate, n-butyl acetate and ethyl 3-ethoxypropionate.

The formulation is uniformly applied to a substrate by known coating processes, for example centrifuging, dipping, knife application, curtain coating, brush application, screen printing, spraying, especially by electrostatic spraying and reverse roll coating.

The coating thickness and type of substrate depend on the desired field of application, The coating thickness is generally within the range from about 0.1 µm to higher than 100 µm, e.g. from 1 µm to 30 µm, preferably from 4 µm to 20 µm.

An other field in which the novel composition may be used is metal coating, for example coating metal sheets and tubes, tins or bottle caps. The metals to be coated can be uncoated or precoated. Suitable substrates are especially metals, such as aluminium or tinplate.

The novel white compositions are distinguished by having very good resistance to yellowing. Another advantage is that the heavy metal anions normally used in the technology, for example SbF_6 anions, are not present in these compounds.

The novel formulations are cured by irradiation with light in the wavelength of 200-600 nm. Where necessary, the formulation can be subjected to a heat treatment after irradiation. The thermal aftertreatment is conveniently carried out in the temperature range from 50-250°C, e.g. from 100-220°C, preferably from 150-210°C.

Accordingly, this invention also relates to a process for the polymerisation of compositions described above, which comprises irradiating the composition with light in the wavelength of 200-600 nm, and to a corresponding process in which the irradiation is followed by a heat treatment.

The UV irradiation for curing the novel formulation is usually carried out using light in the wavelength from 200-600 nm. Suitable radiation comprises, for example, sunlight or light from artificial light sources. A large number of widely different types of light sources can be used, including point sources and arrays of reflector lamps. Examples are: carbon arc lamps, xenon arc lamps, mercury medium, high and low pressure lamps which are doped, where required, with metal halides (metal halogen lamps), microwave-excited metal vapour lamps, excimer lamps, superactinic fluorescent tubes, fluorescent lamps, argon glow lamps, flash lamps, photographic floodlights, electron beams and X-rays. Examples of suitable lamps are fusion lamps, such as fusion H (main emissions: mercury medium pressure spectrum), fusion D (main emissions: 350-450 nm), fusion V (main emissions: 400-450 nm) or fusion M (main emissions: 360-370 nm and 400-410 nm). The distance between lamp and substrate to be irradiated can vary depending on the purpose of application and type or strength of lamp, for example from 2 cm to 150 cm. Other suitable lamps are laser light sources, for example excimer laser. It is also possible to use lasers in the visible range. Irradiation using fusion lamps, e.g. fusion H, fusion D, fusion V or fusion M, is particularly interesting.

This invention also relates to the use of the above compositions and to a process for the preparation of coatings, paints, printing inks, powder coatings, laminating adhesives, dental compositions, in particular white enamel formulations.

In another of its aspects, this invention relates to a coated substrate which is coated on at least one surface with one of the above compositions, and to a coated substrate to which the novel composition is applied at a coating thickness of at least 0.1-100 μm , e.g. 1-30 μm , preferably 4-15 μm .

The following Examples illustrate the invention in more detail. As in the remainder of the description and in the patent claims, parts and percentages are by weight, unless otherwise stated. If alkyl radicals or alkoxy radicals containing more than three carbon atoms are given without their isomeric form, then they refer to the respective n-isomers.

Example 1: Preparation of p-isobutylphenylphenyl iodonium hexafluorophosphate

A 1.5 l flask, equipped with reflux condenser, thermometer, stirrer and nitrogen inlet, is charged with 400 g (1.24 mol) of (diacetoxyiodo)benzene in 800 ml of acetic acid and, after heating to 40°C, 365.6 g (1.92 mol) of p-toluenesulfonic acid are added in portions over 3 h. The reaction mixture is stirred overnight at 40°C, cooled to room temperature and filtered. The filter cake is washed with water and dried at 60°C under high vacuum, giving 372.4 g of hydroxy(tosyloxy)iodobenzene.

In a 750 ml flask, equipped with reflux condenser, thermometer, stirrer and nitrogen inlet, 157 g (0.4 mol) of hydroxy(tosyloxy)iodobenzene and 67.15 g (0.5 mol) of isobutylbenzene are heated in a mixture of 12 ml of acetic acid and 40 ml of acetonitrile for 48 hours to 85°C. After cooling the reaction mixture to room temperature, 500 ml of water are added and the mixture is extracted with dichloromethane. After drying the organic phases with magnesium sulfate and filtration, the solvent is removed under vacuum. A solid is precipitated by treatment with hexane. Filtration gives 131.2 g of 4-isobutylphenylphenyl iodonium tosylate as a beige solid.

In a 750 ml flask, equipped with reflux condenser, thermometer, stirrer and nitrogen inlet, 40.7 g (80 mmol) of 4-isobutylphenylphenyl iodonium tosylate and 29.5 g (160 mmol) of potassium hexafluorophosphate in 500 ml of acetone are refluxed overnight. The cooled suspension is filtered and the filtrate is concentrated under vacuum. 200 ml of dichloromethane are added and the solution is washed with water. After drying over magnesium sulfate and filtration, the solvent is stripped off under vacuum, giving 36.5 g of p-isobutylphenylphenyl iodonium hexafluorophosphate in the form of a colourless oil. The $^1\text{H-NMR}$ spectrum (measured in dimethylsulfoxide- d_6) exhibits displacement signals at the following

values [ppm]: 8.22 (4H, m, ArH), 7.64 (1H, m, ArH), 7.53 (2H, m, ArH), 7.34 (2H, m, ArH), 2.47 (2H, m, 2 CH₂), 1.82 (1H, m, CH(CH₃)₂), 0.82 (6H, d, J=6.2 Hz, 2 CH₃).

Elemental analysis C₁₆H₁₈F₆IP:

calculated	C 39.86%	H 3.76%	F 23.64%	I 26.32%	P 6.42%
found	C 40.14%	H 3.89%	F 23.63%	I 26.20%	P 6.28%

The compounds of the following Examples 2-6 are prepared in analogy to the method of Example 1 from the corresponding substituted aromatic compounds.

Example 2: (4-Hexylphenyl)phenyl iodonium hexafluorophosphate

Prepared from hexylbenzene. The title product is obtained as a brown oil. ¹H-NMR measured in CD₃CN [ppm]: 8.02 (4H, m, ArH), 7.71 (1H, m, ArH), 7.53 (2H, m, ArH), 7.36 (m, 2H, ArH), 2.65 (2H, t, J=7.7 Hz, ArCH₂), 1.55 (2H, m, CH₂), 1.28 (6H, m, (CH₂)₃), 0.85 (3H, t, J= 6.5Hz, CH₃). According to ¹H-NMR, the product contains about 8% of the 2-hexyl isomeric product.

Example 3: (4-Octylphenyl)phenyl iodonium hexafluorophosphate

Prepared from octylbenzene. The title product is obtained as a reddish oil. ¹H-NMR measured in CD₃CN [ppm]: 8.0 (4H, m, ArH), 7.70 (1H, m, ArH), 7.52 (2H, m, ArH), 7.36 (m, 2H, ArH), 2.65 (2H, t, J=7.7 Hz, ArCH₂), 1.57 (2H, m, CH₂), 1.25 (10H, m, (CH₂)₅), 0.85 (3H, t, J= 6.5Hz, CH₃). According to ¹H-NMR, the product contains about 8% of the 2-octyl isomeric product.

Example 4: (2,4-Dimethoxyphenyl)phenyl iodonium hexafluorophosphate

Prepared from 1,3-dimethoxybenzene. The title product is a solid having a melting point from 129-130°C. ¹H-NMR measured in DMSO-d₆ [ppm]: 8.19 (1H, d, J=8.8Hz H₆), 8.07 (2H, m, H_{2,6}), 7.63 (1H, m, H₄), 7.49 (2H, m, H_{3,5}), 6.80 (1H, m, H₃), 6.69 (1H, dd, J=8.8 and 2.1Hz, H₅), 3.94 (3H, s, OCH₃), 3.83 (3H, s, OCH₃).

Example 5: (2,4-Diethoxyphenyl)phenyl iodonium hexafluorophosphate

Prepared from 1,3-diethoxybenzene. The title product is a solid having a melting point of 158°C. ¹H-NMR measured in DMSO-d₆ [ppm]: 8.17 (1H, d, J=8.8Hz H₆), 8.05 (2H, m, H_{2,6}), 7.64 (1H, m, H₄), 7.50 (2H, m, H_{3,5}), 6.75 (1H, m, H₃), 6.66 (1H, dd, J=8.8 and 2.5Hz, H₅), 4.14 (4H, m, 2OCH₂), 1.33 (6H, m, 2CH₃).

Example 6: (2,4-Diisopropoxyphenyl)phenyl iodonium hexafluorophosphate

Prepared from 1,3-diisopropoxybenzene. The title product is a solid having a melting point of 125°C. ¹H-NMR measured in DMSO-d₆ [ppm]: 8.15 (1H, d, J=8.8Hz H₆), 8.03 (2H, m, H_{2'6'}), 7.63 (1H, m, H_{4'}), 7.50 (2H, m, H_{3'5'}), 6.73 (1H, m, H₃), 6.66 (1H, dd, J=8.8 and 2.2Hz, H₅), 4.78 (2H, m, 2OCH), 1.23 (12H, m, 4CH₃).

Example 7: Preparation of bis(p-isobutylphenyl)iodonium hexafluorophosphate

In a 6 l flask, equipped with reflux condenser, thermometer, stirrer and nitrogen inlet, 211.2 g (1.57 mol) of isobutylbenzene and 140.3 g (0.65 mol) of potassium iodate are cooled to 0°C in a mixture of 1850 ml of acetic acid and 525 ml of acetic anhydride. A mixture consisting of 385 ml of acetic acid and 310 ml of sulfuric acid is added dropwise. The mixture is stirred overnight at room temperature and 39.15 g of sodium bisulfate in 2000 ml of water are added. The solution is extracted with hexane and dichloromethane. The organic phases are dried over magnesium sulfate and filtered and the solvent is stripped off under vacuum, giving 304.9 g of bis(4-isobutylphenyl)iodonium bisulfate in the form of a brown oil.

In a 1.5 l flask, equipped with reflux condenser, thermometer, stirrer and nitrogen inlet, a mixture consisting of 152.4 g (0.31 mol) of bis(4-isobutylphenyl)iodonium bisulfate and 68.7 g (0.37 mol) of potassium hexafluorophosphate and 750 ml of water is stirred for 5 h. The solution is extracted with dichloromethane and the organic phases are then washed with water. Drying over magnesium sulfate, filtration and removal of the solvent by evaporation gives 107.4 g of bis(4-isobutylphenyl)iodonium hexafluorophosphate in the form of a brown resin. The ¹H-NMR spectrum (measured in CDCl₃) exhibits displacement signals at the following values [ppm]: 7.85 (4H, m, ArH), 7.20 (4H, m, ArH), 2.42 (4H, d, J=7.2 Hz, 2 CH₂), 1.79 (2H, m, 2 CH(CH₃)₂), 0.82 (12H, d, J=6.6 Hz, 4 CH₃).

The compounds of the following Examples 8-13 are prepared in analogy to the methods of Example 7 from the corresponding substituted aromatic compounds.

Example 8: Bis(4-butylphenyl)iodonium hexafluorophosphate

Prepared from n-butylbenzene. The title product is an orange resin. ¹H-NMR measured in CD₃CN [ppm]: 7.95 (4H, m, ArH), 7.35 (4H, m, ArH), 2.65 (4H, t, J=7.7 Hz, 2CH₂), 1.54 (4H, m, 2CH₂), 1.30 (4H, m, 2 CH₂), 0.89 (6H, t, J=7.2 Hz, 2CH₃).

Example 9: Bis(4-hexyl-phenyl)iodonium hexafluorophosphate

This is a resin prepared from hexylbenzene. ^1H -NMR measured in CD_3CN [ppm]: 7.94 (4H, m, ArH), 7.34 (4H, m, ArH), 2.64 (4H, t, $J=7.7$ Hz, 2CH_2), 1.56 (4H, m, 2CH_2), 1.27 (12H, m, 6CH_2), 0.85 (6H, t, $J=6.5$ Hz, 2CH_3).

Example 10: Bis(4-octylphenyl)iodonium hexafluorophosphate

This is a resin prepared from octylbenzene. ^1H -NMR measured in CD_3CN [ppm]: 7.95 (4H, m, ArH), 7.34 (4H, m, ArH), 2.64 (4H, t, $J=7.7$ Hz, 2CH_2), 1.56 (4H, m, 2CH_2), 1.26 (20H, m, 10CH_2), 0.85 (6H, t, $J=6.6$ Hz, 2CH_3).

Example 11: Bis(4-isopropylphenyl)iodonium hexafluorophosphate

Prepared from 4-isopropylphenol. ^1H -NMR signals measured in $\text{DMSO}-d_6$ [ppm]: 8.14 (4H, m, ArH), 7.40 (4H, m, ArH), 2.92 (2H, sept, $J=6.9$ Hz, 2CH), 1.16 (12H, d, $J=6.9$ Hz, 4CH_3).

Example 12: Bis[4(1,1-dimethylprop-1-yl)phenyl]iodonium hexafluorophosphate

Prepared from 4(1,1-dimethylprop-1-yl)phenol. ^1H -NMR signals measured in $\text{DMSO}-d_6$ [ppm]: 8.14 (4H, m, ArH), 7.48 (4H, m, ArH), 1.61 (4H, m, 2CH_2), 1.21 (12H, s, 4CH_3), 0.56 (6H, m, 2CH_3).

Example 13: Bis(4- C_3 - C_{14} alkylphenyl)iodonium hexafluorophosphate

Prepared from a mixture of phenols substituted in 4-position by C_8 - C_{14} alkyl. ^1H -NMR signals measured in CDCl_3 [ppm]: 7.88 (4H, m, ArH), 7.30 (4H, m, ArH), 2.80-2.35 ($\approx 2\text{H}$, m), 1.75-1.35 ($\approx 12\text{H}$, m), 1.35-0.65 ($\approx 30\text{H}$, m).

Example 14: Preparation of p-butoxyphenylphenyl iodonium hexafluorophosphate

A 350 ml flask, equipped with reflux condenser, thermometer, stirrer and argon inlet, is charged with 100 g (0.31 mol) of diacetoxiodobenzene in 200 ml of acetic acid, to which, after heating to 40°C , 45.8 g (0.48 mol) of p-toluenesulfonic acid are added in portions over 3h. The reaction solution is stirred overnight at 40°C , cooled to room temperature and filtered. The filter cake is washed with water and dried at 60°C under vacuum, giving 71.2 g of hydroxy(tosyloxy)iodobenzene.

In a 200 ml flask, equipped with reflux condenser, thermometer, stirrer and argon inlet, 14.1 g (0.036 mol) of hydroxy(tosyloxy)iodobenzene and 5.1 g (0.034 mol) of 4-butoxybenzene are heated for 2h to 40°C in a mixture consisting of 5 ml of acetonitrile and 2 ml of

acetic acid. After cooling the reaction mixture to room temperature, 100 ml of water are added and the mixture is extracted with methylene chloride. The organic phases are dried over magnesium sulfate, filtered and concentrated in a rotary evaporator. A solid is precipitated by treatment with hexane. Filtration gives 17.0 g of p-butoxyphenylphenyl iodonium tosylate in the form of a beige solid having a melting point of 169-171°C.

In a 200 ml flask, equipped with reflux condenser, thermometer, stirrer and argon inlet, 17.0 g (0.032 mol) of butoxyphenylphenyl iodonium tosylate and 6.6 g (0.036 mol) of potassium hexafluorophosphate are stirred overnight in 50 ml of acetone at room temperature. The resulting suspension is filtered and the filtrate is concentrated in a rotary evaporator. 50 ml of methylene chloride are added and the solution is washed with water. After drying over magnesium sulfate and filtration, the solvent is stripped off under vacuum. A solid is precipitated by treatment with hexane. Filtration gives 15.0 g of p-butoxyphenylphenyl iodonium hexafluorophosphate in the form of a beige solid having a melting point of 101-103°C.

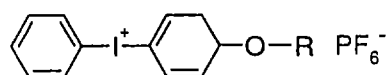
Elemental analysis:

calculated	C 38.56%	H 3.64%	F 22.88%	P 6.22%	J 25.47%
found	C 39.84%	H 3.72%	F 21.61%	P 6.18%	J 25.32%

Examples 15-16:

The compounds of Examples 15-16 are prepared in analogy to the method of Example 14, using the corresponding educts. The compounds and their physical data are listed in the following Table 1.

Table 1:



Example	R	Melting point	Elemental analysis [%]	
			calculated	found
15	2-methylpropyl	resin	C:	38.56
			H:	03.64
			F:	22.88
			P:	06.22
			I:	25.47
16	dodecyl	87 - 89 °C	C:	47.23
			H:	05.70
			F:	17.04
			P:	04.82
			I:	20.71

Example 17:

A white enamel formulation is prepared by mixing the following components:

35.3 % of diglycidyl ether of bisphenol A (ARALDIT GY 250, Ciba Spezialitätenchemie, Switzerland),

14.1 % of trimethylolpropane triglycidyl ether,

9.4 % of C_{12/14}alkyl glycidyl ether,

39.2 % of rutile titanium dioxide (R-TC2, Tioxide, UK),

1.5 % of p-isobutylphenylphenyl iodonium hexafluorophosphate (see Example 1),

0.5 % of isopropylthioxanthone.

The mixture is heated to 60°C and shaken for 6 minutes. After heating it once more to 60°C and shaking it for another 6 minutes, it is stirred for 30 minutes at 60°C. The formulation is applied to a 300 µm aluminium sheet using a 12 µm spiral applicator. Irradiation is carried out using a UV processor under two 80 W/cm mercury medium pressure lamps. The highest belt speed is determined at which the sample is cured with the surface still remaining tack-free. The higher the belt speed, the more reactive the formulation. Moreover, immediately after irradiation and also after subjecting the sample to a final heat treatment for 5 minutes at 180°C in a circulating air oven, the yellowing of the coating is determined via the Yellowness Index (YI) in accordance with ASTM D-1925-70. The lower the YI value, the less yellowing of the coating.

This formulation is cured tack-free at a belt speed of 12.5 m/min. Immediately after irradiation, the measured YI value is -2.5, and after the subsequent heat treatment it is -3.4.

Example 18

A white enamel formulation is prepared by mixing the following components:

17.0 parts of diglycidyl ether of bisphenol A (ARALDIT GY 250, of Ciba Spezialitätenchemie, Switzerland),

17.0 parts of trimethylolpropane triglycidyl ether,

13.0 parts of C_{12/14}alkyl glycidyl ether,

50.0 parts of rutile titanium dioxide (R-TC2, Tioxide, UK),

2.0 parts of p-isobutylphenylphenyl iodonium hexafluorophosphate (see Example 1),

1.0 parts of isopropylthioxanthone

2.0 parts of dispersant (Disperbyk 110; Byk Chemie, Germany)

0.5 parts of wax (polyfluo 540).

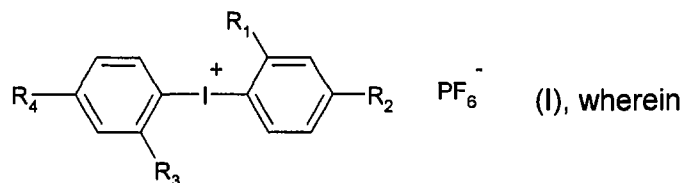
- 22 -

The mixture is heated to 60°C and shaken for 6 minutes. After heating it once more to 60°C and shaking it for another 6 minutes, it is stirred for 30 minutes at 60°C. The formulation is applied to 300 µm aluminium sheets using a 12 µm spiral applicator. Irradiation is carried out using a UV processor under a 120W/cm microwave-excited M-Fusion lamp (of Fusion UV Systems) by passing the sample to be cured on a belt under the lamps. The highest belt speed is determined at which the sample is cured with the surface still remaining tack-free. At a belt speed of 10 m/min, the sample is cured with a tack-free surface.

What is claimed is

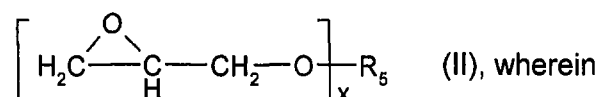
1. A ultraviolet-curable, cationically polymerisable composition, which comprises
 - (a) mono-, bis- or higher aliphatic or aromatic glycidyl ethers,
 - (b) titanium dioxide,
 - (c) at least one iodonium hexafluorophosphate salt as photoinitiator, and
 - (d) a sensitiser compound,
 provided that the composition does not comprise any cationically curing material other than glycidyl ethers.

2. A composition according to claim 1, wherein the photoinitiator (c) is a compound of formula I



R₁, R₂, R₃ and R₄ are each independently of one another hydrogen, C₁-C₂₀alkyl or unsubstituted or hydroxyl-substituted C₁-C₂₀alkoxy, with the proviso that at least one of **R₁, R₂, R₃** or **R₄** is not hydrogen.

3. A composition according to claim 2, wherein in the compound of formula **R₂** is C₁-C₁₂alkyl and **R₁, R₃ and R₄** are hydrogen.
4. A composition according to claim 1, wherein the sensitiser compound (d) is a compound selected from the group consisting of anthracenes, xanthenes, benzophenones and thioxanthenes.
5. A composition according to claim 4, wherein the sensitiser compound (d) is a thioxanthone derivative.
6. A composition according to claim 1, wherein the glycidyl ether (a) is a compound of formula II



- 24 -

x is a number from 1 to 6; and

R₅ is a mono- to hexavalent alkyl or aryl radical.

7. A composition according to claim 1, wherein the proportion of the component (a) is 40-70%, that of the titanium dioxide (b) is 20-60%, that of the photoinitiator (c) is 0.5-10% and that of the sensitizer compound (d) is 0.1-3%.

8. A coated substrate which is coated on at least one surface with a composition according to claim 1.

9. A coated substrate according to claim 8, to which the composition according to claim 1 is applied at a coating thickness of 0.1-100 μm .

10. A process for the photopolymerisation of a composition according to claim 1, which comprises irradiating the composition with light in the wavelength of 200-600 nm.

11. A process according to claim 10, wherein a heat treatment is carried out after the irradiation.

12. A process according to claim 10 for the preparation of coatings, paints, printing inks, powder coatings, laminating adhesives or dental compositions, in particular of white enamel formulations.

13. Use of a composition according to claim 1 for the preparation of coatings, paints, printing inks, powder coatings, laminating adhesives or dental compositions, in particular of white enamel formulations.