

HEAT CURABLE COMPOSITIONS AND  
METHOD OF CURING SAME

The present invention relates to heat curable cationically polymerizable organic materials, such as an epoxy resin, cyclic ether, phenol-formaldehyde resin, which use an aromatic onium salt initiator, which is an aromatic halonium salt, or a Group Va or Group VIa onium salt in further combination with a reducing agent, such as a dicyclopentadienyl iron.

The heat curable compositions of the present invention comprise (A) a cationically polymerizable organic material, (B) from 0.5% to 25% by weight of (A) of a reducing agent and (C) from 0.1% to 15% by weight of the heat curable composition of an aromatic onium salt selected from the class consisting of aromatic halonium salts, Group Va onium salts and Group VIa onium salts.

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Aromatic onium salts can be employed as photoinitiators to effect the cure of an epoxy resin.

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Epoxy resins also can be heat cured without the use of radiant energy if desired. However, the heat cure of the

epoxy resin employing the aforescribed aromatic onium salts was considerably slower than by using a source of radiant energy, such as ultraviolet light. It has now been discovered that considerably faster heat cures of epoxy resins as well as a wide variety of other cationically polymerizable organic materials can be obtained using aromatic onium salts if the aromatic onium salt is used in combination with a reducing agent.

The aromatic onium salts as used in the practice of the present invention, are included within the formula,

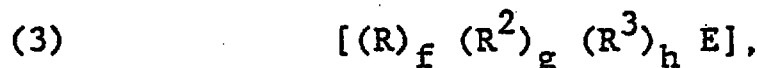


where J is a non-nucleophilic counterion defined more particularly below, and Y is a cation selected from

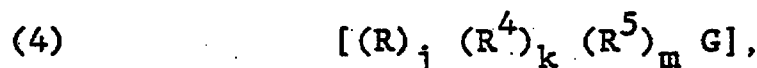
                     an aromatic halonium cation,



an aromatic Group Va cation,



and an aromatic Group VIa cation,



where R is a monovalent aromatic organic radical,  $R^1$  is a divalent aromatic organic radical,  $R^2$  and  $R^4$  are monovalent organic aliphatic radicals selected from alkyl, cyclo alkyl and substituted alkyl,  $R^3$  and  $R^5$  are polyvalent organic radicals forming a heterocyclic or fused ring structure selected from aliphatic radicals and aromatic radicals with E or G, D is Cl, Br or F,                      E is a Group Va element selected from N, P, As, Sb and Bi, G is a Group VIa element selected

from S, Se and Te,

"a" is <sup>0 or 2</sup> ~~a whole number equal to 0 or 2,~~

"b" is <sup>0 or 1</sup> ~~a whole number equal to 0 or 1~~

and the sum of "a" + "b" is <sup>ew</sup> ~~equal to~~

2 or the valence of D,

"f" is <sup>0, 1, 2, 3, or 4</sup> ~~a whole number equal to 0 to 4 inclusive,~~

"g" is <sup>0, 1 or 2</sup> ~~a whole number equal to 0 to 2 inclusive,~~

"h" is <sup>0, 1 or 2</sup> ~~a whole number equal to 0 to 2 inclusive,~~

and the sum of "f" + "g" + "h" is <sup>ew</sup> ~~a value~~

~~equal to~~ 4 or the valence of E,

"j" is <sup>0, 1, 2 or 3</sup> ~~a whole number equal to 0 to 3 inclusive,~~

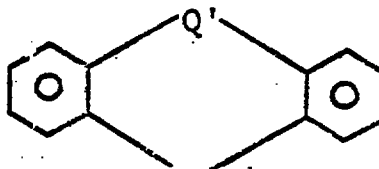
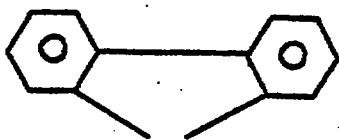
"k" is <sup>0, 1 or 2</sup> ~~a whole number equal to 0 to 2 inclusive, and~~

"m" is <sup>0 or 1</sup> ~~a whole number equal to 0 or 1,~~

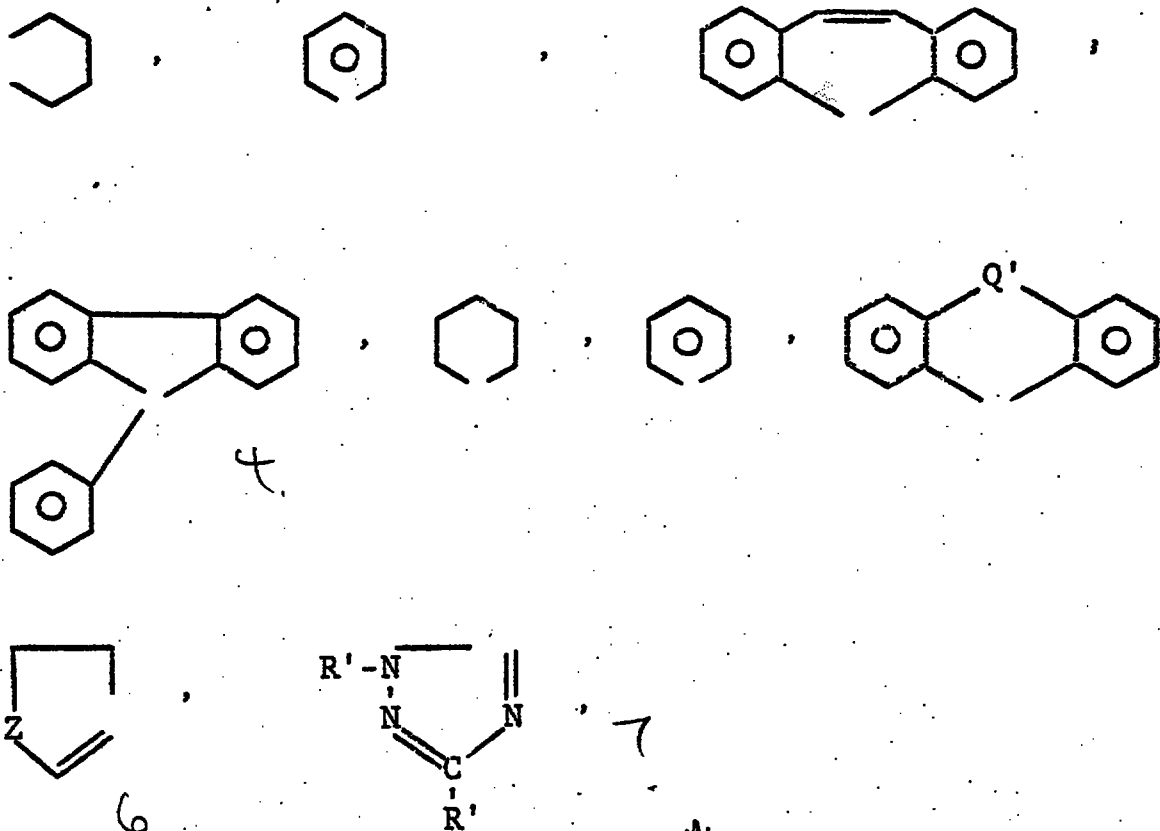
where the sum of "j" + "k" + "m" is <sup>ew</sup> ~~a value~~

~~equal to~~ 3 or the valence of G.

Radicals included by R can be the same or different, aromatic carbocyclic or heterocyclic radicals having from 6 to 20 carbon atoms, which can be substituted with from 1 to 4 monovalent radicals selected from C<sub>(1-8)</sub> alkoxy, C<sub>(1-8)</sub> alkyl, nitro, chloro, etc., R is more particularly phenyl, chloro-phenyl, nitrophenyl, methoxyphenyl, pyridyl. Radicals included by R<sup>1</sup> are divalent radicals, such as



R<sup>2</sup> and R<sup>4</sup> radicals include C<sub>(1-8)</sub> alkyl, such as methyl, ethyl, etc., substituted alkyl, such as -C<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub>, -CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>, -CH<sub>2</sub>COCH<sub>3</sub>, Q' is defined below, R<sup>3</sup> and R<sup>5</sup> radicals include such structures as



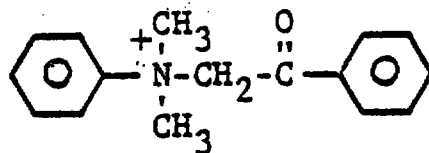
where  $Q'$  is selected from 0,  $(CH_2)_n$ ,  $-\text{CH}_2\text{CH}_2-$  and S,  $n$  is an integer equal to 1-4 inclusive;  $Z$  is selected from  $-O-$ ,  $-S-$  and  $-\text{N}-$ , and  $R'$  is selected from hydrogen,  $C_{(1-8)}$  alkyl,  $C_{(6-13)}$  aryl.

Non-nucleophilic counterions included by J of formula (1) are  $MQ_d$  anions, where M is a metal or metalloid, Q is a halogen radical, and d is an integer such as 4-6 inclusive. In addition, J of formula (1), also can include non-nucleophilic counterions such as perchlorate,  $CF_3SO_3^-$  and  $C_6H_4SO_3^-$ , etc. In instances where the cationically polymerizable material is a phenol-formaldehyde resin, or other formaldehyde condensation resin such as urea, J of formula (1) can be a halide counterion such as  $Cl^-$ ,  $Br^-$ ,  $F^-$ , etc., as well as nitrate, phosphate.

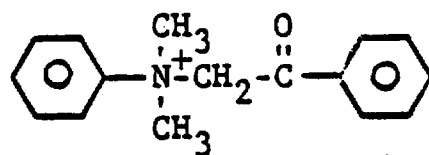
Metal or metalloids included by M of the non-nucleophilic counterion,  $MQ_d$  previously defined and included within J

of formula (1) are transition metals such as Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, Sc, V, Cr, Mn, Cs, Cd rare earth elements such as the lanthanides, for example, Pr, Nd, etc., antinides, such as  
5 Th, Pa, U, Np, etc., and metalloids such as B, P, As. Complex anions included by  $MO_d$  are, for example,  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $SbF_6^-$ ,  $FeCl_4^-$ ,  $SnCl_6^{=}$ ,  $SbCl_6^-$ ,  $BiCl_5^{=}$ .

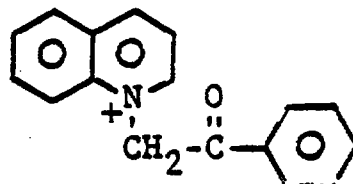
Group VA onium salts included by formula (1) and having formula (3) cations are for example,



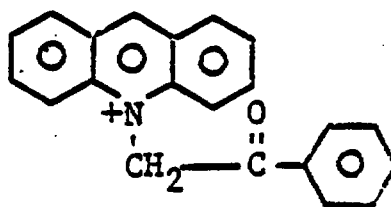
$\text{BF}_4^-$



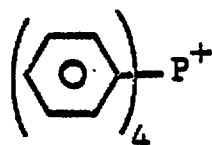
$\text{SbF}_6^-$



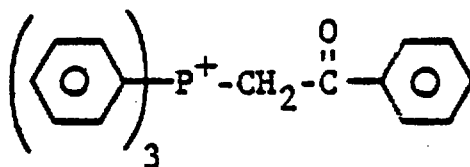
$\text{BF}_4^-$



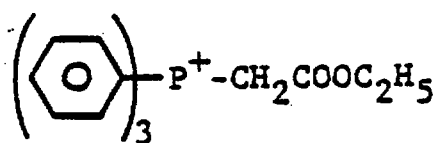
$\text{BF}_4^-$



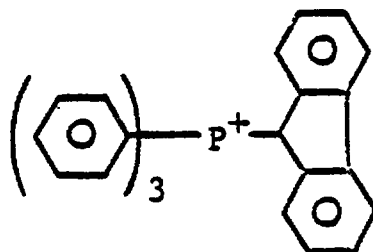
$\text{BF}_4^-$



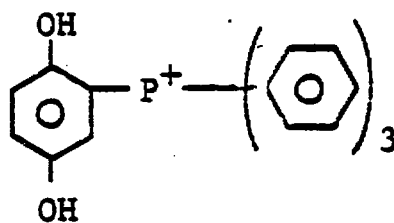
$\text{AsF}_6^-$



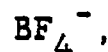
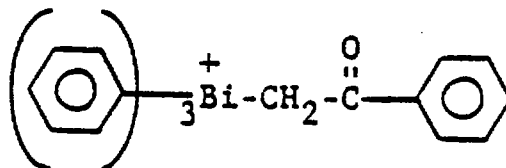
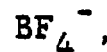
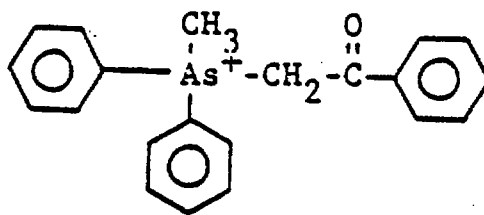
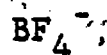
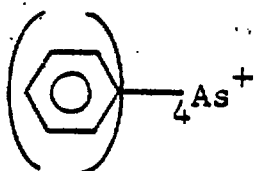
$\text{PF}_6^-$



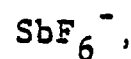
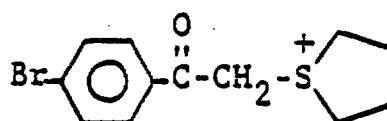
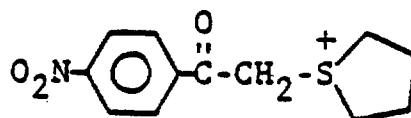
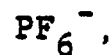
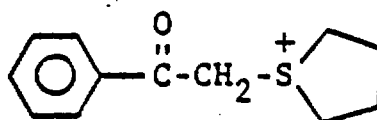
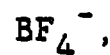
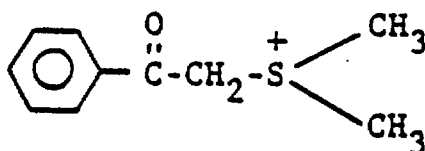
$\text{BF}_4^-$

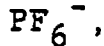
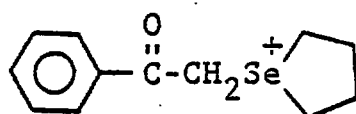
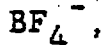
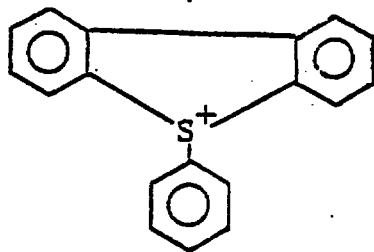
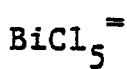
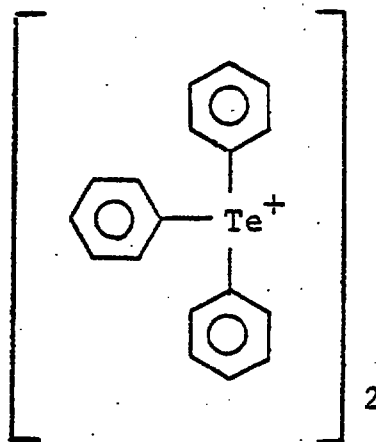
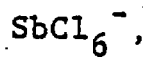
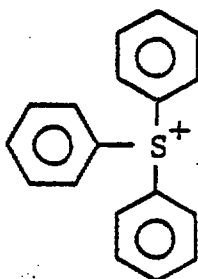
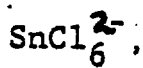
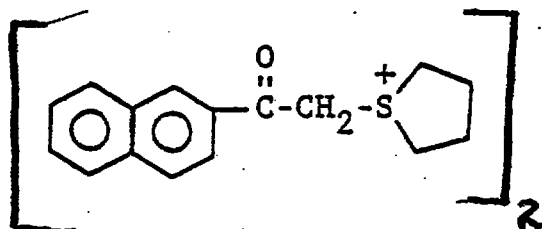
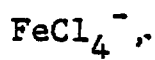
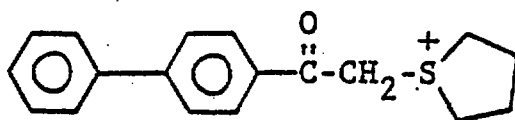


$\text{BF}_4^-$



Group VIa onium salts included by formula (1) and having formula (4) cations are, for example,





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The term "epoxy resin" as utilized in the description of the curable 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 resins (Novolak resins) 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 dioxide, limonene dioxide, 1,2-cyclohexene oxide, glycidyl acrylate, glycidyl methacrylate, styrene oxide, allyl glycidyl ether, may be added as viscosity modifying agents.

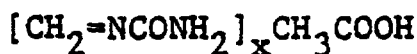
In addition, the range of these compounds can be extended to include polymeric materials containing terminal or pendant epoxy groups. Examples of these compounds are vinyl copolymers containing glycidyl acrylate or methacrylate as one of the comonomers. Other classes of epoxy containing polymers amenable 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. 80 632-5 (1959). As described in the literature, epoxy resins can also be modified in a number of standard ways such as reactions with amines, carboxylic acids, thiols, phenols, alcohols, as shown in U.S. patents 2,935,488; 3,235,620; 3,369,055; 3,379,653; 3,398,211; 3,403,199; 3,563,850; 3,567,797; 3,677,995. Further examples of

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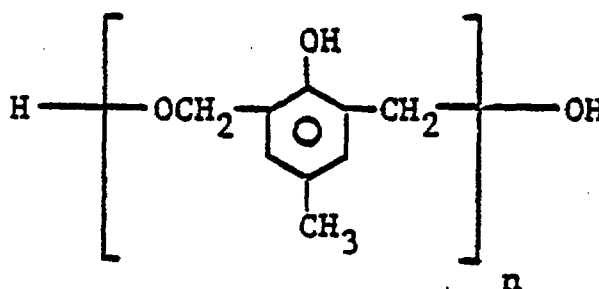
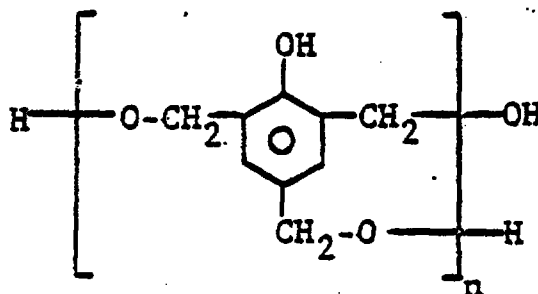
epoxy resins which can be used are shown in the Encyclopedia of Polymer Science and Technology, Vol. 6, 1967, Interscience Publishers, New York, pp. 209-271.

Additional cationically polymerizable organic materials which can be used in the heat curable compositions are thermosetting formaldehyde resins, cyclic ethers, lactones, lactams, cyclic acetals, vinyl organic prepolymers.

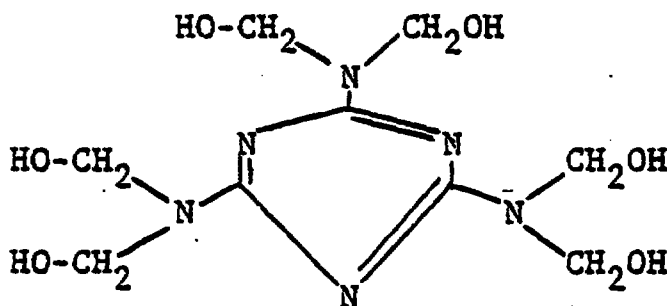
Included by thermosetting organic condensation resins of formaldehyde which can be used in the practice of the present invention are, for example, urea type resins, such as

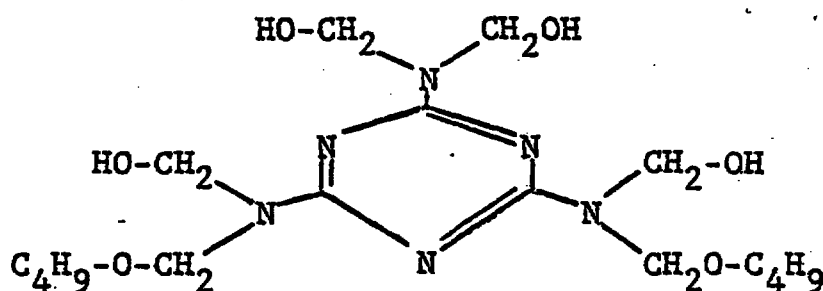


phenol-formaldehyde type resins, such as



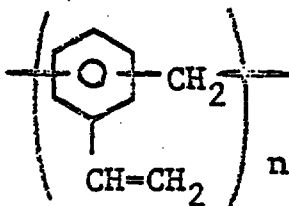
where x and n are integers having a value of 1 or greater than 1;





In addition, there can be used melamine resins, thiourea resins, urea aldehyde resins, cresol-formaldehyde resins in combination 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,  $\text{CH}_2=\text{CH}-\text{O}-(\text{CH}_2-\text{CH}_2\text{O})_n-\text{CH}=\text{CH}_2$ , 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 trivinyl ether, trimethylolpropane trivinylether, prepolymers having the formula,



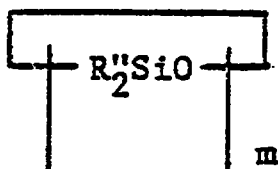
, and

low molecular weight polybutadiene having a viscosity of from 200 to 10,000 centipoises at 25°C. 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 U.S. Patent

3,673,216, assigned to the same assignee as the present invention; oxolanes such as tetrahydrofuran, oxepanes, oxygen containing spiro compounds, trioxane, dioxolane.

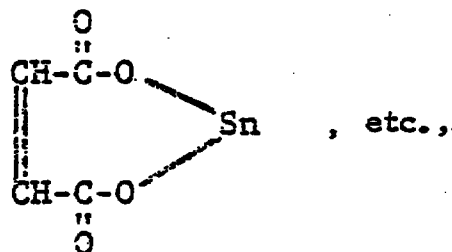
In addition to cyclic ethers there are also included cyclic esters such as  $\beta$ -lactones, for example propiolactone, cyclic amines, such as 1,3,3-trimethyl-azetidine and organosilicon cyclics, for example, materials included by the formula,



where R'' can be the same or different monovalent organic radical such as methyl or phenyl and m is an integer equal to 3 to 8 inclusive. An example of an organosilicon cyclic is hexamethyl trisiloxane, octamethyl tetrasiloxane. The products made in accordance with the present invention are high molecular weight oils and gums.

Included by the reducing agents which can be used in combination with the aromatic onium salts of the present invention, are for example, thiophenols, reducing sugars, ascorbic acid, citric acid, iron salts, such as  $(\text{C}_5\text{H}_5)_2\text{Fe}$ ,  $(\text{C}_7\text{H}_{15}\text{CO}_2)_2\text{Fe}$ , cobalt salts, such as  $(\text{C}_7\text{H}_{15}\text{CO}_2)_2\text{Co}$ ,  $\text{Co}_2(\text{CO})_6[(\text{C}_6\text{H}_5)_3\text{P}]_2$ .

In addition to iron and cobalt salts, there also can be used tin salts, such as  $(\text{C}_7\text{H}_{15}\text{CO}_2)_2\text{Sn}$ ,



and copper salts, such as CuI, CuBr and CuCl.

The heat curable compositions of the present invention can be made by blending the cationically polymerizable organic material with an effective amount of the aromatic onium salt and

in further combination with the reducing agent. In instances where the cationically polymerizable organic material is an epoxy resin, cyclic ether, cyclic ester and the like, as previously defined, the aromatic onium salt used is shown by formula (1), where J is an  $\text{MQ}_4$  anion or  $\text{CF}_3\text{SO}_3^-$  and  $\text{C}_6\text{H}_5\text{SO}_3^-$ . However, in instances where the cationically polymerizable material is a formaldehyde condensation resin as previously defined, J can also be halide, etc., as previously described. The resulting curable compositions can be in the form of a varnish having a viscosity of from 1 centipoise to 100,000 centipoises at 25°C, or a free flowing powder. The curable compositions can be applied to a variety of substrates by conventional means and cured to the tack-free state within from .5 to 20 minutes, depending upon the temperature employed, which can vary from 25°C to 250°C.

Depending upon the compatibility of the onium salts with the epoxy resin as well as the reducing agent, the onium salts can be dissolved or dispersed along with the reducing agent into an organic solvent, such as nitromethane, acetonitrile, etc., prior to incorporation. In instances where the epoxy resin is a solid, incorporation of the onium salts can be achieved by dry milling or by melt mixing.

Formation of the onium salt in situ also can be achieved if desired. Experience has shown that the proportion of onium salt to epoxy resin can vary widely inasmuch as the salt is substantially inert, unless activated. Effective results can be achieved if a proportion of from 1% to 15% by weight of onium salt is employed, based on the weight of curable composition.

The curable compositions may contain inactive ingre-

dients, such as inorganic fillers, dyes, pigments, extenders, viscosity control agents, process aids, UV-screens, in amounts of up to 100 parts of filler per 100 parts of epoxy resin. The curable compositions can be applied to such substrates as metal, rubber, plastic, molded parts or films, paper, wood, glass cloth, concrete, ceramic.

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.

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.

A mixture of 3% by weight of tetramethylenephencyl sulfonium hexafluoroarsenate and 97% by weight of Epon 828, a diglycidyl ether of bisphenol-A of Shell Chemical Company, were heated in a vial to 150°C. After 20 minutes of heating, there was no evidence of gelation.

The above procedure was repeated, except that the mixture contained, in addition to the above-mentioned ingredients, 3% by weight of pentachlorothiophenol. It was found that a cured tack-free product was obtained by heating the mixture for 5 minutes at 150°C. Those skilled in the art know that the aforementioned curable mixture would be suitable for encapsulating electronic components.

Example 2

A uniform mixture of 3 parts of tetramethylenephenyacyl sulfonium hexafluoroantimonate and 7 parts of Epon 828 was found to convert to the solid tack-free state after being heated in a vial at 150°C for 15 minutes. Another sample of the same mixture was blended with 3 parts of pentachlorothiophenol per 100 parts of mixture. It was found that cure of the resulting mixture to a tack-free state was achieved in 2.5 minutes at 150°C.

Example 3

A blend of 97 parts of Epon 828 and 3 parts of tetramethylenephenyacyl sulfonium hexafluoroantimonate was blended with 3 parts of thiophenol. It was found that a tack-free cure was obtained after 5 minutes at 150°C. Another blend was made following the same procedure, except that thiosalicylic acid was substituted for the thiophenol. A similar cure of the mixture was achieved after 3 minutes at 150°C.

Example 4

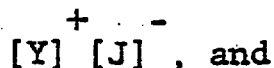
A blend of 97 parts of Ciba Geigy 179\* and 3 parts of phenacyltriphenylphosphonium hexachloroantimonate was heated in a glass vial at 130°C. It was found that after 20 minutes, no significant change in the mixture occurred.

The above procedure was repeated, except that 3 parts of pentachlorothiophenol was added to the mixture. It was found that a tack-free product was obtained after 5 minutes at 130°C.

\* Ciba Geigy 179 is a cycloaliphatic bis-epoxy material

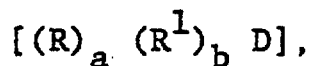
CLAIMS

1. Heat curable compositions comprising  
 (A) a cationically polymerizable organic material,  
 (B) an aromatic onium salt of the formula

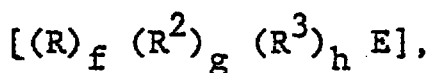


- (C) a reducing agent,

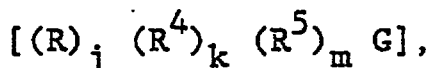
where there is present in the heat curable composition, based on the weight of (A), from 0.1% to 15% by weight of (B) and from 0.5% to 25% by weight of (C), J is a non-nucleophilic counterion, Y is a cation selected from ~~the class consisting~~ of an aromatic halonium cation,



an aromatic Group Va cation,



and an aromatic Group VIA cation,



where R is a monovalent aromatic organic radical,  $R^1$  is a divalent aromatic organic radical,  $R^2$  and  $R^4$  are monovalent organic aliphatic radicals selected from alkyl, cyclo alkyl and substituted alkyl,  $R^3$  and  $R^5$  are polyvalent organic radicals forming a heterocyclic or fused ring structure selected from aliphatic radicals and aromatic radicals with E or G, D is a Cl, Br or F ~~\_\_\_\_\_~~ E is a Group Va element selected from N, P, As, Sb and Bi, G is a Group VIA element selected from S, Se and Te,

"a" is 0, 1 or 2,

"b" is 0 or 1,



and the sum of "a" + "b" is either equal to 2 or the valence of D,

"f" is 0, 1, 2, 3 or 4;

"g" is 0, 1 or 2;

5 "h" is 0, 1 or 2 and the sum of "f" + "g" + "h" is either equal to 4 or the valence of E;

"j" is 0, 1, 2 or 3;

"k" is 0, 1 or 2;

"m" is 0 or 1, where the sum of "j" + "k" +

10 "m" is either equal to 3 or the valence of G.

2. A heat curable composition in accordance with claim 1, where the cationically polymerizable organic material is an epoxy resin (as hereinbefore defined).

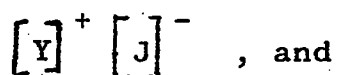
15 3. A heat curable composition in accordance with claim 1, where the cationically polymerizable organic material is a phenol-formaldehyde resin.

4. A heat curable composition in accordance with claim 1, where the reducing agent is a thiophenol.

20 5. A method which comprises heating a curable composition to a temperature in the range of between 25°C to 250°C comprising:

(A) a cationically polymerizable organic material,

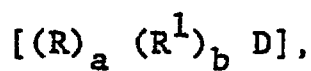
25 (B) from 0.1% to 15% by weight of (A) of an aromatic onium salt having the formula



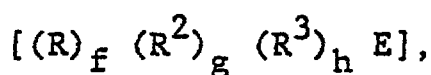
(C) from 0.5% by weight of (A) of a  
30 reducing agent,



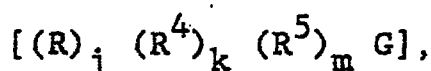
where there is present in the heat curable composition, based on the weight of (A), from 0.1% to 15% by weight of (B) and from 0.5% to 25% by weight of (C), J is a non-nucleophilic counterion, Y is a cation selected from the class consisting of an aromatic halonium cation,



an aromatic Group Va cation,



10 and an aromatic Group VIa cation,



where R is a monovalent aromatic organic radical,  $R^1$  is a divalent aromatic organic radical,  $R^2$  and  $R^4$  are monovalent organic aliphatic radicals selected from alkyl, cyclo alkyl and substituted alkyl,  $R^3$  and  $R^5$  are polyvalent organic radicals forming a heterocyclic or fused ring structure selected from aliphatic radicals and aromatic radicals with E or G, D is F, Cl, or Br, E is Group Va element selected from N, P, As, Sb and Bi, G is a Group VIa element selected from S, Se and 20 Te,

"a" is 0, 1 or 2,

"b" is 0 or 1, and the sum of "a" + "b" is either equal to 2 or the valence of D,



"f" is 0, 1, 2, 3 or 4,

"g" is 0, 1 or 2,

"h" is 0 or 2; and the sum of "f" + "g" + "h" is either equal to 4 or the valence of E,

5

"j" is 0, 1, 2 or 3,

"k" is 0, 1 or 2,

"m" is 0 or 1, where the sum of "j" + "k" + "m" is either equal to 3 or the valence of G.

10

6. A heat curable composition as claimed in claim 1 substantially as hereinbefore described in any one of the Examples.

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