

ONIUM SALTS WITH WEAKLY COORDINATING IMIDAZOLIDINE ANION AS CATIONIC INITIATORS

BACKGROUND OF THE INVENTION

The present invention relates to novel onium imidazolidine organometallic complexes which are cationic initiators of polymerization, and to the use of such novel onium salts for the polymerization or crosslinking of functional polymers or monomers by photochemical activation, or activation under an electron beam.

Onium salts or salts of organometallic complexes are well known as initiators of the cationic polymerization of monomers or of polymers substituted by functional groups of the epoxy or vinyl ether type, and any other cationically polymerized media and the like (U.S. Pat. Nos. 4,450,360; 4,576,999 and 4,640,967; Canadian Patent No. 1,274, 646; European Application EP-A-203, 829). It has been observed that the best results are obtained when the anion of the initiator salt is SbF_6^- ; or tetrakis(pentafluorophenyl) borate, $(\text{C}_6\text{F}_5)_4\text{B}^-$. Recently, a new group of photoinitiators containing gallate anion, $(\text{C}_6\text{F}_5)_4\text{Ga}^-$ whose performance is similar to that of the analogous tetrakis(pentafluorophenyl)borate has been discovered (U.S. Pat. No. 6,166,233).

The present invention relates also to ultraviolet-curable compositions containing epoxy and/or vinyl ether functional groups and onium salts as photoinitiator. More particularly, it relates to cationically polymerizable and/or crosslinkable compositions comprising novel, easily synthesized iodonium salts with high solubility and high catalytic activity.

SUMMARY OF THE INVENTION

Good homogeneity and high curing activity are exhibited by cationically polymerizable and/or crosslinkable compositions comprising an epoxy-

functional resin and a catalytically effective amount of an onium salt such as iodonium, sulfonium, phosphonium, ferrocenium or diazonium of formula (I)



where Q is an onium cation; A is imidazolidine anion of formula (II)



where LN is imidazolidine, Mt is B, Ga, In or Tl;

R¹ are identical or different and represent a monovalent aromatic hydrocarbon radical having from 6 to 14 carbon atoms with at least one electron-withdrawing element or group such as -CF₃, -NO₂ or -CN, or with at least two halogen atoms; In another embodiment of the present invention A is a monocarborane anion of the formula CB₁₁H_nX_{12-n} wherein X is halogen or CF₃.

DETAILED DESCRIPTION OF THE INVENTION

The onium imidazolidine salts of the present invention include a cationic component and an anionic imidazolidine moiety of formula (I)

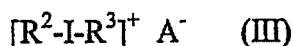


Where Q⁺ is an 'onium cation and A⁻ is an imidazolidine anion of formula (II)



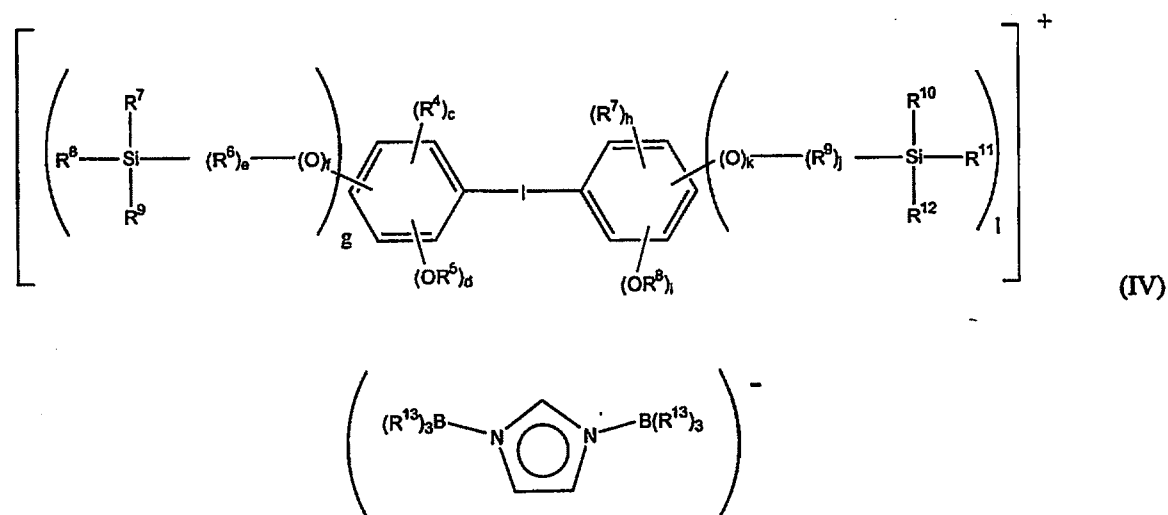
where LN is imidazolidine group, Mt is B, Ga, In or Tl; R¹ are identical or different and represent a monovalent aromatic hydrocarbon radical having from 6 to 14 carbon atoms with at least one electron-withdrawing element or group such as -CF₃, -NO₂ or -CN, or with at least two halogen atoms.

The cationic moiety could be any of the cations of onium salts such as iodonium, pyrylium, thiapyrylium, sulphonium, phosphonium, ferrocenium or diazonium ions and the like. Preferred onium salts are diaryliodonium salts of formula (III)



where R^2 and R^3 are each independently a monovalent aromatic radical having from 6 to 24 carbon atoms. The monovalent aromatic radicals R^2 and R^3 may be unsubstituted or substituted with any group that does not interfere with catalyst function. Preferred substituents include C_{1-18} alkyl, C_{1-18} alkoxy, and trialkylsilane-terminated C_{1-18} alkyl; each of these substituents can be uninterrupted or interrupted by one or more oxygen and/or sulfur atoms.

Highly preferred iodonium salts for use in the UV-curable compositions are iodonium imidazolide salts given by formula (IV)



where

R^4 , R^5 , R^7 and R^8 are independently an alkyl group having from 1 to 18 carbons uninterrupted or interrupted by one or more oxygen and/or sulfur atoms;

R^6 and R^9 are independently a divalent aliphatic hydrocarbon radical having from 1 to 18 carbon atoms per radical, which is either uninterrupted or interrupted by one or more oxygen and/or sulfur atoms;

R^7 , R^8 , R^9 , R^{10} , R^{11} and R^{12} are independently a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, which is uninterrupted or interrupted by one or

WO 03/062208

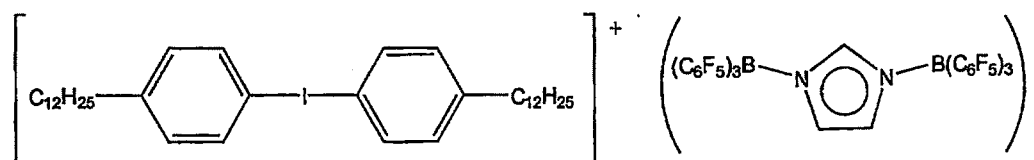
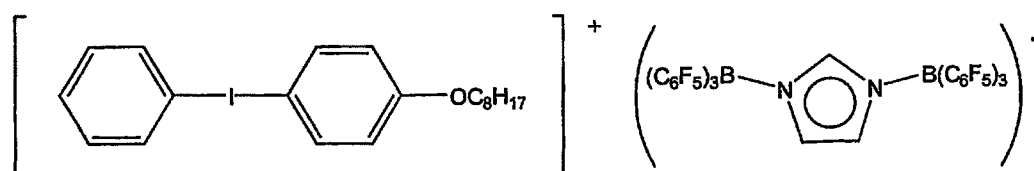
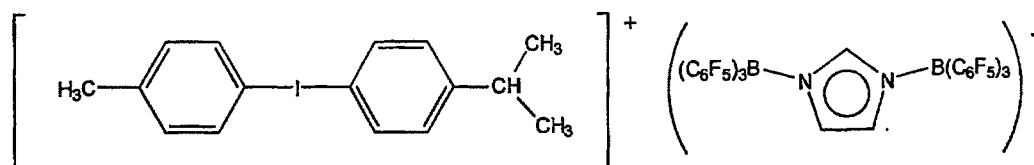
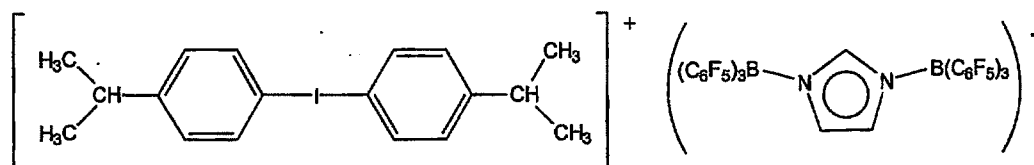
PCT/US02/38227

more oxygen and/or sulfur atoms, or which may be further functionalized with halogen or hydroxy groups.

R^{13} are identical or different and selected from the group of substituted phenyls consisting of $-C_6F_5$, $-C_6H_4(CF_3)$, and $-C_6H_3(CF_3)_2$;

c, d, g, h, i and l are independently 0, 1, 2, 3, 4 or 5, with the proviso that each of the sums $c+d+g$ and $h+i+l$ not exceed 5.

Examples of especially preferred compounds include



The initiator salts of the present invention are useful for polymerizing or crosslinking, by radiation (especially under ultraviolet light or electron beam) monomers or

polymers bearing functional groups such as epoxy groups, oxetane groups, vinyl ether groups, or any other cationically polymerizable monomers and the like. Generally, cationically polymerizable monomers and prepolymers are disclosed in U.S. Pat. No. 5,639,802, which is incorporated herein by reference. The monomers can be made monofunctional, difunctional, or multifunctional. These may also be high molecular weight prepolymers and oligomers. Examples of cationically polymerizable compounds further include epoxy compounds, vinyl or allyl monomers, vinyl or allylic prepolymers, vinyl ethers, vinyl ether functional prepolymers, cyclic ethers including oxetanes, cyclic esters, cyclic sulfides, melamine formaldehyde, phenolic formaldehyde, cyclic organosiloxanes, lactanes and lactones, cyclic acetals, epoxy functional silicone oligomers, vinyl ether functional silicone oligomers, and oxetane functional silicone oligomers. The onium imidazolide salts can additionally be used as thermal polymerization initiators, or as combination ultraviolet light or electron beam and thermal polymerization initiators.

Representative examples of compositions that may be polymerized using the onium imidazolide salts of the present invention are described in U.S. Pat. No. 5,639,802. In addition, these may also include bis-phenol-A-epoxy resins, cycloaliphatic epoxides, oxetanes, epoxidized olefins such as polybutadiene epoxide, epoxidized organic oils such as epoxidized soybean oil and the like.

The onium imidazolide salt is added to the cationically polymerizable material in an amount sufficient to initiate polymerization or crosslinking and generally ranges from about 0.01 to 20 parts by weight per 100 parts by weight of the polymerizable material.

The compositions of the invention are useful as radiation polymerizable coatings for paper, metal, plastic or glass and are particularly useful in applications where the properties of a silicone coating are desired.

Photosensitizers allow one to utilize the onium imidazolides of the present invention for photopolymerization on exposure to longer wavelengths of light. The iodonium imidazolides may employ separate photosensitizers or sensitizers and accelerators described in the prior art for sensitizing and accelerating cationic polymerization

reactions. If a compound is serving as a photosensitizer only it must absorb light energy that can, in some form, be transferred to imidazolid reacting species that does not absorb light energy of the same wavelength. Representative examples of photosensitizers that may be used include benzophenones, acetophenone acetals, benzoin ethers, substituted or nonsubstituted thioxanthenes, fluorones, etc. Additionally, photosensitizers may function as electron transfer donors in an oxidative chain as shown in U.S. Patent Application filed on even date herewith claiming priority of U.S. Provisional Application Ser. No. 60/137,115 "Accelerator/Sensitizers for Cationic Systems". In this embodiment, the crucial step is the formation of an excited state of the photosensitizer that is capable of electron donation to the ground state of the onium imidazolid. The formed radical cation of the photosensitizer deprotonates to form an oxy radical and an additional proton thus accelerating the cationic polymerization. Representative, but nonlimiting examples of sensitizer/accelerators useful in the invention include naphthols, dihydroxynaphthalenes; polyhydroxy phenols, such as cresols, gallols, pyrogallols, etc.; di (C1- C10)alkoxynaphthalenes; C1-C10 alkoxyhydroxynaphthalenes; naphthyl glycidyl ethers and the like.

Because in the charge transfer reaction with the onium imidazolid the sensitizer-accelerator generates both free radicals and cations, it is possible to utilize a combination of free radical polymerizable and cationic polymerizable monomers. Examples of free radical polymerizable monomers include both monomers having one or more ethylenically unsaturated groups, such as vinyl or allyl groups, and polymers having terminal or pendant ethylenic unsaturation. Such compounds are easily identifiable to those skilled in the art and include acrylates.

If solvents are used to dissolve the photosensitizer/accelerator or an onium imidazolid they may be selected from the group yielding α -hydroxy alkylsubstituted carbon centered radicals upon UV induced cleavage. These radicals will further deprotonate to form a ketone. The proton released will participate in the cationic polymerization. Thus, the solvent may act as an accelerator as well. Some examples of

the useful solvents include diacetone alcohol, 2-hydroxy-2-methyl-1-phenyl- propan-1-one and the like.

Iodonium imidazolid salts of the present invention are preferred photo-initiators for epoxy-functionalized siloxane resins due to their excellent solubility in the siloxane polymers. Epoxy-functionalized siloxane polymers suitable for curing by iodonium salts of the present invention are described in US Patent Nos. 4,279,717, 5,397,813 and 5,583,195 of Eckberg et al., which are incorporated herein by reference. Preferred epoxy-functionalized siloxane polymers and silane monomers include β -(3,4-epoxycyclohexyl)ethyltrimethoxy silane, dialkylepoxysiloxo- chain-stopped polydialkyl-alkylepoxysiloxane copolymers (such as materials sold as UV9315 and UV9400 by General Electric Silicones), and trialkylsiloxo- chain-stopped polydialkyl-alkylepoxysiloxane copolymers (such as the material sold as UV9300 by General Electric Silicones), epoxy functional siloxane resin (such as the material sold as UV9430 by General Electric Silicones, and further described in US Patent No. 5,360,833 to Eckberg et al.), blends of epoxy functional siloxane copolymers with vinyl and/or propenyl ethers (such as those described in US Patent No. 5,650,453 to Eckberg et al.).

The siloxane compositions can additionally contain other additives and adjuvants, such as adherence modulators (linear silicone polymers or resins bearing vinyl, epoxy, vinyl ether, alcohol and the like functional groups), reactive diluents, pigments, photosensitizing agents, anchorage additives, fungicidal, bactericidal and antimicrobial agents, corrosion inhibitors and the like.

The compositions according to the invention can be used as such or in solution in an organic solvent. The compositions advantageously exhibit a viscosity not exceeding 5,000 mPa.sec, preferably not exceeding 2000 mPa.sec at 25°C. They are useful for providing antiadherent coatings on cellulosic materials, films, paints, for encapsulation of electrical and electronic components, for coatings on textiles and for sheathing optical fibers. They are very particularly advantageous when they are used,

as such, to produce a material, such as metal sheet, glass, plastic or paper that is nonadherent to other materials to which it would normally adhere.

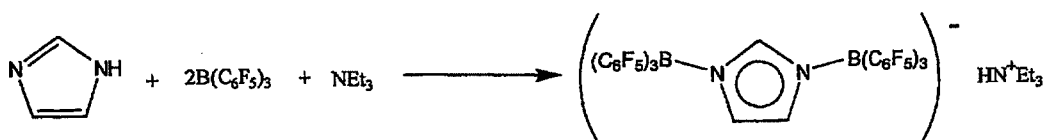
Thus, the present invention also features a process for the production of articles (sheets for example) that are nonadherent to surfaces to which they normally adhere, comprising coating an amount of the subject composition, generally from 0.1 to 5 g/m², onto at least one face surface thereof, and crosslinking the composition by supplying energy, as, for example, UV radiation or electron beam.

The present invention also features the final articles (sheets for example) comprising a solid material (metal, glass, plastic, paper, and the like), at least one surface of which is coated with a composition as described above, which composition is photocrosslinked or cross-linked by an electron beam.

In order to further illustrate the present invention and the advantages thereof, the following specific examples are given, it being understood that some are intended only as illustrative and in nowise limitative.

The iodonium imidazolid salts of the invention can be prepared by synthetic procedures such as those described in the synthetic examples, below.

SYNTHETIC EXAMPLE 1



Synthesis of Triethylammonium imidazolid

Tris(pentafluorophenyl)borane (3.008 g, 5.88 mmol), 0.2 g of imidazole (2.94 mmol) and added 0.297 mg (2.94 mmol) of triethylamine were partly dissolved in 50 mL of toluene. This mixture was refluxed for 5 hours to give a white powder. The white solid was collected on the frit, washed with hexane, and dried under reduced pressure to give 3.22 g of product. Yield 91.9%.

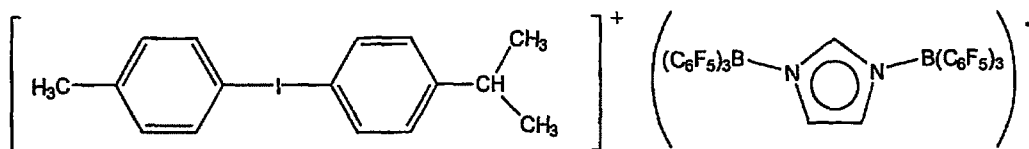
SYNTHETIC EXAMPLE 2

Synthesis of (4-isopropylphenyl)-4'-methylphenyliodonium imidazolid

[(C₆F₅)₃B-C₃H₃N₂-B(C₆F₅)₃] [HNEt₃] (0.41 g, 0.344 mmol) was dissolved in 15 mL of methylene chloride. To this solution, (4-isopropylphenyl)-4'-methylphenyliodonium chloride (0.14 g, 0.378 mmol) in 15 mL of methylene chloride was added at room temperature. The solution was stirred for 2 h in the dark. The precipitate was filtered, and the solvent removed to give a viscous oil (0.53 g). The crude product was chromatographed through a short plug of silica gel by elution with a mixture of CH₂Cl₂ and hexane (1:1) to give a white powder (0.45 g, 92% yield); m.p. 172-174 °C. ¹H NMR (CDCl₃, TMS) δ 1.25 (d, 6H, *J* = 7.0 Hz, CH₃), 2.47 (s, 3H, CH₃), 3.00 (m, 1H, *J* = 7.4 Hz, CH), 6.76 (s, 2H, C₃H₃N₂), 7.49 (s, 1H, C₃H₃N₂), 7.38 (d, 2H, *J* = 8.4 Hz, C₆H₄), 7.42 (d, 2H, *J* = 8.8 Hz, C₆H₄), 7.80 (d, 2H, *J* = 8.6 Hz, C₆H₄), 7.81 (d, 2H, *J* = 8.6 Hz, C₆H₄); ¹³C NMR (CDCl₃) δ 23.5, 25.3, 36.2, 109.1, 109.2, 125.8, 130.3, 134.2, 136.5, 136.8, 148.5, 158.9; ¹¹B NMR (CDCl₃, BF₃·Et₂O) δ -8.73 (s, 2B); ¹⁹F NMR (CDCl₃, CFCl₃) δ -165.01 (s, 2F), -159.23 (s, 1F), -132.49 (s, 2F). Anal. Calcd for C₅₅H₂₁B₂F₃₀IN₂: C, 46.25; H, 1.48. Found: C, 46.45; H, 1.58.

EXAMPLE 1

Solubilities and photoactivities were determined for these new iodonium salts and for four comparative iodonium salts in an epoxyfunctional polydimethyl siloxane copolymer M^{Ep}D^{Ep}_xD_yM^{Ep} material sold as UV9315 by General Electric Silicones. The structure of the imidazolid iodonium salt (compound 1) is presented below:



The comparative iodonium salts are as follows:

Compound 2 – (4-isopropylphenyl)-4'-methylphenyliodonium hexafluoroantimonate

WO 03/062208

PCT/US02/38227

Compound 3 - (4-isopropylphenyl)-4'-methylphenyliodonium chloride

Compound 4 - (4-isopropylphenyl)-4'-methylphenyliodonium
tetrakis(pentafluorophenyl)borate, obtained as Rhodosil 2074 from Rhodia.

Compound 5 - (4-isopropylphenyl)-4'-methylphenyliodonium
tetrakis(pentafluorophenyl)gallate

The solubility of each iodonium salt was evaluated visually at 0.25% weight percent in UV9315. The same catalyst concentration was used for the photoactivity determination. Borate (compound 4) was dissolved at 0.25 % by weight in an epoxy silicone resin (GE Silicones UV9315) and used as a standard. The other iodonium salts were prepared at molar concentrations equal to borate 4. A 0.5 mil film of these solutions was applied onto PK paper, and the sample was passed under a focused UV lamp (System LC-06-T3 from American Ultraviolet Co.) using a conveyor belt capable of operation at variable speed. The intensity of the UV lamp was 125 Watts/in². Firmly placing a thumb on the surface and dragging across the length of the coating was used to test the level of curing of the film. Any tackiness or smearing of the coating or transfer of the film to thumb was classified as a failure. The maximum speed of the conveyor belt that would provide curing without failure was determined and recorded.

Solubility and photoactivity results are presented in Table 1.

Table 1. Solubility and Photoactivity Test Results

Compound No.	Solubility in UV9315	Photoactivity in UV9315 (Maximum fpm of conveyer where smear-free cure is observed)
1	Very good	28
2*	insoluble	3
3*	insoluble	0
4*	Good	28
5*	Good	28

*Comparison

Example 2

Photoactivities were determined for the new iodonium salt and for the four comparative iodonium salts in cycloaliphatic epoxide (UVR6110, trademark of Union Carbide Div. Dow Chemical Co) using FTIR. Solution of gallate (compound 5) in monomer UVR 6110 at 1.00% (wt) was prepared and used as a standard. The other iodonium salts were prepared at molar concentrations equal to gallate 5. A drop of each solution in monomer UVR 6110 was placed between two pieces of polyethylene plates spaced with a Teflon spacer (0.015mm). The liquid film was irradiated at different doses under a UV lamp (System LC-06-T3 from American Ultraviolet Co.). The IR peaks at 790 and 1730 cm^{-1} were followed by FTIR and integrated as a function of dose. The peak at 1730 cm^{-1} was selected as the internal standard, and the conversion was calculated from eq. 2, where $(A_{790}/A_{1730})_0$ and $(A_{790}/A_{1730})_n$ are the area ratios of peaks at 790 and 1730 cm^{-1} at beginning and at dose n, respectively.

WO 03/062208

PCT/US02/38227

$$\text{Conversion} = [1 - (A_{790}/A_{1730})_0 \div (A_{790}/A_{1730})_n] \times 100\%$$

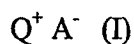
A close examination showed that a slight difference in compounds 1-5 followed the order of gallate 5 > borate 4 > imidazolidine 1 > antimonate 2 >> chloride 3.

The general conclusion from both Examples is that compositions of the invention provide good catalyst solubility and photoactivity in organic epoxy and especially epoxy-functional siloxane systems.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustration and not limitation.

CLAIMS

1. A composition, comprising: (a) a cationically polymerizable or crosslinkable resin; and (b) from 0.01 to 20 parts by weight per 100 parts by weight of (a) of an onium salt of formula (I)

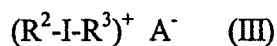


wherein Q^+ is a onium cation selected from iodonium, pyrylium, thiapyrylium, sulphonium, phosphonium, ferrocenium or diazonium ions, A is imidazolidine anion of formula (II)



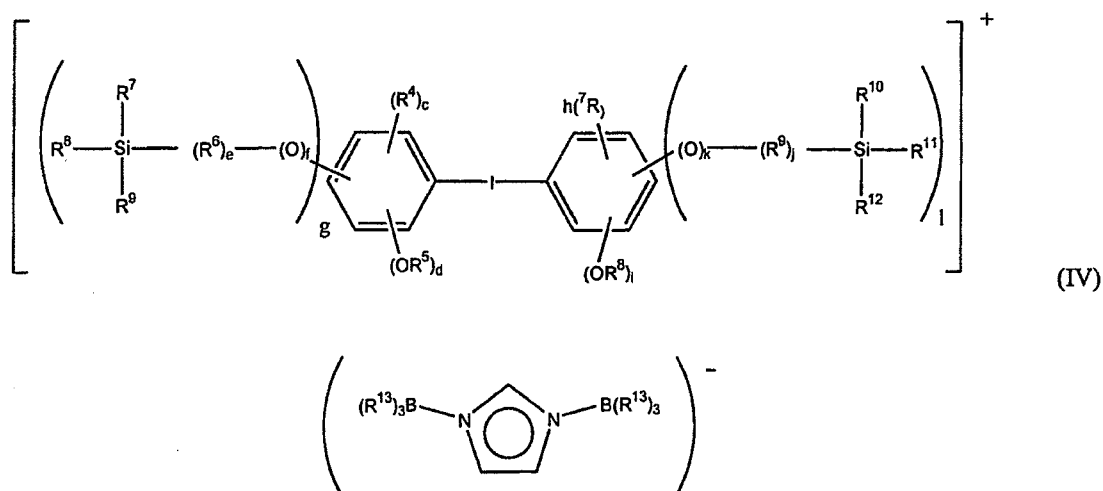
wherein LN is imidazolidine group, Mt is B, Ga, In or Tl; R^1 are identical or different and represent a monovalent aromatic hydrocarbon radical having from 6 to 14 carbon atoms with at least one electron-withdrawing element or group selected from $-CF_3$, $-NO_2$ or $-CN$, or with at least two halogen atoms.

2. A composition according to claim 1, wherein said onium salt is an iodonium salt of formula



wherein R^2 and R^3 are each independently a monovalent aromatic radical having from 6 to 24 carbon atoms.

3. A composition according to claim 1, wherein said onium imidazolidine salts are given by formula (IV)



wherein

R^4 , R^5 , R^7 and R^8 are independently an alkyl group having from 1 to 18 carbons wherein said alkyl group may contain ether or thioether groups;

R^6 and R^9 are independently a divalent aliphatic hydrocarbon radical having from 1 to 18 carbon atoms per radical, wherein said alkyl group may contain ether or thioether groups;

R^7 , R^8 , R^9 , R^{10} , R^{11} and R^{12} are independently a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, wherein said alkyl group may contain ether or thioether groups;

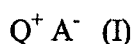
R^{13} are identical or different and selected from the group of substituted phenyls consisting of $-C_6F_5$, $-C_6H_4(CF_3)$, and $-C_6H_3(CF_3)_2$;

c, d, g, h, i and l are independently 0, 1, 2, 3, 4 or 5, with the proviso that each of the sums $c+d+g$ and $h+i+l$ not exceed 5.

4. A composition according to claim 1, wherein said cationically polymerizable or crosslinkable resin comprises a monomer or polymer said monomer or polymer

possessing a functional group selected from the group consisting of epoxy groups, vinyl ether groups, and oxetane groups.

5. A composition, comprising: (a) a cationically polymerizable or crosslinkable epoxy-functional or vinyl ether- functional siloxane resin; and (b) from 0.1 to 20 parts by weight per 100 parts by weight of (a) of an onium salt of formula (I)

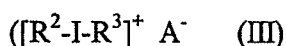


wherein Q^+ is a onium cation selected from iodonium, pyrylium, thiapyrylium, sulphonium, phosphonium, ferrocenium or diazonium ions, A is imidazolidine anion of formula (II)



wherein LN is imidazolidine group, Mt is B, Ga, In or Tl; R^1 are identical or different and represent a monovalent aromatic hydrocarbon radical having from 6 to 14 carbon atoms with at least one electron-withdrawing element or group selected from $-CF_3$, $-NO_2$ or $-CN$, or with at least two halogen atoms.

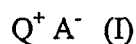
6. A composition according to claim 5, wherein said onium salt is an iodonium salt of formula



wherein R^2 and R^3 are each independently a monovalent aromatic radical having from 6 to 24 carbon atoms.

7. A method of preparing a cross-linked coating comprising:

(a) applying to a substrate a solution comprising an cationically polymerizable resin containing 0.01 to 20 weight percent of an onium salt of formula (I)



wherein

Q is an onium cation selected from the group consisting of iodonium, sulfonium, phosphonium, ferrocenium and diazonium;

A is imidazolidine anion of formula (II)



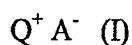
wherein LN is imidazolidine group, Mt is B, Ga, In or Tl; R^1 are identical or different and represent a monovalent aromatic hydrocarbon radical having from 6 to 14 carbon atoms with at least one electron-withdrawing element or group selected from $-\text{CF}_3$, $-\text{NO}_2$ or $-\text{CN}$, or with at least two halogen atoms.

(b) shining ultraviolet light or electron beam radiation on said substrate thereby

(c) forming a cured coating.

8. A method of preparing a cross-linked siloxane coating comprising:

(a) distributing on a substrate an epoxy-functionalized siloxane resin containing 0.01 to 20 weight percent of an onium salt of formula (I)



wherein

Q is an onium cation selected from the group consisting of iodonium, sulfonium, phosphonium, ferrocenium and diazonium;

A is imidazolidine anion of formula (II)



wherein LN is imidazolidine group, Mt is B, Ga, In or Tl; R^1 are identical or different and represent a monovalent aromatic hydrocarbon radical having from 6 to 14 carbon atoms with at least one electron-withdrawing element or group selected from $-\text{CF}_3$, $-\text{NO}_2$ or $-\text{CN}$, or with at least two halogen atoms.

(b) shining ultraviolet light or electron beam radiation on said substrate thereby

(c) forming a cured coating.

9. A coating prepared according to the method of claim 7 or 8.
10. An article bearing a coating of the composition of claim 1.
11. An article bearing a coating of the composition of claim 5.
12. An article bearing the crosslinked composition of claim 1.
13. An article bearing the crosslinked composition of claim 5.