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(57) Abstract

Curable organic resin compositions, such as epoxy resins, are provided, based on the use of dialkyl hydroxy arylsulfonium salts in combination with certain organic oxidants such as iodoso-aromatic esters, or the use of certain amines or transition metals in combination with organic peroxides. The curable compositions can provide flexible or rigid organic resin foam when used with a volatile organic solvent as a result of exothermic heat of cure.

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Description

CURABLE ORGANIC RESIN COMPOSITIONS AND FOAMING METHOD

Cross Reference to Related Applications

RD-10800 for Heat Curable Compositions, filed concurrently herewith, RD-11424, filed on or about November 20, 1978, for Curable Organic Resin Compositions and Foaming Method, which is a continuation-in-part of Serial No. 861,127, filed December 16, 1977, for Curable Organic Resin Compositions and Foaming Method, now abandoned, copending application Serial No. 861,128, for Heat Curable Compositions, filed December 16, 1977, which is a continuation-in-part application of Serial No. 781,785, filed March 28, 1977, for Heat Curable Epoxy Compositions and Method for Curing Same, now abandoned, copending application Serial No. 841,351 , filed October 12, 1977, for Heat Curable Compositions, which is a continuation in-part of Serial No. 689,247, filed May 24, 1976, for Epoxy Compositions and Method of Curing Same, now abandoned, where all of the aforesaid applications are assigned to the same assignee as the present invention.

Background of the Invention

The present invention relates to heat curable compositions and to a foaming method. More particularly, the present invention relates to the cure of a variety of cationically polymerizable materials, such as epoxy resins, with dialkylhydroxyarylsulfonium salts, in combination with certain organic oxidants, for example, iodoso-aromatic compounds, or organic peroxides with organic amine, or transition metal accelerators.

In my copending application RD-11424, filed on or about November 20, 1978, for Curable Organic Resin Compositions

and Foaming Method, a diaryliodonium salt is used in combination with a copper salt and certain reducing agents, such as ascorbic acid, Sn^{+2} compounds, or activated α-hydroxy compounds to effect the cure of a variety of cationically polymerizable organic compositions such as epoxy resins, phenol-formaldehyde resins, etc.

The present invention is based on the discovery that certain dialkylhydroxyarylsulfonium salts of the formula,

$$[R\ (R^1)_a\ S]^+[Y]^- \quad (1),$$

where R is a $C_{(6-20)}$ aromatic radical having from 1 to 3 nuclearly bonded hydroxy radicals, R^1 can be the same or different $C_{(1-8)}$ alkyl radical or an alkylene radical capable of forming a cycloaliphatic or heterocyclic ring, Y is a non-nucleophilic anion, a is an integer equal to 1 or 2, and when R^1 is alkyl, a is 2, and when R^1 is alkylene, a is 1, also can be used to effect the cure of a variety of cationically polymerizable organic materials, when such arylsulfonium salts are used in combination with certain organic oxidants, for example, iodosoaromatic compounds, quinones, etc., and organic peroxides used in combination with organic amine or transition metal accelerators.

Statement of the Invention

There is provided by the present invention, curable compositions comprising

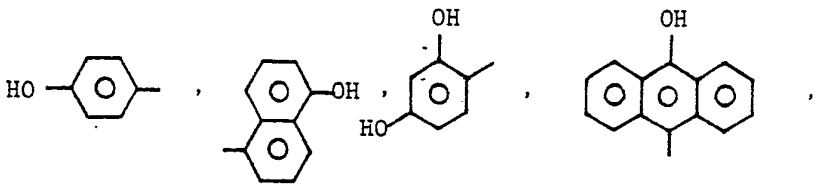
(A) cationically polymerizable organic material, and

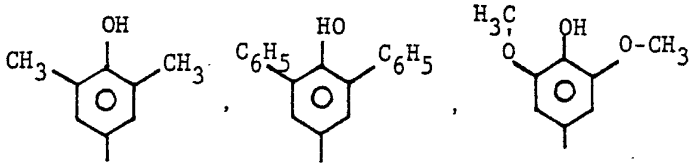
(B) an effective amount of a curing agent consisting essentially of a dialkylhydroxyarylsulfonium salt of formula (1), and an organic oxidant selected from iodosoaromatic organic compounds, quinones and organic peroxides having a decomposition accelerator selected from organic amines and

and transition metals.

Anions included by Y of formula (1) are, for example, MQ_d, where M is a metal or metalloid, Q is a halogen radical and d is an integer having a value of from about 4-6 inclusive. Besides epoxy resins, formula (1) sulfonium salts also have been found to be useful in curing cyclic ethers, lactones, lactams and cyclic acetals, etc., where the sulfonium salts also can have non-nucleophilic counterions such as perchlorate, $CF_3SO_3^-$ and $C_6H_4SO_3^-$. Again, the cationically polymerizable material can be a phenol-formaldehyde, urea-formaldehyde or melamine-formaldehyde resin, Y of formula (1) also can include in addition to MQ_d and other non-nucleophilic counterions previously recited, halide counterions such as Cl, Br, F and I as well as nitrate, phosphate, etc.

Radicals included by R of formula (1) are, for example,



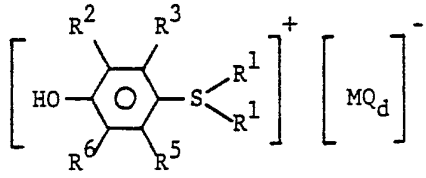


, etc.

R^1 radicals include CH_3-, C_4H_9-, $-(CH_2)_4$-, $-(CH_2)_5$-, $-CH_2-CH_2-O-CH_2-CH_2$-, $-CH_2-CH_2-S-CH_2CH_2$-, $C_6H_5-CH_2$-, C_2H_5-, etc. Complex anions included by MQ_d are, for example, BF_4^-, PF_6^-,

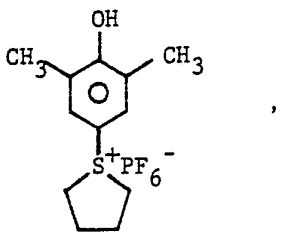
AsF_6^-, SbF_6^-, $FeCl_4^-$, $SnCl_6^-$, $SbCl_6^-$, $BiCl_5^=$, AlF_6^{-3}, $GaCl_4^-$, InF_4^-, $TiF_6^=$, ZrF_6^-, etc., where M is a transition metal such as Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, Sc, V, Cr, Mn, Cs, rare earth elements such as the lanthanides, for example, Ce, Pr, Nd, etc., actinides, such as Th, Pa, U, Np, etc., and metalloids such as B, P, As, etc.

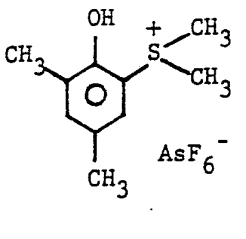
Preferably the salts included by formula (1), are

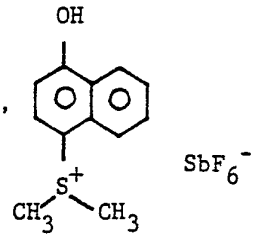
(2) 

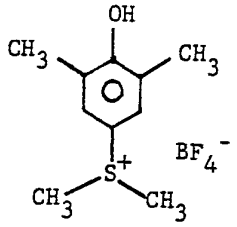
where R^1, M, Q and d are as previously defined, and R^2-R^6 are the same or different monovalent radicals selected from hydrogen, $C_{(1-8)}$ alkyl, $C_{(1-8)}$ alkoxy, nitro, chloro, hydroxy, etc.

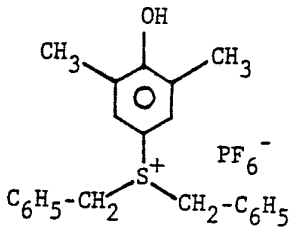
Dialkylhydroxyphenylsulfonium salts included by formulas (1) and (2) are

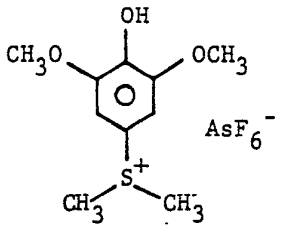












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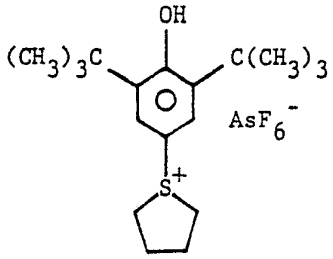

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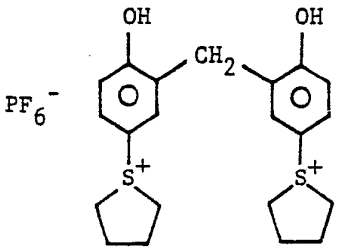

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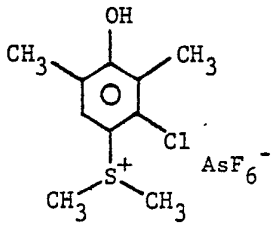

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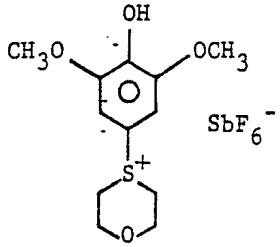


, etc.

Methods for making some of the dialkyl hydroxyarylsulfonium salts of formulas (1) and (2) are shown in U.S. patents 4,058,400 and 4,058,401, and in my copending applications Serial No. 833,146, filed September 14, 1977 and Serial No. 954,196, filed October 24, 1978.

There is also provided by the present invention, a foaming method which comprises,

(1) agitating a curable composition comprising,

(C) a cationically polymerizable organic material

(D) an effective amount of a curing agent consisting essentially of the dialkylhydroxyarylsulfonium salt of formulas (1) or (2), and an organic oxidant selected from an iodosoaromatic compound, a quinone, and an organic peroxide having a decomposition accelerator selected from an organic amine and a transition metal, and

(E) 1% to 30% by weight of (C), (D) and (E) of a volatile inert organic solvent, and

(2) thereafter allowing the ingredients of the resulting mixtures to react resuting in the production of exothermic heat and the simultaneous evaporation of the organic solvent and the cure of the cationically polymerizable organic resin.

The organic oxidant which is utilized in the practice of the invention can be employed in the curable compositions at from 0.1 % to 10% by weight of composition and preferably at from 1% to 5% by weight.

Included by the iodoso-aromatic compounds which can be used in combination with the dialkylhydroxyarylsulfonium salt are, for example, iodosobenzene diacetate, iodosobenzene, 4-nitroiodosobenzene, 4-chloroiodosobenzene diacetate, 4-methoxyiodosobenzene, 4-iodosobiphenyl, 2-chloroiodosobenzene diacetate. The organic oxidant used in the practice of the invention also can consist of organic peroxides in combination with accelerators such as organic amines, for example, N,N-dimethylaniline, diphenylamine, N,N'-tetramethylbenzidine, N,N'-diphenylphenylene-

1,4-diamine, N-phenylpiperadine, Michler's ketone, N-phenyldiethanolamine, etc. In addition to the aforementioned organic amine accelerators which can be used at from 0.1% to 50% by weight. based on the weight of organic peroxide, there also can be used as organic peroxide decomposition accelerators carboxylic acid compounds of transition metals, for example, cobalt napthenate, copper napthenate, cobalt stearate, stannous octoate, iron stearate, zinc octoate, cobalt laurate, iron palmitate, stannous caproate, etc., at 0.1% to 50% by weight of organic peroxides. Organic peroxides include ketone peroxides, peroxy acids, dibasic acid peroxides, aldehyde peroxides, alkyl peroxides, hydroperoxides, alkyl peroxyesters, diperoxide derivatives, for example, t-butyl peroxypivalate, ortho-dichlorobenzoyl peroxide, caprylyl peroxide, lauroyl peroxide, decanoyl peroxide, propionyl peroxide, acetyl peroxyesters, diperoxide derivatives, for example, t-butyl peroxypivalate, 2,4-dichlorobenzoyl peroxide, caprylyl peroxide, decanoyl peroxide, propionyl peroxide, acetyl peroxide, t-butyl peroxyisobutyrate, meta-chlorobenzoyl peroxide, benzoyl peroxide, hydroxyheptyl peroxide, chlorohexanone peroxides, 2,5-dimethylhexyl-2,5-di(peroxybenzoate), di-t-butyl diperphthalate, t-butyl peracetate, t-butylperbenzoate, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, t-butyl hydroperoxide, di-t-butyl peroxide, methyl ethyl ketone peroxide, p-methane hydroperoxide, cumene hydroperoxide, 2,5-dimethylhexyl-2,5-dihydroperoxide, t-butyl hydroperoxide, peracetic acid, perbenzoic acid, m-chloroperbenzoic acid, etc.

Cationically polymerizable organic materials which can be used to make the heat curable compositions of the present invention include epoxy resins, thermosetting organic condensation resins of formaldehyde, vinyl organic prepolymers, cyclic ethers, etc.

The term "epoxy resin" as utilized in the description of the cationically polymerizable compositions of the present invention, includes any monomeric, dimeric or oligomeric or polymeric epoxy material containing one or a plurality of epoxy functional groups. For example, those resins which result from the reaction of bisphenol-A (4,4'-isopropylidenediphenol) and epichlorohydrin, or by the reaction of low molecular weight phenol formaldehyde resin (Novolak resin) with epichlorohydrin, can be used alone or in combination with an epoxy containing compound as a reactive diluent. Such diluents as phenyl glycidyl ether, 4-vinylcyclohexene oxide, glycidyl acrylate, glycidyl methacrylate, styrene oxide, allyl glycidyl ether, etc., may be added as viscosity modifying agents.

In addition, the range of these compounds can be extended to include polymeric materials containing terminal or pendant epoxy groups. Examples of these compounds are vinyl copolymers containing glycidyl acrylate or methacrylate as one of the comonomers. Other classes of epoxy containing polymers amenable to cure using the above catalysts are epoxy siloxane resins, epoxy-polyurethanes and epoxy-polyesters. Such polymers usually have epoxy functional groups at the ends of their chains. Epoxy-siloxane resins and method for making are more particularly shown by E. P. Plueddemann and G. Fanger, J. Am. Chem. Soc. 80 2632-5 (1959). As described in the literature, epoxy resins can also be modified in a number of standard

ways such as reaction with amines, carboxylic acids, thiols, phenols, alcohols, etc., as shown in patent 2,935,488; 3,235,620; 3,369,055; 3,379,653; 3,398,211; 3,403,199; 3,563,840; 3,567,797; 3,677,995; etc. Further coreactants which can be used with epoxy resins are hydroxy terminated flexibilizers such as hydroxyterminated polyesters, shown in the Encyclopedia of Polymer Science and Technology, Vol. 6, 1967, Interscience Publishers, New York, pp. 209-271 and particularly p. 238.

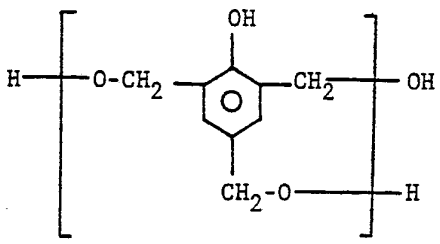
Included by the thermosetting organic condensation resins of formaldehyde which can be used in the practice of the present invention are, for example, urea type resin, such as

$$[CH_2=N\text{-}CONH_2]_x.H_2O \quad ,$$

$$[CH_2=NCONH_2]_xCH_3COOH \quad ,$$

$$[CH_2=NCONHCH_2NHCONHCH_2OH]_2 \quad ;$$

phenol-formaldehyde type resin; such as



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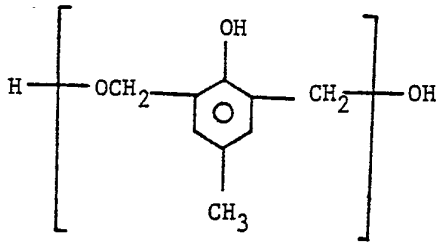

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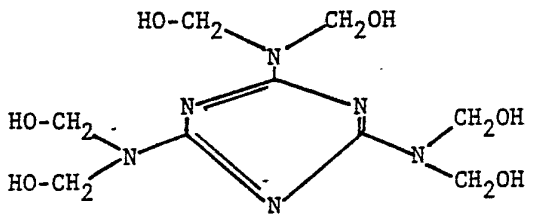
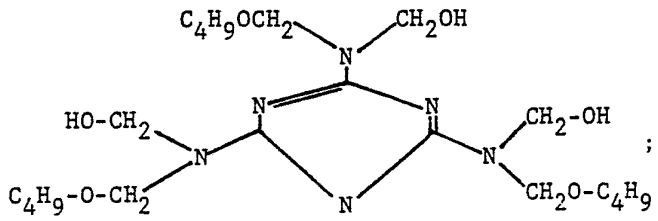
where x and n are integers having a value of 1 or greater;





alkoxy silanes having the formula,

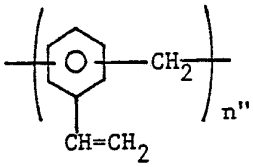
$$(R^7O)_m \, Si \, (R^8)_n \, ,$$

where R^7 is a $C_{(1-7)}$ alkyl radical, R^8 is selected from R^7 radicals and $C_{(6-13)}$ aryl radicals and halogenated derivatves, m is an integer equal to 1 to 4, n is an integer equal to 0 to 3 inclusive and m + n is equal to 4.

In addition, there can be used melamine thiourea resins, melamine, or urea aldehyde resins, cresol-formaldehyde resins and combinations with other carboxy, hydroxyl, amino and mercapto containing resins, such as polyesters, alkyds and polysulfides.

Some of the vinyl organic prepolymers which can be used to make the polymerizable compositions of the present invention are, for example, $CH_2=CH-O-(CH_2-CH_2O)_{n'}-CH=CH_2$, where n' is a positive integer having a value up to about 1000 or higher; multi-functional vinylethers, such as 1,2,3-propane

trivinyl ether, trimethylolpropane trivinylether, prepolymers having the formula,

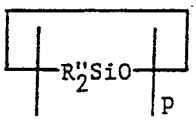


, and

low molecular weight polybutadiene having a viscosity of from 200 to 10,000 centipoises at 25°C, etc. Products resulting from the cure of such compositions can be used as printing inks and other applications typical of thermosetting resins.

A further category of the organic materials which can be used to make the polymerizable compositions are cyclic ethers which are convertible to thermoplastics. Included by such cyclic ethers are, for example, oxetanes such as 3,3-bis-chloromethyloxetane, alkoxyoxetanes as shown by Schroeter Patent 3,673,216, assigned to the same assignee as the present invention; oxolanes such as tetrahydrofuran, oxepanes, oxygen containing spiro compounds, trioxane, dioxolane, etc.

In addition to cyclic ethers, there are also included cyclic esters such as β-lactones, for example propiolactone, cyclic amines, such as 1,3,3-trimethyl-azetidine and organo-silicone cyclics, for example, materials included by the formula,



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where R" can be the same or different monovalent organic radical such as methyl or phenyl and p is an integer equal to 3 to 8 inclusive. An example of an organosilicone cyclic is hexamethyl trisiloxane, octamethyl tetrasiloxane, etc. The product made in accordance with the present invention are high molecular

weight oils and gums.

In particular instances, depending upon the compatability of the dialkylhydroxyarylsulfonium salt with the organic material, the sulfonium salt can be dissolved or dispersed in an organic solvent such as nitromethane, acetonitrile, methylene chloride, etc., prior to its incorporation into the organic material. Experience has shown that the proportion of sulfonium salt to organic material can vary widely inasmuch as the salt is substantially inert, unless activated.

In the practice of the invention, the curable compositions can be made by effecting contact between the dialkyl hydroxyarylsulfonium salt, the cationically polymerizable organic resin and the organic oxidant as previously defined. There can be used 0.1 to 10% by weight of the dialkyl hydroxyarylsulfonium salt based on the weight of cationically polymerizable organic material. In certain situations, a volatile organic solvent also can be utilized in combination with the aforementioned ingredients to produce a foam, based on the vaporization of the organic solvent due to the generation of exothermic heat of reaction while the cationically polymerizable organic resin is curing.

It has been found that contact between the various ingredients of the curable mixture of the present invention can be effected if the dialkylhydroxyarylsulfonium salt is contacted with the organic oxidant in the presence of the cationically polymerizable organic material. For example, the sulfonium salt can be combined with an epoxy resin to produce a stable mixture while the organic oxidant can separately be employed in combination with an epoxy resin which also has

infinite shelf stability. In instances where a foam is desired, a volatile organic solvent can be combined with either of the aforementioned stable mixtures or can be introduced separately during the mixing of the respective mixtures. Suitable volatile organic solvents which can be employed to produce rigid or flexible foams in the practice of the present invention are, for example, acetone, hexane, trichlorofluoromethane, n-pentane, 2-methylhexane, dichloromethane, 1,1,2-trichlorotrifluoroethane, methyl alcohol, ethyl alcohol, methyl ethyl ketone, etc. In addition to such volatile solvents, there are also included thermally unstable compounds such as ethylene carbonate, ammonium nitrite, benzoyl peroxide, cyclohexanone peroxide, methyl ethyl ketone peroxide, 2,2'-azobis(2-methylpropionitrile), azobisformamide, etc.

The foamable mixture can be injection molded into suitable receptacles, such as refrigerator doors and the like to provide for the production of insulating foams. Thorough mixing of the ingredients has been found to facilitate the production of a uniform foam which can be achieved by the employment of a mechanical stirrer or agitator, as generally utilized in the art.

In instances where a flexible foam is desired, the above described epoxy resin can be combined with polycaprolactones or any hydroxy terminated polyester or polyetherpolyol to render the foams made in accordance with the present invention more flexible. Typical hydroxy-terminated polycaprolactones are Niax polyols, manufactured by the Union Carbide Corporation. There can be utilized from 1 to 50 parts of the hydroxyterminated polyester per part of the epoxy resin and preferably from 1 to 10 parts. Included by the hydroxy-termin-

ated polyester which can be employed in the practice of the present invention to flexibilize cured epoxy resin films or foams are compounds of the formula,

$$H\text{---}\left(O\text{-}CH_2\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_4\overset{\overset{O}{\|}}{C}\right)_t\text{---}OH \quad ,$$

where t is an integer having an average value of from 1 to 100.

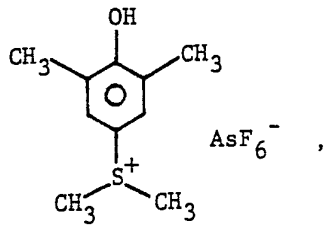
As previously indicated, the curable compositions of the present invention also can be used in coating applications and in the production of rigid or flexible films. In addition to the cationically polymerizable organic resin which includes any of the aforementioned epoxy resins, as well as the organic cyclics as previously defined, as well as additives, such as polycaprolactones for flexibilizing the films and foams made therefrom, there also can be combined with such ingredients fillers in a proportion by weight of from 0 to 500 parts of such filler per 100 parts of the cationically polymerizable organic resin. Suitable fillers include, for example, talc, alumina, sand, silica, ground quartz, wood flour, carbon black, glass fibers, mica, barium sulfate, titanium dioxide, etc.

In addition, the above curable compositions may include additives to enhance surface properties and to control foam cell size. Among such additives are polyalkylene oxide surfactants and silicone fluids.

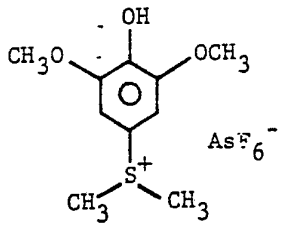
In order that those skilled in the art will be better able to practice the present invention, the following exampls are given by way of illustration and not by way of limitation. All parts are by weight.

Example 1.

Various dialkyl hydroxyarylsulfonium salts were used in combination with iodosobenzene diacetate as curing agents for 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexene carboxylate. The sulfonium salt was added to the respective mixtures at 3% by weight and the iodosobenzene diacetate was utilized at 6% by weight based on the total weight of the respective mixtures. The sulfonium salts used were dimethyl-4-hydroxy-3,5-dimethylphenylsulfonium hexafluoroarsenate of the formula,



and dimethyl-4-hydroxy-3,5-dimethoxyphenylsulfonium hexafluoroarsenate of the formula,



The respective mixtures were then stirred under ambient conditions and allowed to rest. Each of the mixtures gelled within three minutes to form a hard crosslinked mass.

Example 2.

A mixture of the epoxy resin of Example 1 and 3% by weight of dimethyl-4-hydroxy-3,5-dimethoxyphenylsulfonium hexafluoroarsenate was stirred with a peracetic acid solution in toluene containing about 0.5% by weight of cobalt napthanate. The mixture was then vigorously stirred and allowed to

stand under atmospheric conditions. There was obtained a hard crosslinked mass within 5 minutes.

Example 3.

Acetone was added to a mixture while it was stirred consisting of 3% by weight of dimethyl-4-hydroxy-3,5-dimethoxy phenylsulfonium hexafluoroarsenate, 6% by weight of iodosobenzene diacetate and about 91% by weight of 3,5-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate. The resulting mixturen containing 10% by weight of acetone was allowed to rest under atmospheric conditions. After 10 minutes there was obtained a low density rigid foam useful as a thermal insulator.

Example 4.

A mixture composed of 10 parts of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate, 0.15 part 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and 0.15 part of dimethyl-4-hydroxy-3,5-dimethoxyphenyl-sulfonium hexafluoroarsenate was rapidly stirred until the mixture became uniform. The mixture was then allowed to stand. The mixture thereafter turned an intense red color and it gelled after 5 minutes while generating exothermic heat of reaction.

Example 5.

There was added 1.5 part of iodosobenzene diacetate and 1.5 part of dimethyl-4-hydroxy-3,5-dimethoxy-phenylsulfonium hexafluoroarsenate to 10 parts diethyleneglycol divinyl ether. The mixture polymerized rapidly and cured to a hard polymeric mass within 8 minutes. The curable composition is useful as a potting resin.

Example 6.

The above example was repeated except triethyleneglycol divinyl ether was used as the cationically polymeriz-

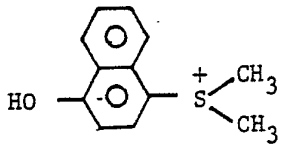
able organic material.

Example 7.

There was added 0.15 part of dimethyl-3,5-dimethyl-4-hydroxyphenylsulfonium hexafluoroarsenate and 0.15 part of 3-chloroiodosobenzene diacetate, to 5 parts of 4-vinylcyclohexene dioxide. The mixture was stirred until the ingredients were dissolved and then allowed to stand in the dark. A hard crosslinked product was obtained after 2 hours.

Example 8.

There were added 0.1 part of methyl ethyl ketone peroxide, as a 60% solution in dimethylphthalate (Lucidol Lupersal® DDM) and 0.01 part of cobalt napthenate (Mooney Chemicals 12% Cobalt Chem-all) to a mixture of 5 parts of 4-vinylcyclohexene dioxide and 0.15 part of the sulfonium salt



On standing for 8 hours, the resulting fluid mixture hardened.

Example 9.

A mixture of 10 parts of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carbonylate, 0.15 part of dimethyl-3,5-dimethoxy-4-hydroxyphenylsulfonium hexafluoroarsenate and 0.15 part of o-chloranil was allowed to rest under ambient conditions in the dark. After standing for 7 hours, the mixture converted to a hard solid. Those skilled in the art would know that the mixture would be useful as an encapsulating compound.

Example 10.

There were added 0.30 part of dimethyl-3,5-dimethoxy-4-hydroxyphenylsulfonium hexafluoroarsenate, 0.15 part of t-butylhydroperoxide and 0.005 part of copper napthenate (6.0% solution in mineral spirits) to 10 parts of 4-vinylcyclohexene dioxide. The mixture hardened spontaneously after standing for 8 hours in the dark at room temperature.

The above procedure was repeated, except that dimethyl-3,5-dimethyl-4-hydroxyphenylsulfonium hexafluoroarsenate was substituted for the above mentioned sulfonium catalyst. The same results were obtained. In addition, similar results were obtained when t-butylhydroperoxide was substituted with methylethyl ketone peroxide.

Example 11.

There were added 0.3 part dimethyl-3,5-dimethoxy-4-hydroxy phenylsulfonium hexafluoroarsenate, 0.1 part of diphenylamine and 0.3 part of 40% peracetic acid to 10 parts of ERL 4221 (3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate). An immediate exothermic reaction resulted followed by gellation of the epoxy resin.

Example 12.

The above procedure was repeated, except that the Epon 828, a diglycidyl ether of 4,4'-isopropylidine diphenol was used as the epoxy resin. It was found that the mixture gelled in 5 hours. Those skilled in the art would know that the formulation was useful as an adhesive or encapsulating resin.

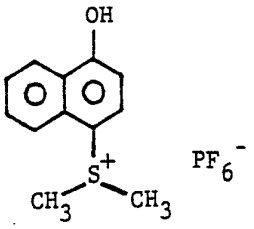
Example 13.

There were added 0.3 part of dimethyl-3-methyl-4-hydroxyphenylsulfonium hexafluoroarsenate, 0.02 part of

diphenylamine and 0.3 part of 40% peracetic acid to 10 parts of Methylon resin (a phenol-novolak resole made by the General Electric Company). The mixture hardened to the insoluble cured state on standing for 15 hours.

Example 14.

A mixture consisting of 100 parts Epon 828, 0.2 part of diphenylamine and 6 parts of 40% peracetic acid was combined with 3 parts of



The mixture was stirred and then poured into a 6 in. x 3/4 in. x 1/4 in. silicone rubber mold. On standing for 8 hours, a hard crosslinked molded part was obtained.

Although the above examples are directed to only a few of the compositions of the present invention, it should be understood that the present invention is directed to a much broader class of curable compositions and method for making foams as shown by the description preceding these examples.

Claims

1. Curable Compositions comprising

(A) cationically polymerizable organic material, and

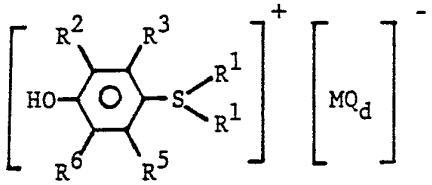
(B) an effective amount of a curing agent consisting essentially of dialkylhydroxyarylsulfonium salt of the formula,

$$[R\ (R^1)_a\ S]^+[Y]^-\ ,$$

and an organic oxidant selected from iodoso-aromatic organic compounds, quinones and organic peroxides having a decomposition accelerator selected from organic amines and transition metals,

where R is a $C_{(6-20)}$ aromatic radical having from 1 to 3 nuclearly bonded hydroxy radicals, R^1 can be the same or different $C_{(1-8)}$ alkyl radical or an alkylene radical capable of forming a cycloaliphatic or heterocyclic ring, Y is a non-nucleophilic anion, a is an integer equal to 1 or 2, and when R^1 is alkyl, a is 2, and when R^1 is alkylene, a is 1.

2. A curable composition in accordance with claim 1, where the dialkylhydroxyarylsulfonium salt has the formula,



where R^1 is a $C_{(1-8)}$ alkyl radical, M is a metal or metalloid, Q is a halogen radical, R^2-R^6 are monovalent radicals selected

from hydrogen, $C_{(1-8)}$ alkyl, $C_{(1-8)}$ alkoxy, nitro, and chloro, and d is an integer equal to 4-6 inclusive.

3. A curable composition in accordance with claim 1, where the sulfonium salt is dimethyl-4-hydroxyl-3,5-dimethylphenylsulfonium hexafluoroarsenate.

4. A curable composition in accordance with claim 1, where the cationically polymerizable organic material is an epoxy resin.

5. A curable composition in accordance with claim 1, where the organic oxidant is iodosobenzene diacetate.

6. A curable composition in accordance with claim 1, where the cationically polymerizable material is a vinyl ether.

7. A curable composition in accordance with claim 1, where the cationically polymerizable material is a phenol-novolak resole.

8. A curable composition in accordance with claim 1, where the organic oxidant is a quinone.

9. A curable composition in accordance with claim 1, where the organic oxidant is an organic amine accelerated organic peroxide.

10. A curable composition in accordance with claim 1, where the organic oxidant is a transition metal compound accelerated organic peroxide.

11. A foaming method which comprises,

(1) agitating a curable composition comprising

(C) a cationically polymerizable organic material,

(D) an effective amount of a curing agent consisting essentially of a dialkylhydroxyarylsulfonium salt of the formula,

$$[R\ (R^1)_a\ S]^+[Y]^-\ ,$$

and an organic oxidant selected from an iodosoaromatic compound, a hydroquinone, and an organic peroxide having a decomposition accelerator selected from an organic amine and compound of a transition metal, and

(E) 1% to 30% by weight of (C), (D) and (E) of a volatile inert organic solvent, and

(2) thereafter allowing the ingredients of the resulting mixtures to react resulting in the production of exothermic heat and the simultaneous evaporation of the organic solvent and the cure of the cationically polymerizable organic resin,

where R is a $C_{(6-20)}$ aromatic radical having from 1 to 3 nuclearly bonded hydroxy radicals, R^1 can be the same or different $C_{(1-8)}$ alkyl radical or an alkylene radical capable of forming a cycloaliphatic or heterocyclic ring, Y is a non-nucleophilic anion, a is an integer equal to 0 or 2, and when R^1 is alkyl, a is 2, and when R^1 is alkylene, a is 1.

12. A method in accordance with claim 7, where the volatile organic solvent is acetone.

13. A method in accordance with claim 7, where the cationically polymerizable organic material is an epoxy resin.

14. A method in accordance with claim 7, where the iodoso aromatic compound is iodosobenzene diacetate.

AMENDED CLAIMS
(received by the International Bureau on 20 May 1980 (20.05.80))

1. Heat curable compositions comprising

(A) cationically polymerizable organic material, and

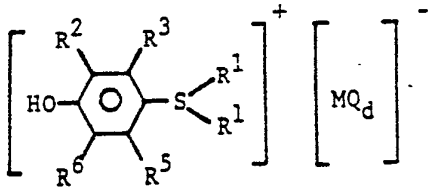
(B) an effective amount of a curing agent consisting essentially of 0.1 to 10% by weight of (A) of a dialkylhydroxyarylsulfonium salt of the formula,

$$[R\ (R^1)_a\ S]^+\ [Y]^-\ ,$$

and 0.1 to 10% by weight of the heat curable composition of an organic oxidant selected from iodosoaromatic organic compounds, and organic peroxides having 0.1 to 50% by weight of organic peroxide of a decomposition accelerator selected from organic amines and transition metals,

where R is a $C_{(6-20)}$ aromatic radical having from 1 to 3 nuclearly bonded hydroxy radicals, R^1 can be the same or different $C_{(1-8)}$ alkyl radical or an alkylene radical capable of forming a cycloaliphatic or heterocyclic ring, Y is a non-nucleophilic anion, a is an integer equal to 0 or 2, and when R^1 is alkyl, a is 2, and when R^1 is alkylene, a is 1.

2. A curable composition in accordance with Claim 1, where the dialkylhydroxyarylsulfonium salt has the formula,



where R^1 is a $C_{(1-8)}$ alkyl radical, M is a metal or metalloid, Q is a halogen radical, R^2-R^6 are monovalent radicals selected from hydrogen, $C_{(1-8)}$ alkyl, $C_{(1-8)}$ alkoxy, nitro, and chloro, and d is an integer equal to 4-6 inclusive.

3. A curable composition in accordance with Claim 1, where the sulfonium salt is dimethyl-4-hydroxyl-3,5-dimethylphenyl-sulfonium hexafluoroarsenate.

4. A curable composition in accordance with Claim 1, where the cationically polymerizable organic material is an epoxy resin.

5. A curable composition in accordance with Claim 1, where the organic oxidant is iodosobenzene diacetate.

6. A curable composition in accordance with Claim 1, where the cationically polymerizable material is a vinyl ether.

7. A curable composition in accordance with Claim 1, where the cationically polymerizable material is a phenol-novolak resole.

8. Heat curable compositions comprising

(C) cationically polymerizable organic material,

and

(D) 0.1 to 10% by weight of the cationically polymerizable organic material of a dialkylhydroxyarylsulfonium salt of the formula,

$$[R\ (R^1)_a\ S]^+[Y]^-\ ,$$

and 0.1 to 10% by weight of the heat curable composition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone,

where R is a $C_{(6-20)}$ aromatic radical having from 1 to 3 nuclearly bonded hydroxy radicals, R^1 can be the same or different $C_{(1-8)}$ alkyl radical or an alkylene radical capable of forming a cycloaliphatic or heterocyclic ring, Y is a non-nucleophilic anion, a is an integer equal to 1 or 2, and when R^1 is alkyl, a is 2, and when R^1 is alkylene, a is 1.

9. A curable composition in accordance with Claim 1, where the organic oxidant is an organic amine accelerated organic peroxide.

10. A curable composition in accordance with Claim 1, where the organic oxidant is a transition metal compound accelerated organic peroxide.

11. A foaming method which comprises,

(1) agitating a curable composition comprising

(C) a cationically polymerizable organic material,

(D) an effective amount of a curing agent consisting essentially of a dialkylhydroxyarylsulfonium salt of the formula,

$$[R\ (R^1)_a\ S]^+[Y]^-\ ,$$

and an organic oxidant selected from an iodosoaromatic compound, a hydroquinone, and an organic peroxide having a decomposition accelerator selected from an organic amine and compound of a transition metal, and

(E) 1% to 30% by weight of (C), (D) and (E) of a volatile inert organic solvent, and

(2) thereafter allowing the ingredients of the resulting mixtures to react resulting in the production of exothermic heat and the simultaneous evaporation of the organic solvent and the cure of the cationically polymerizable organic resin,

where R is a $C_{(6-20)}$ aromatic radical having from 1 to 3 nuclearly bonded hydroxy radicals, R^1 can be the same or different $C_{(1-8)}$ alkyl radical or an alkylene radical capable of forming a cycloaliphatic or heterocyclic ring, Y is a non-nucleophilic anion, a is an integer equal to 0 or 2, and when R^1 is alkyl, a is 2, and when R^1 is alkylene, a is 1.

12. A method in accordance with Claim 11, where the volatile organic solvent is acetone.

13. A method in accordance with Claim 11, where the cationically polymerizable organic material is an epoxy resin.

14. A method in accordance with Claim 11, where the iodoso aromatic compound is iodosobenzene diacetate.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US80/00096

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. 3-C08J9/00
US CL; 521/113, 121, 128, 149, 178, 181; (continued)

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	521/113, 121, 128, 149, 178, 181; 526/193, 208, 212, 222, 227, 332; 528/89, 90, 143, 408

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A, 3,412,046 PUBLISHED 19 NOVEMBER 1968 PAYNE	1-14
A	US, A, 4,058,400 PUBLISHED 15 NOVEMBER 1977 CRIVELLO	1-14
A	US, A, 4,058,401 PUBLISHED 15 NOVEMBER 1977 CRIVELLO	1-14
A	US, A, 4,069,054 PUBLISHED 17 JANUARY 1978 SMITH	1-14
A	POLYMER, VOL. 19, OCTOBER, 1978, ABDUL-RASOUL et al., pages 1219-1222	1-14

* Special categories of cited documents: [15]

"A" document defining the general state of the art
"E" earlier document but published on or after the international filing date
"L" document cited for special reason other than those referred to in the other categories
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but on or after the priority date claimed
"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention
"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
5 March 1980	18 APR 1980
International Searching Authority [1]	**Signature of Authorized Officer** [20]
ISA/US	M. Foelak

Form PCT/ISA/210 (second sheet) (October 1977)

INTERNATIONAL SEARCH REPORT

International Application No PCT/US80/00096

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

(Continued...) 526/193, 208, 212, 222, 227, 332; 528/89, 90, 143, 408

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols

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Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

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International Searching Authority [1]	Signature of Authorized Officer [20]
	M. Foelak

Form PCT/ISA/210 (second sheet) (October 1977)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers....., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers....., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

GROUP I Claims 1-10 directed to curable compositions

GROUP II Claims 11-14 directed to a method of foaming
SEE FORM PCT/ISA/206 for reasons

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.