

SPECIFICATION

Heat Curable Compositions

The present invention relates to heat curable compositions comprising a cationically polymerizable organic material, such as an epoxy resin, and an effective amount of a diaryliodonium salt used in combination with a cocatalyst which is a copper salt, an organic acid or mixtures thereof.

Diaryliodonium salts of the formula,



can be used in combination with a copper salt, such as copper benzoate to effect the thermal cure of an epoxy resin, where R is a monovalent aromatic organic radical, R' is a divalent aromatic organic radical, M is a metal or metalloid, Q is a halogen radical, a is 0 or 2, b is 0 or 1 and the sum of a+b is equal to 2 or the valence of I, c=d-e, e equals the valence of M and is an integer equal to 2-7 inclusive and d>e and is an integer having a value up to 8.

We also have found that heat curable cationically polymerizable materials can be made by incorporating into epoxy resins, the diaryliodonium salt of formula (I) in combination with organic acids, such as aromatic organic carboxylic acids. In addition, we have further found that besides epoxy resins, other cationically polymerizable materials, such as cyclic ethers, lactones, lactams, cyclic acetals, can be thermally cured with combinations of such organic acids, copper salt or mixtures thereof with iodonium salts of formula (I), or iodonium salts having a non-nucleophilic counterion such as perchlorate, $CF_3SO_3^-$ and $C_6H_4SO_3^-$. Again, where the cationically polymerizable material is a phenol-formaldehyde resin, urea-formaldehyde or melamine-formaldehyde, iodonium salts can be used having in addition to MQ_d and the other non-nucleophilic counterions previously recited, halide counterions such as Cl^- , Br, F and I, as well as nitrate and phosphate.

There is provided by the present invention, a curable composition comprising by weight

(A) a cationically polymerizable organic material, and

(B) from 0.1% to 35% of the curable composition of a catalyst selected from the class consisting of

(i) a mixture of

(a) a diaryliodonium salt of the formula



and

(b) from 0.01 part to 10 parts, per part of (a), of a copper salt,

(ii) a mixture of

(c) the diaryliodonium salt of formula (II),

(d) from 0.1 part to 15 parts, per part of (c), of organic acid (excluding ascorbic acid) organic acid anhydride (excluding ascorbic acid anhydride) or mixtures thereof and

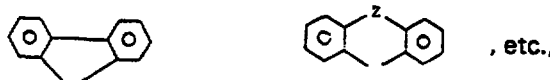
(iii) a mixture of

(e) the diaryliodonium salt of formula (II),

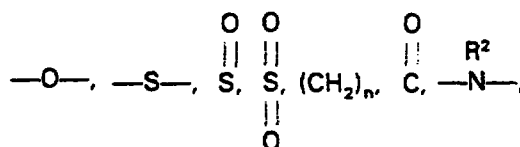
(f) from .01 part to 10 parts, per part of (e) of the copper salt of (b), and

(g) from 0.1 part to 15 parts, per part of (e), of the organic acid (excluding ascorbic acid), organic acid anhydride excluding ascorbic acid anhydride or mixtures thereof of (d),

where R, R', a, b and c are as previously defined, and Y is a non-nucleophilic counterion as defined above. Radicals included by R of formulas (I) and (II) can be the same or different aromatic carbocyclic radicals having from 6 to 20 carbon atoms, which can be substituted with from 1 to 4 monovalent radicals selected from C_{1-8} alkoxy, C_{1-8} alkyl, nitro, chloro, R is more particularly, phenyl, chlorophenyl, nitrophenyl, methoxyphenyl, pyridyl. Radicals included by R' of formulas (I) and (II) are divalent radicals such as



where Z is selected from

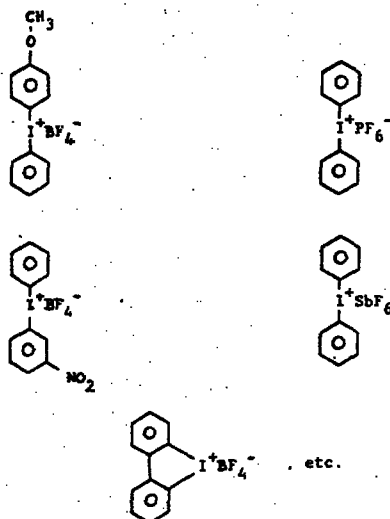


R² is C_{1-8} alkyl or C_{18-13} aryl, and n is an integer equal to 1-8 inclusive.

Metal or metalloids included by M of formulas (I) and (II) are transition metals 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, Cd, Pr, Nd, actinides, such as Th, Pa, U, Np, and metalloids such as B, P, As.

Complex anions included by $\text{MO}_6^{(d-e)}$ are, for example BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , FeCl_4^- , SnCl_6^{2-} , SbCl_6^- , BiCl_5^- .

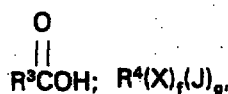
Iodonium salts included by formulas (I) and (II) are, for example,



Iodonium salts of formula (I) can be made by the procedure in Crivello U.S. Patent 3,981,897, where contact between an aryl halonium bisulfate and the corresponding hexafluoroacid or salt can be effected under aqueous conditions. Iodonium salts of formulas (I) and (II) also can be made by the procedures described by O. A. Ptitsyna, M. E. Pudcva et al, Dokl., Akad. Nauk, SSSR, 163 383 (1964); Dokl., Chem., 163 671 (1965), F. Marshall Beringer, M. Drexler, E. M. Gindler, etc., J. Am. Chem. Soc., 75 2705 (1953).

Copper salts which can be used include, for example, Cu(I) salts such as copper halides, e.g., Cu(I) chloride Copper (II) salts such as Cu(II) benzoate, Cu(II) acetate, Cu(II) stearate, Cu(II) glyconate, Cu(II) citrate.

Organic acids and organic acid anhydrides which have been found effective in combination with the diaryliodonium salts of formulas (I) and (II) are included by the formulas,



where R^3 is a monovalent organic radical selected from $\text{C}_{(1-8)}$ alkyl and $\text{C}_{(6-13)}$ aryl, R^4 is a polyvalent organic radical selected from $\text{C}_{(2-8)}$ aliphatic and $\text{C}_{(6-13)}$ aryl, X is selected from carboxy and sulfonate, J is



f is an integer equal to 0 to 4 inclusive, g is equal to 0 to 2 and when g is 0, f is equal to 2 to 4, and when g is 1, f is equal to 1 or 2. Some of the organic acids and organic acid anhydrides which can be used are, for example, aliphatic carboxylic acids such as acetic acid, 2-ethylhexanoic acid, hexanoic acid, oleic acid, stearic acid, palmitic acid, succinic acid, azelaic acid, aromatic carboxylic, for example, benzoic acid, salicylic acid, terephthalic acid, phthalic acid, trimellitic acid, trimellitic anhydride, pyromellitic dianhydride, o-toluic acid; sulfonic acids such as benzene sulfonic acid, p-toluene sulfonic acid, 4-nitrobenzene sulfonic acid.

The term "epoxy resin" as utilized in the description of the cationically polymerizable compositions of the present invention, is defined as 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 phenolformaldehyde 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 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 polymer 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 epoxysiloxane resins, epoxy-

polyurethanes and epoxy-polyesters. Such polymers usually have epoxy functional groups at the ends of their chains. Epoxysiloxane 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 reaction with amines,

5 carboxylic acids, thiols, phenols, alcohols, as shown in U.S. 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. Further coreactants which can be used with epoxy resins are hydroxy terminated flexibilizers such as hydroxy terminated

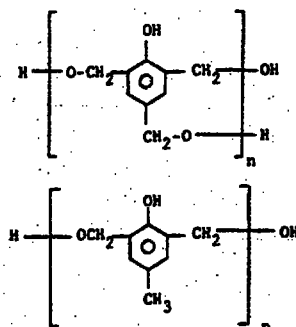
polyesters, shown in the Encyclopedia of Polymer Science and Technology, Vol. 6, 1967, Interscience Publishers, New York, pp. 209—279 and particularly p. 238.

10 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

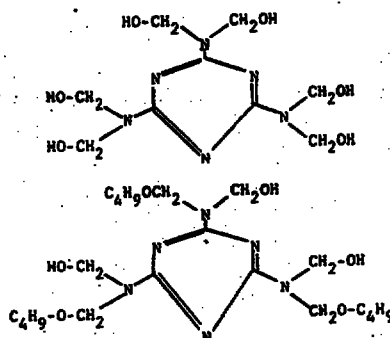


15 phenol-formaldehyde type resin such as

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



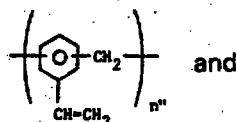
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In addition, there can be used melamine thiourea resins, melamine, or urea aldehyde resins, cresol-formaldehyde resins and combinations with other carboxy, hydroxyl, amino and mercapto containing resins, such as polyesters, alkyds and polysulfides.

Some of the vinyl organic prepolymers which can be used to make the polymerizable compositions of the present invention are, for example, $\text{CH}_2=\text{CH}-\text{O}-(\text{CH}_2-\text{CH}_2\text{O})_{n'}-\text{CH}=\text{CH}_2$,

25 where n' is a positive integer having a value up to about 1000 or higher; multi-functional vinylethers, such as 1,2,3-propane trivinylether, trimethylolpropane trivinylether, prepolymers having the formula,



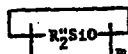
30 low molecular weight polybutadiene having a viscosity of from 200 to 10,000 centipoises at 25°C, etc. Products resulting from the cure of such compositions can be used as printing inks and other applications typical of thermosetting resins.

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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.

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 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, 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 polymerizable organic material with at least an effective amount (i.e. at least 0.1% by weight) of the diaryliodonium salt and in further combination, as previously defined, with the other cocatalysts which are the copper salt, organic acid, organic acid anhydride, etc. 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 diaryliodonium 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 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.

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

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

Various blends of Shell Epon 828, bisphenol-A-diglycidyl ether, and a diaryliodonium-Cu(II) salt catalyst were heated for about 5 minutes to determine their respective cure temperatures, "CT". A wide variety of diaryliodonium MO_6 salts of formula (I) in combination with several Cu(II) salts were utilized. The following table shows the results obtained where the weight percent is shown of diaryliodonium salt and the Cu(II) salt in the respective blends, based on total weight of mixture, and "Ph" is phenyl.

	Iodonium Salt (2%)	Cu(II) Salt (WT%)	CT(°C)	
40	Ph_2IAsF_6	None	215	40
	Ph_2IAsF_6	benzoate (0.04)	112	
	Ph_2IAsF_6	benzoate (0.5)	105	
	Ph_2ISbF_6	None	171	
	Ph_2ISbF_6	benzoate (0.5)	105	
45	Ph_2IBF_4	None	210	45
	Ph_2IBF_4	benzoate (0.5)	135	
	Ph_2IAsF_6	stearate (0.2)	148	
	Ph_2IAsF_6	stearate (0.5)	115	
	$(4\text{-t-butPh})_2\text{IAsF}_6$	benzoate (0.5)	106	
50	$(4\text{-Cl-Ph})_2\text{IA2F}_6$	benzoate (0.5)	106	50
	$(4\text{-CH}_3\text{-Ph})_2\text{IAsF}_6$	benzoate (0.5)	108	
	Ph_2IAsF_6	acetate (0.5)	142	

In the above table, cure was determined by applying the curable mixture onto a steel substrate and heating it in an oven until the applied curable mixture formed a tack-free cured film.

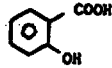
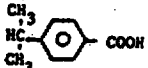
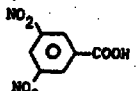
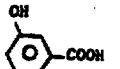
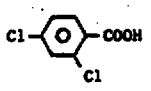
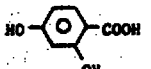
Example 2

A mixture of bisphenol-A diglycidyl ether and 3% by weight of diphenyliodonium hexafluoroarsenate was respectively blended with 3% of benzoic acid and 6 and 10% of trimellitic anhydride by weight. The resulting curable mixtures were then heated at a rate of 10°C per minute to determine the minimum temperature required to gel the bis-epoxide. It was found that a temperature of 225°C was required to gel the bis-epoxide when the mixture was free of aromatic carboxylic acid.

However, the 3% by weight benzoic acid mixture gelled at 120°C, while the 6 and 10% trimellitic anhydride mixture gelled at 150—160°C, respectively.

Example 3

A variety of curable mixtures were prepared utilizing 3,4'-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate, 3% by weight of diphenyliodonium hexafluoroarsenate and a range of between about 3%—6% by weight of various organic acids. The mixtures were heated in an oil bath to determine the respective gel times. The temperature of the oil bath was 170°C. The following results were obtained, where "Acid" signifies the organic acid or organic acid anhydride employed.

	Acid	Weight (%)	Gel Time (sec)	
10	None	0	>900	10
	Acetic	6	170	
	Stearic	6	215	
	Benzene sulfonic	6	135	
15	Trimellitic anhydride	6	160	
	Trimellitic anhydride	10	150	15
		6	300	
		3	225	
		6	165	
		3	225	
20		6	165	20
		6	115	
		6	123	

The above results show that a significant reduction in gel time was achieved when the organic acid was utilized in combination with the diaryliodonium salt.

Example 4

There were added 0.2 part of diphenyliodonium hexafluoroarsenate, 0.1 part of benzoic acid and 0.05 part copper benzoate to 10 parts of an allyl ether resole condensation product of phenol and formaldehyde containing multifunctional hydroxy methyl groups (Methylon* 75108 resin of the General Electric Company). The mixture was stirred in an oil bath at 120°C. The mixture gelled and hardened at 120°C to a rigid cross-linked mass within 5 minutes. The composition is useful as a potting material for electrical components.

*Registered Trade Mark.

Example 5

There was added 0.1 part of copper benzoate and 0.2 part of diphenyliodonium hexafluoroarsenate to 10 parts caprolactone. The mixture was heated for 20 minutes at 120°C. The resulting highly viscous reaction mixture was poured into methanol. There was obtained 9.5 parts polycaprolactone having an intrinsic viscosity in methylene chloride of 0.4 dl/g.

Example 6

Ten parts of a mixture of 3% by weight of diphenyliodonium hexafluoroarsenate, 6% by weight of copper benzoate, 51% by weight of cycloaliphatic bisepoxide (CY-179, of the Ciba Geigy Company) and 40% by weight of hydroxyl terminated polyester (R-101—110, of the Hooker Chemical Company) was placed in an aluminum cup. The mixture was heated for 10 minutes at 130°C. On cooling, there was obtained a rubbery material capable of being flexed 180°C without breaking.

Example 7

Graphite cloth (Morganite I produced by the Whittaker Corporation, Costa Mesa, California) was impregnated with the following mixture:

	Epoxy cresol novolac (ECN 1299) of the Ciba Geigy Co.	20 parts	
5	Diphenyliodonium hexafluoroarsenate	3 parts	5
	Diglycidyl ether of bisphenol-A (Epon 828) of the Shell Chemical Company	80 parts	
	Trimellitic anhydride	10 parts	
	Copper benzoate	1 part	

- 10 The cloth was then cut into 4" x 6" pieces. A four layer laminate was made from the aforementioned piece. The laminate was then pressed at 165—170°C at 50 psi for 3 minutes. There is obtained a rigid cured solvent resistant graphite fiber reinforced laminate having excellent mechanical properties. 10

Example 8

- 15 A molding compound was made by mixing 394 parts of a granulated filler-epoxy preblend, 18.75 parts of trimellitic anhydride, 3.75 parts of diphenyliodonium hexafluoroarsenate, 0.15 part of copper stearate, 9 parts of powdered carnauba wax 6 parts of powdered Cornelius wax, and 75 parts of 1/4" chopped glass fiber. The filler-epoxy preblend was based on the use of 8,365 parts of hydrated alumina and 1,050 parts of titanium dioxide, 3,500 parts of pulverized Epi-Rez SU-8 (an epoxy novolac resin of the Celanese Chemical Company) and 875 parts of pulverized Epon 1009, a BPA epoxy resin of the Shell Chemical Company. The filler-epoxy preblend was initially sintered, followed by compounding it 20 with a Sterling extruder. 20

The molding compound was granulated for evaluation after it had been sheeted on a roll mill. The granulated molding material free of particles finer than 20 mesh was molded in accordance with ASTM D955 for 3—5 minutes at 350°F at a pressure of 2000—3000 psi. There were obtained ASTM discs and dog bone specimens providing the following properties:

25	Molding Properties	Dry Powder	Preforms (preheated)	Test Method	25
	Molding Temp.	350°F	350°F		
	Cure Cycle	45 sec.	—		
	Mold Shrinkage		3.6 mil/in	D955 (ASTM)	
30	— 5 in bars				30
	Physical Properties				
	Specific Gravity		1.83—1.85	D570	
	Hardness, Rockwell	M88±10	M110±4	D785	
	Mechanical Properties				
35	Tensile Strength (psi)	4300±300	5100±600	D638	35
	Flexural Strength (psi)	10900±400	9800±500	D790	
	Compressive Strength (psi)	18100±500	17000±1500	D695	
	Drop ball (1/2 lb, in)	10±1	10±1		
	Notched Izod (ft-lb/in)	0.37±.04	0.53±.1	D256	
40	Thermal Properties				40
	HDT	460±7°F	435±13°F	D648	
	Electrical Properties				
	Arc Resistance	199±1	196±2	D495	

Example 9

- 45 There was formulated, 33.5 parts of platy talc, 33.5 parts of hydrated alumina, 13 parts of trimellitic anhydride, 3.9 parts of diphenyliodonium hexafluoroarsenate, 3.6 parts of powdered paraffin wax and 0.6 part of stearic acid with 268 parts of a granulated preblend of hydrated alumina, platy talc and epoxy resin, and 145 parts of epoxy coated glass fiber. The granulated preblend of platy talc and hydrated alumina was initially prepared from a mixture of 140 parts of platy talc, 140 parts of hydrated alumina, 45.75 parts of Epon 1001 BPA epoxy resin of the Shell Chemical Company, and 48.75 parts 50 of ECN 1299, an epoxy cresol novolac resin of the Ciba-Geigy Chemical Company. The epoxy coated glass fiber was prepared from a mixture of 75 parts of chopped glass fibers, 32.5 parts of Epon 1001 and 32.5 parts of ECN 1299. 50

- 55 The above formulation was then dry blended and roll milled at temperatures in the range of between 30—90°C for several minutes. The resulting mixture was then further tumble blended with additional stearic acid after being granulated. 55

Several ASTM specimens were prepared in accordance with the procedures of Example 8. The resulting specimens provided the following properties:

			Test Method	
Molding Properties (Compression)				
5	Molding temperature	350°F		5
	Cure cycle			
	— Dry powder	60 sec.		
	— Preforms (preheated)	40 sec.		
10	Mold shrinkage			
	— 5×1/2×1/2 bars (mils/in)	2.1±0.1	D955 (ASTM)	10
Physical Properties				
	Specific gravity	1.93		
	Water absorption		D570	
	— 25°C (24 hrs. %)	0.06		
15	— 100°C (2 hrs. %)	0.22		15
	Burning characteristics	V-0	UL-94	
	Hardness, Rockwell	M97±10	D785	
Mechanical Properties				
20	Tensile strength (psi)	5700±1700	D638	
	Flexural strength (psi)	11,000±2000	D790	20
	Flexural Modulus (psi×10 ⁶)	1.84±0.14		
	Compressive Strength (psi)	16,000±1900	D695	
	Notched izod (ft-lb/in)	0.57±0.01	D256	
Thermal Properties				
25	Thermal coefficient of expansion (in/in°F×10 ⁻⁵)	14.	D696	25
	Heat deflection temperature (265 psi)	475°F	D648	
30	— Flex. strength (% retention)	9800±1200 (91%±22%)		30
	— Flex. modulus (% retention)	1.84±0.09 (100%±8%)		
Electrical Properties				
	Arc resistance, sec.	199±5	D495	
35	Claims			35
	1. A curable composition comprising by weight			
	(A) a cationically polymerizable organic material, and			
	(B) from 0.1% to 35% of the curable composition of a catalyst selected from the class consisting			
40	of			40
	(i) a mixture of			
	(a) a diaryliodonium salt of the formula,			
	$[(R)_a(R^1)_bI]^+[Y]^-$, and			
	(b) from 0.01 part to 10 parts, per part of (a), of a copper salt,			
45	(ii) a mixture of			45
	(c) the diaryliodonium salt of (a) and			
	(d) from 0.1 part to 15 parts, per part of (c), of organic acid (excluding ascorbic acid), organic acid anhydride (excluding ascorbic acid anhydride), or mixtures thereof and			
	(iii) a mixture of			
50	(e) the diaryliodonium salt of (a)			50
	(f) from .01 part to 10 parts, per part of (e), of the copper salt of (b), and			
	(g) from 0.1 part to 15 parts, per part of (e), of the organic acid (excluding ascorbic acid), organic acid anhydride (excluding ascorbic acid anhydride), or mixtures thereof of (d),			
	where R is a monovalent aromatic organic radical, R ¹ is a divalent aromatic organic radical, a is 0 or 2, b is 0 or 1 and the sum of a+b is equal to 2 or the valence of I, and Y is a non-nucleophilic counterion.			
55	2. A curable composition in accordance with Claim 1, where the cationically polymerizable material is an epoxy resin.			55
	3. A curable composition in accordance with Claim 1, where the cationically polymerizable material is a phenolformaldehyde resin.			



Several ASTM specimens were prepared in accordance with the procedures of Example 8. The resulting specimens provided the following properties:

			Test Method	
	Molding Properties (Compression)			
5	Molding temperature	350°F		5
	Cure cycle			
	— Dry powder	60 sec.		
	— Preforms (preheated)	40 sec.		
10	Mold shrinkage			
	— 5×1/2×1/2 bars (mils/in)	2.1±0.1	D955 (ASTM)	10
	Physical Properties			
	Specific gravity	1.93		
	Water absorption		D570	
15	— 25°C (24 hrs. %)	0.06		15
	— 100°C (2 hrs. %)	0.22		
	Burning characteristics	V-0	UL-94	
	Hardness, Rockwell	M97±10	D785	
	Mechanical Properties			
20	Tensile strength (psi)	5700±1700	D638	20
	Flexural strength (psi)	11,000±2000	D790	
	Flexural Modulus (psi×10 ⁶)	1.84±0.14		
	Compressive Strength (psi)	16,000±1900	D695	
	Notched izod (ft-lb/in)	0.57±0.01	D256	
	Thermal Properties			
25	Thermal coefficient of expansion (in/in°F×10 ⁻⁵)	14.	D696	25
	Heat deflection temperature (265 psi)	475°F	D648	
30	— Flex. strength (% retention)	9800±1200 (91%±22%)		30
	— Flex. modulus (% retention)	1.84±0.09 (100%±8%)		
	Electrical Properties			
	Arc resistance, sec.	199±5	D495	
35	Claims			35
	1. A curable composition comprising by weight			
	(A) a cationically polymerizable organic material, and			
	(B) from 0.1% to 35% of the curable composition of a catalyst selected from the class consisting			
40	of			
	(i) a mixture of			40
	(a) a diaryliodonium salt of the formula,			
	$[(R)_a(R^1)_bI]^+[Y]^-$, and			
	(b) from 0.01 part to 10 parts, per part of (a), of a copper salt,			
45	(ii) a mixture of			45
	(c) the diaryliodonium salt of (a) and			
	(d) from 0.1 part to 15 parts, per part of (c), of organic acid (excluding ascorbic acid), organic acid anhydride (excluding ascorbic acid anhydride), or mixtures thereof and			
	(iii) a mixture of			
50	(e) the diaryliodonium salt of (a)			50
	(f) from .01 part to 10 parts, per part of (e), of the copper salt of (b), and			
	(g) from 0.1 part to 15 parts, per part of (e), of the organic acid (excluding ascorbic acid), organic acid anhydride (excluding ascorbic acid anhydride), or mixtures thereof of (d),			
	where R is a monovalent aromatic organic radical, R ¹ is a divalent aromatic organic radical, a is 0 or 2, b is 0 or 1 and the sum of a+b is equal to 2 or the valence of I, and Y is a non-nucleophilic counterion.			
55	2. A curable composition in accordance with Claim 1, where the cationically polymerizable material is an epoxy resin.			55
	3. A curable composition in accordance with Claim 1, where the cationically polymerizable material is a phenolformaldehyde resin.			

4. A curable composition in accordance with Claim 1, where the diaryliodonium salt has the formula,



where R is a monovalent aromatic organic radical, R' is a divalent aromatic organic radical, M is a metal or metalloid, Q is a halogen radical, a is 0 or 2, b is 0 or 1 and the sum of a+b is equal to 2 or the valence of I, c=d-e, e equals the valence of M and is an integer equal to 2—7 inclusive and d>e and is an integer having a value up to 8.

5. A curable composition in accordance with any one of the preceding claims where a mixture of copper salt and the diaryliodonium salt is employed.

6. A curable composition in accordance with any one of Claims 1 to 4 where a mixture of organic acid or organic acid anhydride and the diaryliodonium salt is employed.

7. A curable composition in accordance with any one of Claims 1 to 4 where the mixture of organic acid, the diaryliodonium salt and copper salt is employed.

8. A curable composition in accordance with Claim 7, where the organic acid is trimellitic anhydride.

9. A curable composition in accordance with any one of the preceding claims where the diaryliodonium salt is diphenyliodonium hexafluoroarsenate and copper salt is copper benzoate.

10. A curable composition in accordance with Claim 1, comprising by weight of the unfilled epoxy resin (A) a platy talc, hydrated alumina, glass fiber filled epoxy resin, and (B) from 1% to 35% of a mixture of trimellitic anhydride, diphenyliodonium hexafluoroarsenate and copper stearate.

11. A curable composition in accordance with Claim 1 comprising by weight of the unfilled epoxy resin (A) a hydrated alumina, titanium dioxide filled epoxy resin and (B) from 1% to 35% of a mixture of trimellitic anhydride, diphenyliodonium hexafluoroarsenate, and stearic acid.

12. A curable composition as claimed in Claim 1 substantially as hereinbefore described in any one of the Examples.

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