

PATENT SPECIFICATION

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(54) FLAME-RETARDANT COMPOSITIONS

(71) We, FMC CORPORATION, a corporation incorporated in the State of Delaware, United States of America, of 633 Third Avenue, New York, State of New York, United States of America, (assignee of CARL LEONARD WRIGHT and HARRY HOYT BEACHAM), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to flame-retardant compositions made flame retardant by incorporating a polybrominated aromatic hydrocarbon together with a polyethylenically unsaturated monomer in the composition.

Thermosetting polymerizable compositions, commonly termed thermosetting resins, are widely used in making castings, laminates, and molded articles. The high strength to weight ratios of thermoset resins when properly reinforced and cured and the resistance of these compositions to environmental conditions has suggested the use of thermoset compositions in numerous applications, including many applications where combustibility is a serious consideration.

A number of methods have been employed to reduce the rate of combustion of thermoset resin compositions. These methods have included the use of numerous flame-retardant additives including inorganic additives, organic additives, a combination of inorganic and organic additives, the addition of a flame-retardant element that reacts and becomes part of the thermoset resin, and combinations of all these methods.

The use of inorganic fillers to impart flame retardance is attractive on a cost basis. Typical inert flame retardant fillers retard the burning rate to the extent that they act as diluents of the combustible components. However, large

amounts of fillers adversely affect the electrical properties of thermoset resin compositions.

Organic compounds containing halogen and phosphorus atoms such as chlorinated paraffins, chlorinated biphenyls, chlorinated aryl substituted alkyls, phosphorus containing hydrocarbons, and the like have been used for many years to impart flame resistance to plastic compositions including thermoset resins. The chlorinated materials are quite effective as flame retardants.

The flame-retarding mechanism is believed to involve the release of hydrogen chloride at combustion temperatures which snuffs out the flame by exclusion of oxygen. Only highly chlorinated organic materials have been considered since the objective is to provide maximum flame resistance with a minimum of additive material. These highly chlorinated organics, including those which are solid, have a plasticizing action on thermoset compositions. Generally the plasticizing action of the chlorinated organic compounds lowers the heat deflection temperature and otherwise impairs the desirable properties of cured thermosetting resins.

Combinations of chlorinated organic additives with antimony trioxide have been known for a number of years. The effect of certain other metal oxides, such as magnesia or hydrated alumina, combined with antimony oxides in flame-proofing chlorinated polymers was noted by D. C. Thompson et al in an article entitled "Flame Resistance of Neoprene" appearing in the August, 1958 issue of *Rubber-Age*. Combinations of hydrated alumina with antimony oxide and chlorinated organics are widely recognized as effective flame retardants for resinous compositions including thermoset resin compositions.

Satisfactory flame resistance in thermoset polymers has been obtained by using reactive

[Price 25p]

Price 33p

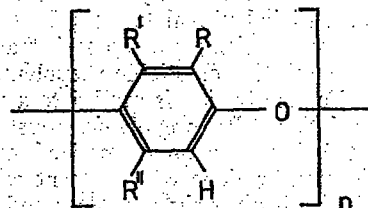
allyl phthalate resins and unsaturated polyester resins, which are typical of the polyethylenically unsaturated materials used in practising this invention, when cured, are known to be plasticized by brominated biphenyls and terphenyls. For example, ordinary 5 moded diallyl phthalate polymer articles containing brominated biphenyls do not have the characteristic "hot hardness" of diallyl 10 phthalate molded articles; when removed from a hot mold, the molded articles containing a brominated biphenyl are soft, like hot rubber, and harden only on cooling. Physical mixtures of highly brominated biphenyls (some with 15 melting points above 150°C) and an allyl prepolymer "ball up" or stick together when ball milled together (though either material alone will ball mill in a conventional manner), thus showing solvation of resin by the polybrominated aromatic hydrocarbon. It is there- 20 fore quite surprising that when at least one mol of a polyethylenically unsaturated monomer is present for every 3 mols of the polybrominated aromatic hydrocarbon, these polybrominated aromatic hydrocarbons can be 25 incorporated into diallyl phthalate prepolymer or unsaturated polyester resin molding compositions which can be cured into articles that are essentially not plasticized by the polybrominated aromatic hydrocarbon. 30

The polybrominated aromatic hydrocarbon and polyethylenically unsaturated materials do not have to be prereacted. These materials may be incorporated into thermosetting resin 35 compositions which are used for making moldings, castings, and laminates without substantially degrading the cured physical properties of the thermosetting resins provided there is at least one mol of polyethylenically 40 unsaturated monomer for every three mols of polybrominated aromatic hydrocarbon in the thermosetting resin composition and the curing temperature is at least 130°C. When cured to the thermoset stage, these novel thermosetting resin compositions exhibit excellent 45 electrical and mechanical properties and are flame resistant. The polybrominated aromatics have little or no plasticizing effect upon the cured thermoset compositions and there is substantially no loss of thermoset properties. 50

Polybrominated aromatic hydrocarbons are commercially available and represent a low cost bromine source for making flame retardant thermoset resin compositions. Surprisingly, compared to the more expensive 55 flame retardant compositions made with polyester or diallyl phthalate resins and diallyl chloredate, the compositions of this invention have somewhat improved electrical properties. These novel compositions can be used 60 with ordinary flame retardant additives and synergists used in flame retardant resin composition, such as antimony trioxide and hydrated alumina.

65 Polyphenylene ether polymers can be used

to replace some or all of the polyunsaturated polymers in these novel compositions in which case it is preferred that at least an additional 0.05 parts by weight of polyethylenically unsaturated monomer is added to the composition 70 for each part of polyphenylene ether polymer. Typical polyphenylene ether polymer have a repeating structural unit of the formula



wherein the oxygen atom of one unit is connected to the benzene nucleus of the adjoining unit; n is a positive integer and is at least 10; R is a hydrogen atom, a hydrocarbon radical free from tertiary alpha-carbon atoms, a halohydrocarbon radical having at least two carbon atoms between the halogen atom and the phenol nucleus and being free from a tertiary alpha-carbon atom, a hydrocarbonoxy radical being free from a tertiary alpha-carbon atom, or a halohydrocarbonoxy radical having at least two carbon atoms between the halogen atom and the phenol nucleus and being free from tertiary alpha-carbon atoms; and R' and R'' are both monovalent substituents which may be any of the radicals given for R and, in addition, halogen. All of the polyphenylene ether polymers currently available have been found to be useful in practising this invention. A method of producing polyphenylene ether polymers by forming self-condensation products of phenylene by reacting oxygen with a phenol is described in U.S. Patent Specification No. 3,306,875. Polyphenylene ether polymers available from the General Electric Company such as "Noryl" and Grades 631-101, 691-111 and 631-111 have been found to be useful in practising this invention. ("Noryl" is a Trade Mark). As far as is known, all known polyethylene ether polymers are useful in practising this invention. 105

To produce a thermosetting composition a free radical initiator should be present in sufficient amounts to convert the (polyethylenically unsaturated monomer, polyethylenically unsaturated polymer and polybrominated aromatic hydrocarbon) compositions to the thermoset state upon the application of heat. Free radical initiation may be accomplished by electron beams or other sources of radiation including actinic light. Conveniently, peroxide catalysts which promote reaction between unsaturated compounds with carbon to carbon double bond unsaturation are used. The peroxide catalyst does not have to exclude homopolymerization, but must be a catalyst that does not produce only homo- 120

5 polymers. When peroxide catalysts and heat are used to cure the compositions, peroxides which have a minimum 10 hour half-life in benzene at a temperature in excess of 100°C should be used to some extent to catalyze the reactions of this invention. Mixed catalysts may be used, but at least part of the catalyst must be a catalyst having a 10 hour half-life at a temperature in excess of 100°C in benzene. Dicumyl peroxide, tertiary butyl perbenzoate, 2,5 - dimethyl - 2,5 - di(*tert.* - butylperoxy) - hexyne - 3 and 2,5 - dimethyl - 2,5 - di(*tert.* - butylperoxy)hexane alone and in combination with benzoyl peroxide have been used. Dicumyl peroxide gives the best results in the novel compositions of this invention. Generally, catalysts well known to cure allyl polymer compositions are useful in practising this invention.

20 A wide variety of water-insoluble, inert fillers may be used in preparing the molded compositions of this invention. Useful fillers include calcium carbonate, both precipitated and wet ground types, calcium silicate (Wollastonite), silica, hydrated clays, calcined clays, chalk, calcium sulfate (anhydrous), barium sulfate, asbestos, glass (powdered), quartz, aluminum trihydrate, aluminum oxide, antimony oxide, magnesium oxide, inert iron oxides and groundstone such as granite, basalt, marble, limestone, sandstone, phosphate rock, travertine, onyx and bauxite. Additionally, inert fibrous materials may be used such as synthetic fibers, glass fibers, asbestos and cellulosic fibers. Up to 200 parts by weight of filler and/or fiber per 100 parts by weight of polyethylenically unsaturated polymerizable materials-polybrominated aromatic hydrocarbon may be used in these molding compositions. Up to 400 parts by weight of fiberglass may be present per 100 parts by weight of polyethylenically unsaturated polymerizable materials-polybrominated aromatic hydrocarbon.

45 Incidental additives widely incorporated in thermosetting molding compounds and laminates such as pigments, release agents, coupling agents, lubricants and other incidental additives may also be incorporated in the compositions of this invention.

50 The novel molding compositions of this invention are prepared in conventional equipment and using techniques well known in the plastics industry to be useful in compounding allylic, epoxy, and polyester molding compounds. The molding compounds may be filled or unfilled and of the premixed powdered, granular or dough type. The polyfunctional polymerizable materials, including polymer and monomer, a polybrominated aromatic hydrocarbon, free radical catalyst and an internal mold release, pigments, inhibitor, and so forth are simply mixed together in a heavy duty mixer. The mixing may be done with or without the use of solvents. However, if solvents

are used, they should be removed from the premixed compound before molding. The molding compositions can be molded under conditions normally used for allyl polymer molding compositions, that is, they may be molded at from about 130° to 180°C for about 1 to 60 minutes. Because of the various viscosities of these novel molding compositions, the molding pressure may vary from near (0) zero to 10,000 pounds per square inch depending on the composition.

70 There are two convenient ways to add the polybrominated aromatic hydrocarbons to the polyethylenically unsaturated polymerizable materials. The preferred method of addition is to add the polybrominated aromatic hydrocarbon with the polyethylenically unsaturated materials as any other additive might be added in a molding compound or laminating solution. Although not the preferred method of addition, the polybrominated aromatic hydrocarbon may be added after it has been pre-reacted with a polyfunctional monomer. This is particularly useful where large amounts of monomer cannot be tolerated, as in high pressure molding compounds. Direct addition of the polybrominated aromatic hydrocarbon in preparation of the molding compound can be done by simply adding a polyethylenically unsaturated monomer and a polybrominated aromatic hydrocarbon to a molding compound prior to or during compounding in place of part of the polymer which would normally be used in the molding compound, providing there is at least one mol by weight of polyethylenically unsaturated monomer present for each three mols of polybrominated aromatic hydrocarbon.

100 The polyethylenically unsaturated polymerizable materials and polybrominated hydrocarbons have been prereacted to form solid reaction products by heating together a mixture of about 3 to 2 mols of polybrominated aromatic hydrocarbon with 2 to 3 mols of a polyethylenically unsaturated monomer in the presence of about 2% by weight of dicumyl peroxide. A number of filled and unfilled reaction products were prepared in a sigma blade mixer equipped with a steam jacket. Steam at a temperature of 160°C was circulated through the jacket. The reactants, and in some cases, filler and catalyst were simply added to the sigma blade mixer with 160°C steam being supplied to the steam jacket and reacted together with agitation. Although the exact temperatures of the mixer blade and side walls was not known and accurate time measurements could not be made, reasonable initiation times, generally less than 10 minutes, were obtained. During the processing the mixtures were highly fluid up to reaction and proceeded through reaction rapidly to a brittle, rubber stage finally breaking into small lumps. No particular advantage was observed for filled compositions. All of

the reactants evaluated appeared to have about the same rate of reaction and the reaction appeared to be complete in a matter of 2 to 5 minutes after initiation. The hard reaction products were ball-milled for a period of 2 hours to produce a finely ground, uniform powder. The ratio of polyethylenically unsaturated monomer to polybrominated aromatic hydrocarbon was varied over ratios from 3 to 2 mols of monomer per 2 to 3 mols of polybrominated aromatic hydrocarbon. These products, due to their high bromine content, were found to impart flame resistance to thermosetting compounds. These novel solid reaction products may be used in thermoplastics such as polyethylene, polyvinyl chloride acrylics and polystyrene, as well as rubber and other organic systems including thermosetting materials such as epoxy resins, polyurethane resins and polyimide resins, where flame resistance is desirable.

These solid reaction products can also be added to unsaturated polyester resin compositions containing a monounsaturated monomer, for example, a "styrene cut polyester." The physical properties of styrene type polyester molding compounds containing the solid reaction products of this invention exceed the United States military specification requirements for Styrene-Polyester Molding compounds.

The materials of this invention permit compounding versatility that has not previously been available. The materials can be used in processing compositions which are to be subjected to either low pressure or high pressure thermosetting conditions. Where it is desirable to incorporate these flame retardant materials into high pressure molding compounds such as in diallyl phthalate systems, the solid pre-reacted products described above are preferred. These materials in the form of a fine powder are easily dispersed in an allyl resin composition in place of part of the allyl prepolymer. A diallyl phthalate molding composition containing the flame retardant pre-reacted products is processed in the same manner as conventional diallyl phthalate molding compounds. Up to 50% of the diallyl phthalate prepolymer can be replaced by these solid reaction products. Where it is desirable to achieve maximum flame retardancy in a molding compound or laminate with a minimum amount of bromine it is advisable to incorporate antimony oxide along with the bromine containing reaction product. Metal oxides such as hydrated alumina may be used with the antimony oxide. It is generally advisable to use a sufficient amount of the reaction product in a molding compound or laminate so that there is about 10 to 20% bromine, based on the weight of the total organic content of the molding compound or laminate for high levels of flame resistance. However, less

bromine is required where low levels of flame resistance can be tolerated.

Where low pressure, long flow laminating, impregnating and molding compositions are desired, the polybrominated aromatic hydrocarbon can be incorporated directly in allyl compositions or polyester compositions provided there is at least one mol by weight of a polyethylenically unsaturated monomer for each three mols of polybrominated aromatic hydrocarbon and a peroxide catalyst which will not initiate the free radical curing at less than 100°C.

Polyphenylene ether polymers can be used to replace up to all of the polyethylenically unsaturated polymer in these novel compositions. When some or all of the polyethylenically unsaturated polymer is replaced with polyphenylene ether polymer, the compositions can be used at coating compositions, as glue lines for adhering materials to reinforced polymeric substrates or adhering two materials together, for use in reinforced laminates and as potting and encapsulating compositions. Although all of the polyethylenically unsaturated polymer can be replaced with polyphenylene ether polymer, it is preferred to retain at least some of the polyethylenically unsaturated polymer in the compositions as the presence of the polyethylenically unsaturated polymer improves the handling characteristics of the compositions.

The novel compositions of the invention are readily used in preparing fiber reinforced laminates, generally fiber glass reinforced, by either the wet lay-up or prepreg techniques. Wet fiber glass lay-ups are prepared by making a liquid blend of the polymerizable materials, i.e., a monomer such as diallyl orthophthalate, a polymer containing carbon to carbon unsaturation and/or a polyphenylene ether polymer, a polybrominated aromatic hydrocarbon, a catalyst, and other modifying ingredients such as dyes, pigments, fillers, inhibitors and glass coupling agents. The liquid blend is poured onto one or more layers of a fibrous non-woven glass mat or woven glass fabric, which has preferably been treated with a glass coupling agent, to impregnate the reinforcing glass; after impregnation the product is laminated under heat and mild pressures according to procedures well known to be useful for curing allyl resin laminates.

A typical slow cure is effected by placing the wet lay-up in a vacuum bag and applying a vacuum of 28 to 30 inches of mercury for about 1 to about 5 hours to remove bubbles; the evacuated lay-up is then preferably augmented by autoclave pressure at 30 to 50 psi for 30 minutes at 82°C, 60 minutes at 120°C, 30 minutes at 150°C, 15 minutes at 160°C, and then cured an additional 60 minutes at 160°C. Thin sections can be cured more rapidly; for example, 30 to 50 psi for 60

minutes at 160°C. The amount of glass in the lay-up can be as high as 80% although the preferred amount of reinforcing glass is 50 to 75% by weight of the laminate.

5 The novel resin compositions of this invention can be employed in the usual process for manufacture of fibrous reinforced thermoset resin laminates using the prepreg technique. A polymerizable liquid, i.e., monomer
10 such as diallyl orthophthalate, a polybrominated aromatic hydrocarbon, a polyphenylene ether polymer, and where desired, a polymer containing carbon to carbon unsaturation such as an allyl prepolymer or a
15 reactive type polyester resin, a catalyst and modifying ingredients such as dyes, pigments, fillers, glass coupling agents and inhibitors are mixed together and used to impregnate a fibrous non-woven mat or a woven fabric.
20 Where glass mats or fabrics are used, it may be desirable to have the glass treated with a glass coupling agent. The use of some solvent is usually required in order to reduce the viscosity of the resin composition to make
25 it suitable for application to the mat or fabric with conventional, commercial saturating or impregnating equipment.

30 It is not necessary to dissolve the polyphenylene ether polymer when such polymer is used in the impregnating compositions of this invention. Simple uniform dispersion of the polyphenylene ether polymer powder in the solvent-monomer-polymerizable resin mixtures
35 suffices. Prepregs are generally more economically processed with 30 to 60 parts of the impregnating composition dispersed in 70 to 40 parts of a suitable solvent such as acetone, methylethyl ketone, methyl isobutyl ketone, toluene, xylene, chloroform, methylene
40 chloride, trichloroethylene, perchloroethylene and mixtures thereof and other solvents known to be useful in preparing allylic prepregs.

45 The mat or fabric is impregnated with a solvent solution of the impregnating composition and then dried to remove the solvent. After impregnation and drying of the impregnated fabric, the laminate is laid up and cured with heat and mild pressure using cure cycles and conditions similar to those used in curing the wet lay-up type laminates. Roving,
50 including glass roving, is similarly pre-impregnated for processing by filament winding techniques into pipe, other cylindrical shapes and hollow tapered and conical shapes. Products
55 made by filament winding are generally cured at about 150°C in 60 minutes. The fiber content of the prepreg laminates varies from about 15 to about 40% by weight for low density fibers and up to about 55 to 75% of the total weight of the cured laminate for
60 glass mat or glass fabric laminates. The fiber content of filament wound constructions such as pipe, when made from impregnated glass roving, is generally about 70 to 80% of the
65 total weight of the cured product.

Reinforced laminates of fibrous materials such as glass cloth, glass mats, synthetic fiber, cloth mats and paper can be copper-clad to produce copper-clad laminates with excellent electrical properties to be used in preparing printed circuits and the like. Copper-clad
70 laminates can be prepared by coating copper sheet with a thermosetting coating of this invention containing a polyphenylene ether polymer and then heating the coating copper
75 sheet at 100° to 170°C for 20 to 30 minutes. The baked resin coated foil is then placed on resin impregnated fibrous materials (on one or both sides) such as glass cloth which
80 has been impregnated with the novel compositions of this invention and then the "laminate" is pressed at 50 to 2,000 psi at 100 to 170°C for at least 5 minutes to convert the resinous materials to the thermoset state. If desired,
85 the coated copper foil can be laminated at a temperature of at least 130°C to almost any thermoset resin base. In accordance with a preferred embodiment, the base material is a thermoset polymer composition which is:

- (a) a thermosetting polyethylenically unsaturated polymer containing 10 to 50% by weight of a polyethylenically unsaturated monomer converted to the thermoset state at an elevated temperature of at least 130°C in the presence of a peroxide catalyst; 90
- (b) a flame-retardant thermosetting composition comprising 5—70 parts by weight of a polyethylenically unsaturated monomer 95—30 parts by weight of a polyethylenically unsaturated polymer or a polyphenylene ether polymer, with 5 to 50 parts by weight per 100 parts of monomer and polymer of a polybrominated aromatic hydrocarbon containing at least 50% by weight combined bromine and whose molecular weight is greater than 200, in which composition there is at least 1 mol of polyethylenically unsaturated monomer for each 3 mols of polybrominated aromatic hydrocarbon, converted to the thermoset state at a temperature of at least 130°C in the presence of a peroxide catalyst; or 100
- (c) a thermosetting composition comprising 10—45% by weight of a polyethylenically unsaturated monomer, 20—75% by weight of a polyethylenically unsaturated polymer, 10—35% by weight of said polyphenylene ether resin, converted to the thermoset state at a temperature of at least 130°C in the presence of a peroxide catalyst. 105

A reinforcing material which is a non-woven fibrous mat, a woven fabric or fiber may be incorporated in the base. A second sheet of copper can be coated and a coated copper 125

sheet laminated to each side of the base. As indicated above, dicumyl peroxide is the preferred catalyst for producing the copper-clad laminates of this invention. The resulting copper-clad laminate has excellent electrical properties and adhesion of the copper to the base material is also excellent. Quite surprisingly when tested, according to NEMA Standards Publication LI-1-1966, but at up to 200°C rather than the standard 25°C, these copper-clad laminates retained essentially all of their electrical properties as measured at room temperature. Reinforced laminates made from those compositions of this invention which contain polyphenylene ether polymers adhere very well to the type of copper foil used in making printed circuit boards without pre-coating the foil. Compositions containing a polybrominated aromatic hydrocarbon apparently "wet" metal surfaces better than similar compositions without the polybrominated aromatic hydrocarbon.

Those compositions of this invention which contain polyphenylene ether resins as a portion of the system are useful as thermosetting coatings. They adhere strongly to a wide variety of substrates including metals, ceramic bases and other resinous substances while providing excellent electrical insulating characteristics. They may be used as conformal coatings for electronic devices or as primer coats to bond additional electrical insulation to the devices. Many molding compounds used in the encapsulation of electronic components do not form good bonds to the devices and to the wire leads, thereby permitting access of moisture. When such devices or leads are first coated with the compositions of this invention, and then heated for 20 to 30 minutes at 100 to 170°C prior to mold encapsulating the device with a thermosetting mold encapsulation composition, said mold encapsulation being done at a temperature of at least 130°C whereby the mold encapsulation composition and the thermosetting composition are converted to the thermoset state, hermetically sealed systems are obtained which resist moisture even on prolonged exposure to boiling water or high pressure steam.

The coatings may be formulated with all polymer components in solution. Useful solvents comprise chlorinated hydrocarbons and aromatic hydrocarbons. Alternatively, the coatings may be formulated as finely divided dispersions of the polymer system in liquid organic media. Useful dispersion media include organic ketones and esters. Dispersed coatings are preferred for most applications since they may be formulated at high polymer

solids levels yet are capable of application by brushing, spraying or roller coating. Coatings containing up to 80 percent solids can be applied by knife coating techniques yet they flow out to smooth adherent insulating varnishes when subjected to oven baking at temperatures of 120°C or higher.

A thermoset article can be produced by saturating a fibrous sheet with a thermosetting composition of the present invention and heating the saturated fibrous sheet at a temperature of at least 130°C for 2 to 30 minutes.

The test methods appearing in the following list were followed in testing the molded and laminated test specimen made from the various compositions disclosed in the Example.

A. Flexural Strength*	ASTM D-790	60
B. Modulus of Elasticity in Flexure (Flex. Mod.)	ASTM D-790	65
C. Tensile Strength	ASTM D-638	70
D. Compressive Strength (Comp. Str.)	ASTM D-695	75
E. Water Absorption	ASTM D-570 (a)	
F. Specific Gravity	ASTM D-792	85
G. Flame Resistance (Burning and Ignition Tests Method 1 and 2)	ASTM D-229	
H. Hardness (Rockwell)	ASTM D-785	90
I. Interlaminar Shear Strength	ASTM D-2733	

* The flexural strengths at 150°C for the unfilled resin systems were obtained after $\frac{1}{2}$ hour conditioning at 150°C. Each individual specimen as held to $\frac{1}{2}$ hour conditioning to avoid any ambiguity that may be caused by post-curing in the test oven. Only maximum flexural yield was measured.

In the Example, all parts and percentages are by weight unless otherwise specified.

Example

Vacuum bag laminates were prepared using diallyl isophthalate prepolymer and monomer, brominated biphenyl and in one example a polyphenylene ether polymer. Woven glass cloth, type 181, was impregnated with the mixtures set forth below and allowed to dry for 48 hours at 25°C. The dry impregnated glass cloth was cut into 12" squares, stacked 18 plies deep with the warp yarns parallel. The impregnated lay-up was molded by the vacuum-bag technique. Full cure was obtained after 15 minutes at 150°C.

Formulation			
5	Diallyl isophthalate monomer	250	350
	Diallyl isophthalate prepolymer	650	310
	Hexabromobiphenyl	200	150
	Dicumyl peroxide	30	30
	Gamma methacryloxypropyl-trimethyl silane	5	5
10	Hydroquinone	0.3	0.3
	Aluminum trihydrate	70	40
	Methyl ethyl ketone	400	400
	Polyphenylether blend (1)	—	285
Physical Properties			
15	Resin content, weight %	29.8	35.1
	Rockwell hardness, M scale	120	122
	Compressive strength, psi	26,400	44,500
	Flexural strength psi @ 25°C	65,800	83,900
	psi @ 205°C	31,100	22,000
20	after 2 hours in boiling water	47,800	76,900
	Flexural Modulus, psi @ 25°C	2.7×10^4	2.8×10^4
	psi @ 205°C	2.6×10^4	1.8×10^4
	after 2 hours in boiling water	2.6×10^4	2.9×10^4
	Tensile strength, psi	52,600	55,300
25	Shear strength, psi @ 25°C	3010	5400
	psi @ 205°C	1740	1470
	Moisture absorption, 48 hours under water at 50°C, wt %	.44 (2)	.08
	Specific gravity	1.974	1.911
	Dielectric constant 10^3 /HZ dry	4.53	4.30
30	10^6 /HZ dry	4.46	4.33
	Burning test ASTM D-635)	Non-burning	Non-burning

- (1) Polyphenylene ether polymer, 200 parts diallyl isophthalate prepolymer, 57 parts, and aluminum trihydrate, 28 parts, ball milled together for 12 hours.
 (2) Sample contained some small voids.

WHAT WE CLAIM IS:—

- 35 1. A flame-retardant composition derived from (a) 10—70 parts by weight of a polyethylenically unsaturated monomer, (b) 90—30 parts by weight of a polyethylenically unsaturated polymer, a polyphenylene ether polymer or a mixture thereof, (c) 5—50 parts by weight per 100 parts by weight of said monomer and polymer, of a polybrominated aromatic hydrocarbon containing at least 50% by weight combined bromine and whose molecular weight is greater than 200, in which composition there is at least 1 mol of polyethylenically unsaturated monomer for each 3 mols of polybrominated aromatic hydrocarbon.
 45 2. A composition as claimed in claim 1 in which the polybrominated aromatic hydrocarbon is used in the form of a reaction product prepared by heating 3 to 2 mols of polybrominated aromatic hydrocarbon containing at least 50% by weight bromine and having a molecular weight of at least 200 with 2 and 3 mols of the polyethylenically unsaturated monomer at a temperature of at least 130°C in the presence of a free radical initiator.
 50 3. A composition as claimed in claim 1 or 2 which also comprises a peroxide catalyst which

has at least a 10 hour half-life in benzene at a temperature in excess of 100°C in sufficient amount to convert the ethylenically unsaturated monomer - polymer - brominated aromatic hydrocarbon mixture to the thermoset state at elevated temperatures.
 4. A composition as claimed in any of claims 1 to 3 which comprises:

- (a) 10 to 50 parts by weight of the polyethylenically unsaturated monomer;
 (b) 5 to 30 parts by weight per 100 parts of (a) plus (c) plus (d) of the polybrominated aromatic hydrocarbon containing at least 50% by weight bromine and having a molecular weight of at least 200, the ratio of monomer to brominated hydrocarbon being at least 1:3 on a molar basis;
 (c) 20 to 60 parts by weight of the polyphenylene ether polymer;
 (d) 0—30 parts by weight of the polyethylenically unsaturated polymer, and
 (e) 2—10 parts by weight per 100 parts of all of (a) plus (b) plus (c) plus (d) of a peroxide catalyst which has a minimum 10 hour half-life in benzene at a temperature in excess of 100°C.



Formulation

5	Diallyl isophthalate monomer	250	350
	Diallyl isophthalate prepolymer	650	310
	Hexabromobiphenyl	200	150
	Dicumyl peroxide	30	30
	Gamma methacryloxypropyl-trimethyl silane	5	5
10	Hydroquinone	0.3	0.3
	Aluminum trihydrate	70	40
	Methyl ethyl ketone	400	400
	Polyphenylether blend (1)	—	285

Physical Properties

15	Resin content, weight %	29.8	35.1
	Rockwell hardness, M scale	120	122
	Compressive strength, psi	26,400	44,500
	Flexural strength psi @ 25°C	65,800	83,900
20	psi @ 205°C	31,100	22,000
	after 2 hours in boiling water	47,800	76,900
	Flexural Modulus, psi @ 25°C	2.7×10^6	2.8×10^6
	psi @ 205°C	2.6×10^6	1.8×10^6
	after 2 hours in boiling water	2.6×10^6	2.9×10^6
	Tensile strength, psi	52,600	55,300
25	Shear strength, psi @ 25°C	3010	5400
	psi @ 205°C	1740	1470
	Moisture absorption, 48 hours under water at 50°C, wt %	.44 (2)	.08
	Specific gravity	1.974	1.911
30	Dielectric constant 10^3 /HZ dry	4.53	4.30
	10^6 /HZ dry	4.46	4.33
	Burning test ASTM D-635)	Non-burning	Non-burning

(1) Polyphenylene ether polymer, 200 parts diallyl isophthalate prepolymer, 57 parts, and aluminum trihydrate, 28 parts, ball milled together for 12 hours.

(2) Sample contained some small voids.

WHAT WE CLAIM IS:—

- 35 1. A flame-retardant composition derived from (a) 10—70 parts by weight of a polyethylenically unsaturated monomer, (b) 90—30 parts by weight of a polyethylenically unsaturated polymer, a polyphenylene ether polymer or a mixture thereof, (c) 5—50 parts by weight per 100 parts by weight of said monomer and polymer, of a polybrominated aromatic hydrocarbon containing at least 50% by weight combined bromine and whose molecular weight is greater than 200, in which composition there is at least 1 mol of polyethylenically unsaturated monomer for each 3 mols of polybrominated aromatic hydrocarbon.
- 45 2. A composition as claimed in claim 1 in which the polybrominated aromatic hydrocarbon is used in the form of a reaction product prepared by heating 3 to 2 mols of polybrominated aromatic hydrocarbon containing at least 50% by weight bromine and having a molecular weight of at least 200 with 2 and 3 mols of the polyethylenically unsaturated monomer at a temperature of at least 130°C in the presence of a free radical initiator.
- 50 3. A composition as claimed in claim 1 or 2 which also comprises a peroxide catalyst which

has at least a 10 hour half-life in benzene at a temperature in excess of 100°C in sufficient amount to convert the ethylenically unsaturated monomer - polymer - brominated aromatic hydrocarbon mixture to the thermoset state at elevated temperatures.

4. A composition as claimed in any of claims 1 to 3 which comprises:

- (a) 10 to 50 parts by weight of the polyethylenically unsaturated monomer;
- (b) 5 to 30 parts by weight per 100 parts of (a) plus (c) plus (d) of the polybrominated aromatic hydrocarbon containing at least 50% by weight bromine and having a molecular weight of at least 200, the ratio of monomer to brominated hydrocarbon being at least 1:3 on a molar basis;
- (c) 20 to 60 parts by weight of the polyphenylene ether polymer;
- (d) 0—30 parts by weight of the polyethylenically unsaturated polymer; and
- (e) 2—10 parts by weight per 100 parts of all of (a) plus (b) plus (c) plus (d) of a peroxide catalyst which has a minimum 10 hour half-life in benzene at a temperature in excess of 100°C.



5. A composition as claimed in any of claims 1 to 4 in which the polybrominated aromatic hydrocarbon is a brominated biphenyl, a brominated terphenyl, tribromobenzene or a brominated naphthalene.
6. A composition as claimed in any of claims 1 to 4 in which the polyethylenically unsaturated monomer is diallyl phthalate, diallyl isophthalate, diallyl chlorendate, diallyl maleate, triallyl cyanurate, triallyl isocyanurate, ethylene glycol dimethacrylate, or divinyl benzene.
7. A composition as claimed in any of claims 2 to 6 in which the free radical initiator used in preparing the polybrominated aromatic hydrocarbon reaction product is a peroxide catalyst which has a 10 hour half-life in benzene at a temperature in excess of 100°C.
8. A composition as claimed in any of claims 3 to 7 in which the peroxide catalyst is dicumyl peroxide, tertiary butyl perbenzoate, 2,4 - dimethyl - 2,5 - di(tertiary - butylperoxy) - hexyne - 3, 2,5 - dimethyl - 2,5 - di(tertiary - butylperoxy) - hexane alone or in admixture with benzoyl peroxide.
9. A composition as claimed in any of claims 1 to 8 in which the polyethylenically unsaturated polymer is diallyl orthophthalate prepolymer, diallyl isophthalate prepolymer, diallyl terephthalate prepolymer, or an unsaturated polyester resin of the type in which at least 50 mole percent of the dibasic carboxylic acid portion of the polyester resin is an unsaturated dicarboxylic acid, and the alcohol component is a glycol containing 2 to 8 carbon atoms, which may be cyclic or acyclic.
10. A composition as claimed in any of claims 1 to 9 which also comprises up to 200 parts by weight per 100 parts by weight of (a), (b) and (c) as defined in claim 1 of in inert, filler which is an inert mineral filler, an inert fibrous filler, a fibrous mat, woven fabric or non-woven fabric.
11. A composition as claimed in any of claims 1 to 9 which also comprises up to 400 parts by weight per 100 parts by weight of polyethylenically unsaturated polymerizable materials—polybrominated aromatic hydrocarbon of fiber-glass.
12. A composition as claimed in any of claims 1 to 11 which also comprises a fluid in which the thermosetting composition is dispersed or dissolved.
13. A composition as claimed in claim 12 in which the fluid is a chlorinated hydrocarbon solvent or aromatic hydrocarbon solvent.
14. A flame-retardant composition according to claim 1 substantially as hereinbefore described with particular reference to the foregoing Example.
15. A method for producing a copper clad laminate which comprises coating a copper sheet with a thermosetting coating composition as claimed in any of claims 3 to 14 and heating said coated copper sheet for 2 to 30 minutes at 100° to 170°C prior to being laminated at a temperature of at least 130°C to a base, whereby the thermosetting coating is converted to the thermoset state.
16. A method as claimed in claim 15 in which the coating composition is as claimed in claim 4.
17. A method as claimed in claim 15 or 16 in which the base material is a thermoset polymer composition which is:
- (a) a thermosetting polyethylenically unsaturated polymer containing 10 to 50% by weight of a polyethylenically unsaturated monomer converted to the thermoset state at an elevated temperature of at least 130°C in the presence of a peroxide catalyst;
 - (b) a flame-retardant thermosetting composition comprising 5—70 parts by weight of a polyethylenically unsaturated monomer 95—30 parts by weight of a polyethylenically unsaturated polymer or a polyphenylene ether polymer, with 5 to 50 parts by weight per 100 parts of monomer and polymer of a polybrominated aromatic hydrocarbon containing at least 50% by weight combined bromine and whose molecular weight is greater than 200, in which composition there is at least 1 mol of polyethylenically unsaturated monomer for each 3 mols of polybrominated aromatic hydrocarbon, converted to the thermoset state at a temperature of at least 130°C in the presence of a peroxide catalyst; or
 - (c) a thermosetting composition comprising 10—45% by weight of a polyethylenically unsaturated monomer, 20—75% by weight of a polyethylenically unsaturated polymer, 10—35% by weight of said polyphenylene ether resin, converted to the thermoset state at a temperature of at least 130°C in the presence of a peroxide catalyst.
18. A method as claimed in any of claims 15 to 17 in which a reinforcing material which is a nonwoven fibrous mat, a woven fabric or fiber is incorporated in the base.
19. A method as claimed in claim 18 in which a second sheet of copper is coated and a coated copper sheet is laminated to each side of said base.
20. A method for producing a copper clad laminate according to claim 15 substantially as hereinbefore particularly described.
21. A method for producing a thermoset article which comprises saturating a fibrous sheet with a thermosetting composition as claimed in any of claims 3 to 14 and heating the saturated fibrous sheet at a temperature of at least 130°C for 2 to 30 minutes.



22. A method as claimed in claim 21 in which the composition is as claimed in claim 4. 20
- 5 23. A method as claimed in claim 21 or 22 which comprises laminating a copper foil sheet in one or both surfaces of said saturated fibrous sheet to form a copper clad laminate. 25
- 10 24. A method as claimed in claim 23 in which a plurality of fibrous sheets are saturated with the thermosetting composition and a plurality of the saturated sheets are laid up to form a multiple ply base carrying a copper foil sheet on one or both surfaces of the laminate. 30
- 15 25. A method for producing a thermoset article according to claim 21 substantially as hereinbefore particularly described.
26. A method for producing a mold encapsulated electrical device with a plurality of leads projecting from the device which comprises coating said device with a thermosetting coating composition as claimed in any of claims 3 to 14, heating said coated device for 2 to 30 minutes at 100 to 170°C prior to mold encapsulating the device with a thermosetting mold encapsulation composition, said mold encapsulation being done at a temperature of at least 130°C whereby the mold encapsulation composition and the thermosetting composition are converted to the thermoset state.
27. A method according to claim 26 substantially as hereinbefore particularly described.
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