



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ³: G03C 1/68	A1	(11) International Publication Number: WO 80/01723 (43) International Publication Date: 21 August 1980 (21.08.80)
(21) International Application Number: PCT/US80/00097 (22) International Filing Date: 1 February 1980 (01.02.80) (31) Priority Application Number: 011,102 (32) Priority Date: 12 February 1979 (12.02.79) (33) Priority Country: US (71) Applicant: GENERAL ELECTRIC COMPANY [US/-US]; 1 River Road, Schenectady, NY 12345 (US). (72) Inventor: CRIVELLO, James, Vincent; R.D.No.1 Carlton Road, Clifton Park, NY 12065 (US). (74) Agents: CECCON, Clario; General Electric Company, 570 Lexington Avenue, New York, NY 10022 (US) et al.		(81) Designated States: BR, DE (European patent), FR (European patent), GB (European patent), JP, NL (European patent). Published <i>With international search report</i> <i>With amended claims</i>
(54) Title: HEAT CURABLE COMPOSITIONS (57) Abstract Heat curable compositions are provided comprising cationically polymerizable organic materials such as epoxy resins, vinyl ethers or phenol formaldehyde resins and thermal curing agents, based on the use of dialkyl hydroxyarylsulfonium salts with an organic oxidant, such as an organic peroxide, azonitriles, etc. The heat curable compositions can be used as injection molding compounds or as a coating composition.		

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DescriptionHEAT CURABLE COMPOSITIONSCross Reference to Related Applications

RD-11473, for Curable Organic Resin Compositions, Foam-
Method and Organic Foams, 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
5 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,
10 for Heat Curable Epoxy Compositions and Method for Curing Same,
now abandoned, copending application Serial No. 940,564, filed
Sept. 8, 1978 for Heat Curable Compositions and Method of Cur-
ing Same which is a continuation-in-part of copending applica-
tion Serial No. 841,351, filed October 12, 1977, for Heat Cur-
15 able 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 appli-
cations are assigned to the same assignee as the present inven-
tion.

Background of the Invention

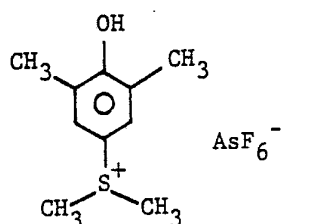
The present invention relates to heat curable compos-
itions comprising a cationically polymerizable organic material,
for example, an epoxy resin, a dialkyl hydroxyarylsulfonium
salt and an organic oxidant.

25 As shown in my copending application Serial No.
940,564, for Heat Curable Compositions and Method for Curing
Same, filed September 8, 1978 and assigned to the same assignee
as the present invention, organic resins, for example, epoxy



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resins can be thermally cured by using an effective amount of an aromatic onium salt such as an aryl iodonium salt and a reducing agent, for example, a thiophenol. The present invention is based on the discovery that such organic resin also can be thermally cured with an organic oxidant, such as an organic peroxide in combination with an effective amount of certain hydroxyaryldialkyl sulfonium salts, for example,



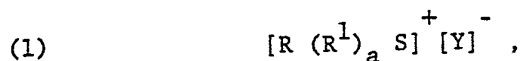
dimethyl-4-hydroxy-3,5-dimethylphenyl sulfonium hexafluoroarsenate.

Statement of the Invention

There is provided by the present invention, heat curable compositions comprising

- (A) a cationically polymerizable organic material,
- (B) an effective amount of a thermal curing agent consisting essentially of an organic oxidant and a dialkyl hydroxy aryl sulfonium salt.

Included by the dialkylhydroxyarylsulfonium salts which can be used in the practice of the present invention are compounds having the formula,



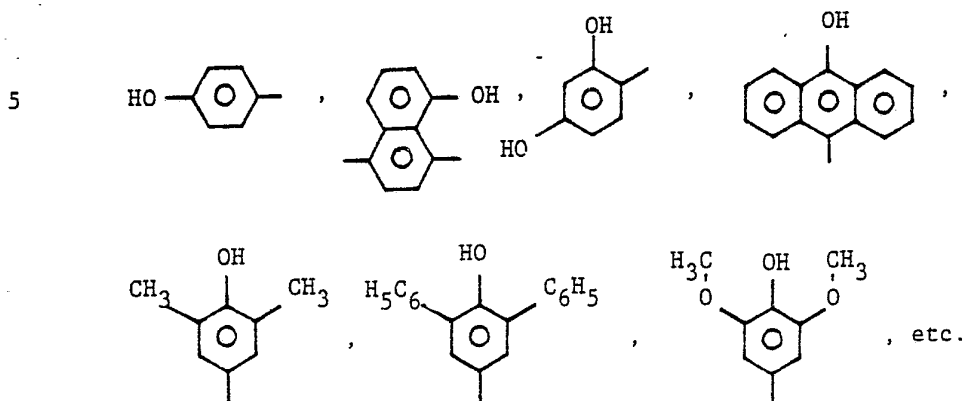
where R is a C₍₆₋₂₀₎ aromatic radical having from 1 to 3 nuclearly bonded hydroxy radicals, R¹ can be the same or different C₍₁₋₈₎ alkyl radical or an alkylene radical capable of forming a cycloaliphatic or heterocyclic ring, Y is a non-nucleo-



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philic 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.

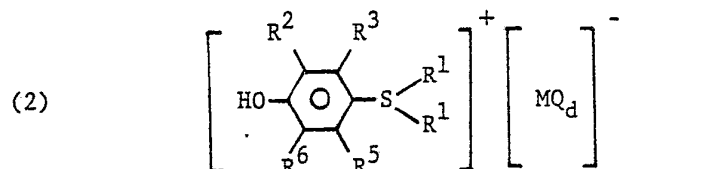
Radicals included by R of formula (1) are, for example,



R^1 radicals include CH_3- , $-C_4H_9-$, C_2H_5- , CH_3O- , $(CH_3)_3C-$, $C_6H_5CH_2-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-CH_2-CH_2-O-CH_2-CH_2-$, $-CH_2-CH_2-S-CH_2-CH_2-$, etc.

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Preferably, the salts included by formula (1), are

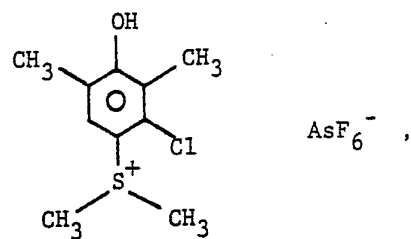
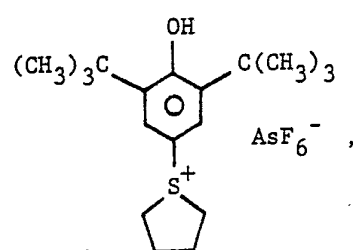
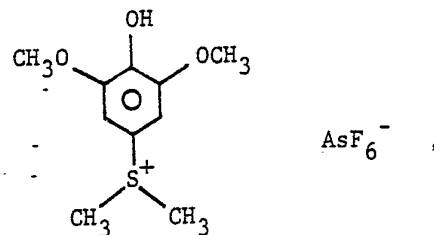
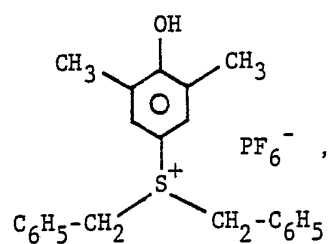
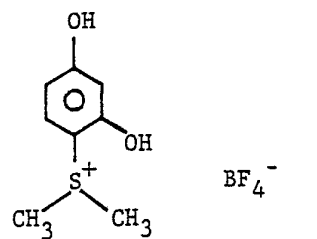
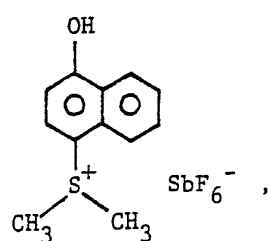
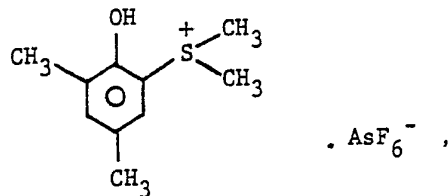
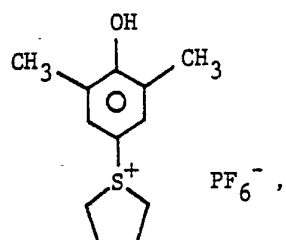


where R^1 , M , Q and d are as previously defined, and R^2-R^6 are monovalent radicals selected from hydrogen, $C_{(1-8)}$ alkyl, $C_{(1-8)}$ alkoxy, nitro, chloro, etc.

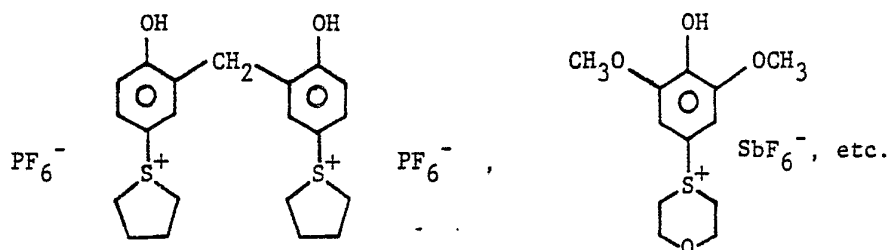
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Dialkyl hydroxyphenylsulfonium salts included by formulas (1) and (2) are,

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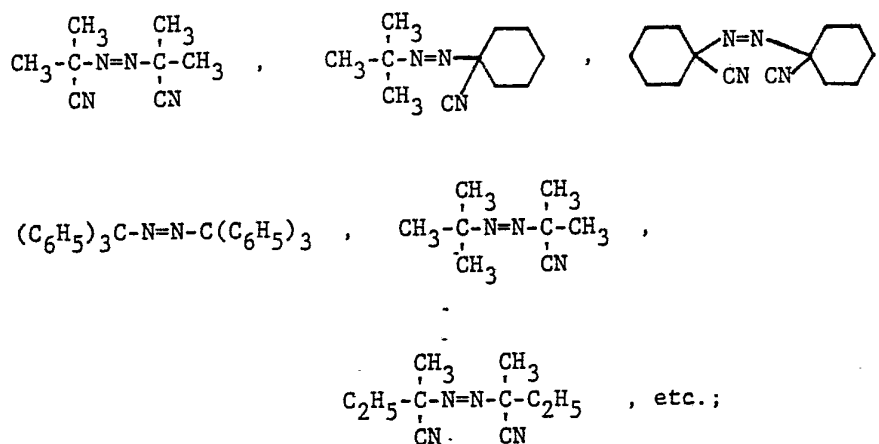
Methods for making some of the dialkyl hydroxy aryl sulfonium salts of formulas (1) and (2) are shown in U.S. patents 4,058,400 and 4,058,401, and in my copending applications Serial Number 833,146, filed September 14, 1977 and Serial Number 954,196, filed October 24, 1978.

Organic oxidants which can be used in the practice of the invention in combination with the dialkylhydroxy arylsulfonium salts of formulas 1 and 2 to effect the cure of the cationically polymerizable organic material are, for example, organic peroxides such as ketone peroxides, peroxy acids, dibasic acid peroxides, aldehyde peroxides, alkyl peroxides, hydroperoxides, alkyl peroxyesters, diperoxide derivatives, for example, t-butyl peroxyphthalate, 2,4-dichlorobenzoyl peroxide, caprylyl peroxide, lauroyl peroxide, decanoyl peroxide, propionyl peroxide, acetyl peroxide, t-butyl peroxyisobutyrate, p-chlorobenzoyl peroxide, benzoyl peroxide, hydroxyheptyl peroxide, cyclohexanone peroxides, 2,5-dimethylhexyl-2,5-di(peroxybenzoate), di-t-butyl diperphthalate, t-butyl peracetate, t-butyl-

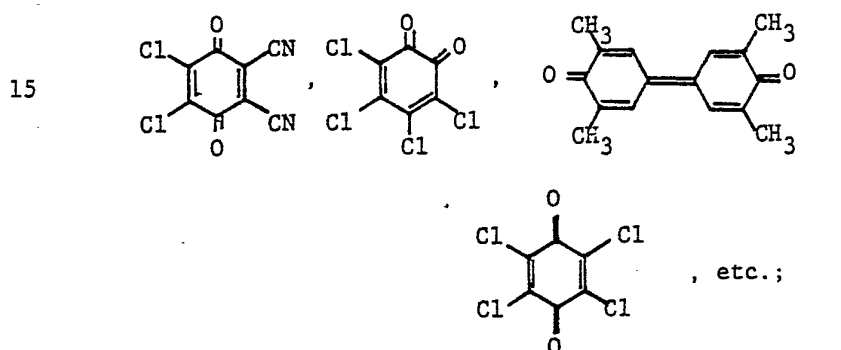
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perbenzoate, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butyl-
peroxy)hexane, t-butyl hydroperoxide, di-t-butyl peroxide,
methyl ethyl ketone peroxide, p-methane hydroperoxide, cumene
hydroperoxide, 2,5-dimethylhexyl-2,5-dihydroperoxide, t-butyl
5 hydroperoxide, peracetic acid, perbenzoic acid, m-chloroper-
benzoic acid, etc.

In addition to organic peroxides, organic oxidants
which also can be used in the practice of the invention
include azo-bis alkyl nitriles and other azo zompounds, such
10 as



quinones, such as



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iodoso aromatic compounds, such as iodosobenzene, 4-nitroiodosobenzene, iodosobenzene diacetate, 4-chloriodosobenzene, 4-methoxyiodosobenzene, 4-iodosobiphenyl, 2-chloriodosobenzene diacetate, etc.

5 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.

10 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
15 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
20 diluent as phenyl glycidyl ether, 4-vinylcyclohexene dioxide, limonene dioxide, 1,2-cyclohexene oxide, glycidyl acrylate, glycidyl methacrylate, styrene oxide, allyl glycidyl ether, etc., may be added as viscosity modifying agents.

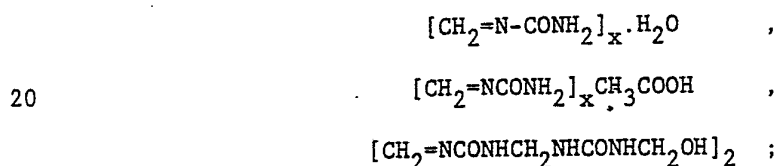
 In addition, the range of these compounds can be
25 extended to include polymeric materials containing terminal or pendant epoxy groups. Examples of these compounds are vinyl copolymers containing glycidyl acrylate or methacrylate as one of the comonomers. Other classes of epoxy containing polymers amenable to cure using the above catalysts are epoxy-



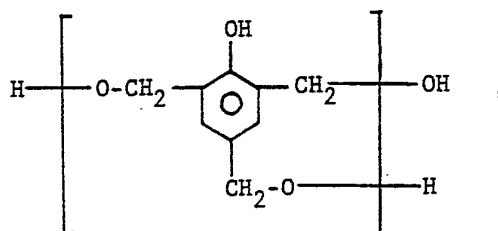
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siloxane resins, epoxy-polyurethanes and epoxy-polyesters. Such polymers usually have epoxy functional groups at the ends of their chains. Epoxy-siloxane resins and method for making are more particularly shown by E. P. Plueddemann and G. Fanger, J. 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 hydroxyl terminated polyethers, hydroxy terminated polyesters, etc., shown in the Encyclopedia of Polymer Science and Technology, Vol. 6, 1967, Interscience Publishers, New York, pp. 209-271 and particularly p. 238.

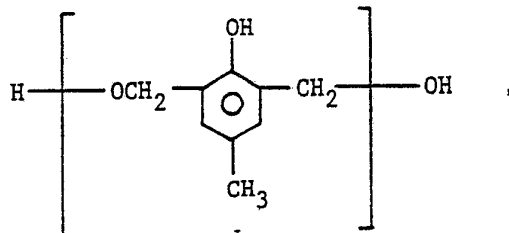
Included by the thermosetting organic condensation resins of formaldehyde which can be used in the practice of the present invention are, for example, urea type resins, such as



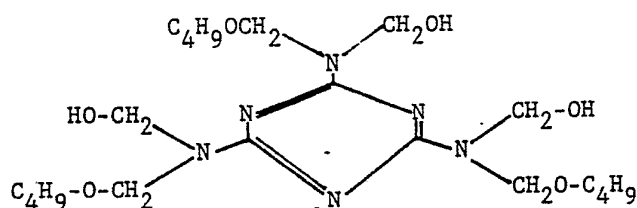
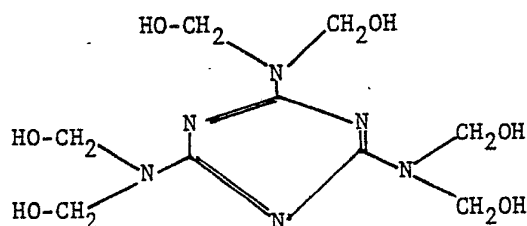
phenol-formaldehyde type resin, such as



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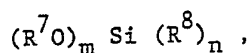


where x and n are integers having a value of 1 or greater;



, etc.

5 alkoxy silanes having the formula,



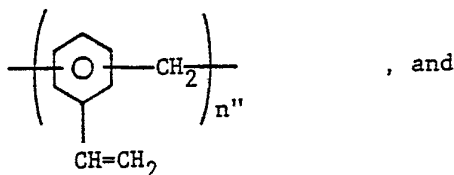
where R^7 is a $\text{C}_{(1-7)}$ alkyl radical, R^8 is selected from R^7 radicals and $\text{C}_{(6-13)}$ aryl radicals and halogenated derivatives,
 10 m is an integer equal to 1 to 4, n is an integer equal to 0 to 3 inclusive and $m + n$ is equal to 4.

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 poly-
 15 sulfides.



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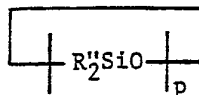
Some of the vinyl organic prepolymers which can be used to make the polymerizable compositions of the present invention are, for example, $\text{CH}_2=\text{CH}-\text{O}-(\text{CH}_2-\text{CH}_2\text{O})_{n'}-\text{CH}=\text{CH}_2$, where n' is a positive integer having a value up to about 1000 or higher; multi-functional vinyl ethers, such as 1,2,3-propane trivinylether, trimethylolpropane trivinylether, prepolymers having the formula,



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,



where R'' can be the same or different monovalent organic radical

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such as methyl or phenyl and p is an integer equal to 3 to 8 inclusive. An example of an organosilicon cyclic is hexamethyl trisiloxane, octamethyl tetrasiloxane, etc. The products made in accordance with the present invention are high molecular weight oils and gums.

The heat curable compositions of the present invention can be made by blending the cationically polymerizable organic material with an effective amount of the thermal curing agent. There can be used 0.1 to 10 percent by weight of the dialkyl hydroxyarylsulfonium salt based on the weight of cationically polymerizable organic material. With respect to the combination of organic oxidant and dialkylhydroxyarylsulfonium salt, there can be used from 1 to 100 parts of organic oxidant, per part of dialkyl hydroxy arylsulfonium salt.

The resulting curable composition can be in the form of a varnish having a viscosity of from 1 to 100,000 centipoises at 25°C or a free flowing powder, depending upon the nature of the cationically polymerizable organic material. The curable compositions can be applied to a variety of substrates by conventional means and cured to the tack-free state within 0.5 to 20 minutes, depending upon the temperature employed.

In certain instances, an organic solvent, such as nitromethane, acetonitrile, can be used to facilitate the mixing of various ingredients. The dialkyl hydroxy arylsulfonium salts can be formed in situ if desired. In addition, the curable compositions may contain inactive ingredients, such as silica, talc, clay, glass fibers, extenders, hydrated alumina, carbon fiber process aids, etc., in amounts of up to 500 parts of filler per 100 parts of cationically polymerizable organic



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material. The curable compositions can be applied to such substrates as metal; rubber, plastic, molded parts or films, paper, wood, glass, cloth, concrete, ceramic, etc.

5 Some of the applications in which the curable compositions of the present invention can be used are, for example, protective, decorative and insulating coatings, potting compounds, printing inks, sealants, adhesives, molding compounds, wire insulation, textile coatings, laminates, impregnated tapes, varnishes, etc.

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

Example 1.

15 A mixture of three parts of dimethyl-4-hydroxy-3,5-dimethoxyphenyl sulfonium hexafluoroarsenate, three parts of benzoylperoxide and 94 parts of Shell Epon 828, a diglycidyl ether of bisphenol-A, was stirred and heated to 160°C. The mixture gelled and hardened within 2.5 minutes.

20 Example 2.

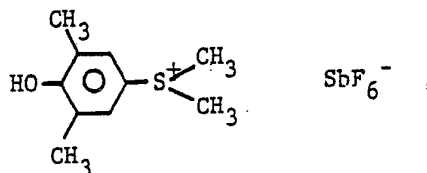
The procedure of Example 1 was repeated, except that Celanese SU8, epoxy novolak resin was substituted for the diglycidyl ether bisphenol-A epoxy resin. The resulting heat curable composition required eight minutes to harden at 120°C.

25 Example 3.

A series of mixtures were prepared utilizing 100 parts of 3,4-epoxycyclohexylmethyl-3,4-epoxy cyclohexane carboxylate, 3 parts of a hexafluoroantimonate salt of the formula,



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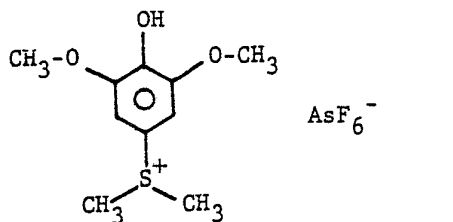
and 3 parts of various organic oxidants. The mixtures were then heated to 130°C to determine gel times. The following results were obtained:

5	<u>Organic oxidant</u>	<u>Gel Time</u>
	None	>7 min.
	benzoyl peroxide	1 min., 30 sec.
	cumene hydroperoxide	2 min., 50 sec.
	2,3-dichloro-5,6-dicyano-quinone	40 sec.
10	azo-bisisobutyronitrile	6 min. 15 sec.
	lauroyl peroxide	4 min. 5 sec.

Example 4.

In accordance with the procedure of Example 3, heat curable mixtures were prepared utilizing 100 parts of ERL 4221 (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxy-

15 late), 3 parts of



and 3 parts of various organic oxidants. The mixtures were heated to 150°C to determine when the mixtures changed from a fluid condition to the solid cured state. The following

20 results were obtained:



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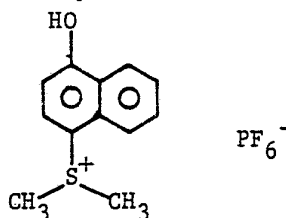
<u>Organic oxidant</u>	<u>Gel Time</u>
None	25 min.
methylethyl ketone peroxide	11 min.
t-butyl hydroperoxide	3 min.

5 Example 5.

A mixture composed of 100 parts of 1,4-butanediol diglycidyl ether, 3 parts of t-butyl hydroperoxide and 3 parts of dimethyl-3,5-dimethoxy-4-hydroxyphenylsulfonium hexafluoro-arsenate was heated at 150°C. The mixture cured to a hard crosslinked resin after 18 minutes. The same mixture free of the t-butyl hydroperoxide did not gel after it was heated for 60 minutes at 140°C.

10 Example 6.

Mixtures were prepared having 100 parts of diethyleneglycol divinyl ether and 3 parts of

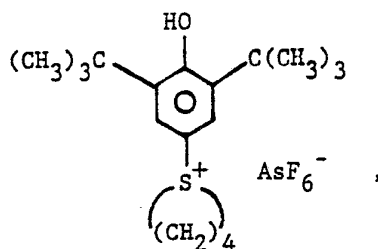


There was added 3 parts of t-butyl hydroperoxide to one of the mixtures. Both mixtures were thoroughly stirred and then heated to 140°C. The mixture containing the peroxide cured after 5 minutes, while the mixture free of peroxide required 15 minutes to cure to a tack-free condition.

20 Example 7.

Mixtures of 100 parts of Methylon[®] resin (a phenol-formaldehyde resole of the General Electric Company) and 3 parts of

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were thoroughly stirred. There was added 3 parts of t-butyl hydroperoxide to one of the mixtures. The mixtures were then heated at 150°C. The mixture having the t-butyl hydroperoxide cured to a hard crosslinked insoluble resin. The mixture free of the organic oxidant remained substantially unchanged.

Although the above examples are directed to only a few of the very many heat curable compositions included by the present invention, it should be understood that the present invention includes a much broader class of heat curable material as shown by the description preceding these examples.

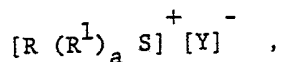
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Claims

1. Heat curable compositions comprising
 - (A) a cationically polymerizable organic material
 - (B) an effective amount of a thermal curing agent consisting essentially of an organic oxidant and a dialkyl hydroxyl arylsulfonium salt.

5

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



10

where R is a C₍₆₋₂₀₎ aromatic radical having from 1 to 3 nuclearly bonded hydroxy radicals, R¹ 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 R¹ is alkyl, a is 2, and when R¹ is alkylene, a is 1.

15

3. A heat curable composition in accordance with claim 2, where Y has the formula,



and M is a metal or metalloid, Q is a halogen radical and d is an integer equal to 4-6 inclusive.

5

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

5. A heat curable composition in accordance with claim 1, where the organic oxidant is benzoyl peroxide.

6. A heat curable composition in accordance with claim 4, where the dialkyl hydroxylarylsulfonium salt is dimethyl-4-hydroxy-3,5-dimethoxyphenylsulfonium hexafluoro-



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arsenate.

7. A heat curable composition in accordance with claim 1, where the cationically polymerizable organic material is a phenolformaldehyde resin.

8. A heat curable composition in accordance with claim 1, where the cationically polymerizable organic material is a diglycidyl ether of bisphenol-A.

9. A heat curable composition in accordance with claim 1, where the cationically polymerizable organic material is a divinyl ether.

10. A heat curable composition in accordance with claim 1, where the dialkylhydroxyarylsulfonium salt is dimethyl-4-hydroxy-3,5-dimethylphenylsulfonium hexafluoroantimonate.



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AMENDED CLAIMS

(received by the International Bureau on 9 June 1980 (09.06.80))

1. Heat curable compositions comprising
 - (A) a cationically polymerizable organic material
 - (B) an effective amount of a thermal curing agent capable of effecting the cure of the cationically polymerizable organic material consisting essentially of an organic oxidant selected from the class consisting of organic peroxides, azo-bis-alkyl-nitriles, and quinones selected from the class consisting of p-chloranil and 3,3',-5,5'-tetramethyl-4,4'-diphenoquinone and a dialkyl hydroxyl arylsulfonium salt having an anion of the formula,



where M is a metal or metalloid, Q is a halogen radical and d is an integer equal to 4-6 inclusive.

2. A heat curable composition in accordance with claim 1, where the cationically polymerizable organic material is an epoxy resin.
3. A heat curable composition in accordance with claim 1, where the organic oxidant is benzoyl peroxide.
4. A heat curable composition in accordance with claim 2, where the dialkyl hydroxylaryl-sulfonium salt is dimethyl-4-hydroxy-3,5-dimethoxyphenylsulfonium hexa-fluoro arsenate.
5. A heat curable composition in accordance with claim 1, where the cationically polymerizable organic material is a phenolformaldehyde resin.



6. A heat curable composition in accordance with claim 1, where the cationically polymericable organic material is a diglycidyl ether of bisphenol-A.

7. A heat curable composition in accordance with claim 1, where the cationically polymerizable organic material is a divinyl ether.

8. A heat curable composition in accordance with claim 1, where the dialkylhydroxyarylsulfonium salt is dimethyl-4-hydroxy-3,5-dimethylphenylsulfonium hexafluoroantimonate.

9. (Cancelled)

10. (Cancelled)



INTERNATIONAL SEARCH REPORT

62/01723

International Application No

PCT/US80/00097

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-G03C 1/68

US CL. 526/193, 208, 212, 222, 227, 332; 528/89, 90, 143, 408

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System

Classification Symbols

US

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	1-10
A	US, A, 4,058,400 PUBLISHED 15 NOVEMBER 1977 CRIVELLO	1-10
A	US, A, 4,058,401 PUBLISHED 15 NOVEMBER 1977 CRIVELLO	1-10
A	US, A, 4,102,687 PUBLISHED 25 JULY 1978 CRIVELLO	1-10
A	US, A, 4,108,747 PUBLISHED 22 AUGUST 1978 CRIVELLO	1-10
A P	US, A, 4,154,872 PUBLISHED 15 MAY 1979 TSAD ET AL	1-10
A P	US, A, 4,161,405 PUBLISHED 17 JULY 1979 CRIVELLO	1-10
A	POLYMER, VOL. 19, OCTOBER, 1978 ABDUL-RASOUL ET AL, PAGES 1219-1222	1-10

^{*} Special categories of cited documents: ¹⁶

"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

05 MARCH 1980

Date of Mailing of this International Search Report ²

17 APR 1980

International Searching Authority ¹

ISA/US

Signature of Authorized Officer ²⁰

MORTON FOELAK