

PATENT SPECIFICATION

(11) 1287 519

NO DRAWINGS

- (21) Application No. 31375/70 (22) Filed 29 June 1970
 (31) Convention Application No. 837 911 (32) Filed 30 June 1969 in
 (33) United States of America (US)
 (45) Complete Specification published 31 Aug. 1972
 (51) International Classification C08F 45/58, 29/44 // B32B 5/28;
 H01L 1/10



- (52) Index at acceptance
 C3P 14D2F 14D2H 14D3C2 14K4 14P1E4 14P4C 14P6X
 4A 4C12B 4C13A 4C16B 4C16C 4C20D1 4C20D3
 4C4A 4C8B 4D2 4D3A 4K4 4P1E3 4P1E4 4P3
 4P4C 4P5 4P6H 4P6X
 B5N 178 17Y 184 189 192 20Y 214 228 239 242 250 253X
 254X 269X 270X 277X 287X 290X 296X 299X
 428 462 466 542 547 55Y 64X 669 670 679 67X
 682 687 68X 697 69X 736 745 748
 C3R 36C10 36C12 36C22 36C23 36C25 36C6X 36C8P
 36L1A 36L1B 36L2X 36L4C 36L6F
 H1K 211 312 412 41Y 421 424 42X 454 463 470

(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 BBACHAM), 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 polychlorinated 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 chlorinated intermediates which become a part of the cured thermoset system, thus avoiding the plasticizing effect experienced when using chlorinated paraffins, chlorinated polyphenyls and the like. An important advance in the chemistry of self-extinguishing or flame retardant thermoset resins occurred as a result of the discovery of a commercial method of making chlorendic acid or anhydride in 1952. Chlorendic acid and anhydride have been esterified to form polyesters similar to those obtained when using phthalic anhydride. Additionally, chlorendic acid and anhydride have been used to prepare reactive monomers, such as diallyl chlorendate, which are useful in flameproofing thermosetting resins such as polyesters and diallylic phthalates without substantially reducing the desirable physical properties of the thermoset resin compositions.

The addition of a reactive flame retardant additive to thermoset resins such as polyesters and diallylic phthalate resins is highly desirable as this method of flameproofing offers flexibility in resin production since it is possible to flameproof general purpose resins rather than to make special flame retardant grade resins. The chlorendic acid based reactive flame retardant materials are expensive and since 1952 no efficient and inexpensive reactive flame retardants for thermoset resins have been widely accepted.

By means of the present invention certain polychlorinated aromatic hydrocarbon compounds are incorporated in thermosetting polymer compositions to make the compositions flame retardant without injuring the desirable physical and electrical properties of the thermosetting compositions when in the thermoset state.

According to the present invention there is provided 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 polychlorinated aromatic compound containing at least 50% by weight combined chlorine and whose molecular weight is greater than 200, in which composition there is at least 1 mole of polyethylenically unsaturated monomer for each 3 mols of polychlorinated aromatic compound.

The compositions of the present invention can also include polymerization initiators, pigments, fillers, reinforcing fibers, release agents, coupling agents and other incidental additives in amounts commonly used in resin, particularly thermosetting resin, compositions.

Where high monomer levels cannot be tolerated, as in high pressure molding compounds, the polychlorinated compound may be pre-reacted with the monomer prior to incorporating the polychlorinated aromatic hydrocarbon in the thermosetting resin composition. The polychlorinated aromatic compound is pre-reacted with the monomer by heating 3 to 2 mols of the polychlorinated aromatic hydrocarbon with 2 to 3 mols of the polyethylenically unsaturated monomer at a temperature of at least 130°C in the presence of a free radical initiator for a period of time sufficient to initiate an exothermic reaction between the polychlorinated aromatic compound and the monomer, generally about 2 to about 10 minutes. These reaction products can be added to thermosetting compositions and thermoplastic compounds as flame retardant additives.

Another feature of the invention is the discovery that certain of the novel compositions adhere strongly to a wide variety of substrates including metals. These compositions, which are useful as thermosetting coatings, generally comprise: (a) 10 to 50 parts by weight of a polyethylenically unsaturated monomer; (b) 5 to 30 parts by weight of a polychlorinated aromatic hydrocarbon containing at least 50% by weight chlorine and having a molecular weight of at least 200, the ratio of monomer to polychlorinated aromatic hydrocarbon being at least 1 to 3 on a molar basis; (c) 20 to 60 parts by weight of a polyphenylene ether polymer; (d) 0 to 30 parts by weight of a polyethylenically unsaturated polymer and (e) 2 to 10 parts by weight per 100 parts by weight 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. Because it is not necessary to dissolve the polyphenylene ether polymer portion of these coating compositions, the compositions may be dispersed in a liquid for ease of application, thus making it possible to prepare coating compositions containing as much as 80 weight % solids. These compositions are useful for coating articles to seal them against moisture, as coating compositions for impregnating glass fabric and the like for making laminates, and because they adhere well to metal, they are useful in adhering metal to metal and metal to plastics such as in preparing a copper clad glass laminate.

All of the compositions of the present invention can be thermoset by free radical initiators at temperatures of at least 130°C for a period of time sufficient to initiate an exothermic reaction during which the polychlorinated

aromatic compound reacts with other components of the compositions and loses its thermoplastic or plasticizing properties.

5 The polychlorinated aromatic hydrocarbons containing at least 50% by weight combined chlorine and having a molecular weight greater than 200, useful in practicing this invention, include but are not limited to, compounds such as chlorinated biphenyls and terphenyls, 10 trichlorobenzene and higher chlorinated benzenes and alkyl substituted benzenes and chlorinated naphthalenes.

Polyethylenically unsaturated polymers useful in practicing this invention include, but are not limited to, diallyl phthalate prepolymers and unsaturated polyester resins. Diallyl 15 phthalate prepolymers useful in practicing this invention include prepolymers made from the diallyl esters of ortho-, iso-, and terephthalic acids. These diallyl phthalates may be manufactured by polymerizing a monomeric material to produce a solution of soluble prepolymer in monomer. Polymerization is carried to a point short of gelation. The prepolymer must then be separated from the unpolymerized monomer. This may be done by treatment with a solvent which dissolves the monomer and precipitates the prepolymer. 25 Such a general process is described in U.S. Patent Specification No. 3,096,310. A conventional method of separating allyl prepolymer from monomer by precipitating the prepolymer in an unreactive liquid precipitant that is a solvent for the monomer and a non-solvent for the prepolymer in a shearing zone is described in U.S. Patent Specification No. 3,030,341. Prepolymers may also be separated from unpolymerized monomer by distillation as disclosed in U.S. Patent Specification No. 3,285,836. The diallyl phthalate prepolymers are solids containing little or no monomer; they can be stored indefinitely in this form since they require catalysts and either heat, actinic light or nuclear particle radiation to convert them to the insoluble or thermoset stage. 45

The unsaturated polyester resins useful in practicing this invention, whether liquid or solid, should be of the reactive type, that is, at least about 50 mole percent of the dibasic acid portion of the polyester resin should be an unsaturated diacid such as maleic or fumaric acid. If these polyester resins are diluted or cut with a monomer, the polyester resin should preferably be cut with a polyfunctional monomer. The alcohol moiety of the polyester is generally a saturated, glycol containing 2 to 8 carbon atoms which may be cyclic or acyclic. 55

60 A reactive unsaturated polyester may be prepared by reacting equimolar amounts of maleic anhydride and diethylene glycol at a temperature above 200°C. Water is azeotropically removed. The distillate is analyzed from time to time for starting ingredients, 65

and a sufficient amount of material may be added to the reactor to maintain the initial proportions of the reacting ingredients. After 8 hours reaction at such a temperature, a polyester is obtained in the form of a viscous liquid with an acid number of about 18. 70

A solid reactive unsaturated polyester can be prepared by reacting equimolar amounts of a mixture of maleic anhydride and isophthalic acid with a 10 weight % excess of propylene glycol. Water is removed azeotropically. The reaction is continued by heating until the acid number of the reaction mixture falls below 5. Excess unreacted propylene glycol is removed under vacuum and a solid polyester is obtained. Polyesters made from chlorendic anhydride and equimolar amounts of maleic anhydride or fumaric acid are well known reactive flame retardant polyesters that can be used in practicing this invention. 85

Polyunsaturated monomers useful in practicing this invention include, but are not limited to, diallyl phthalate, diallyl isophthalate, diallyl chlorendate, diallyl maleate, triallyl cyanurate, triallyl isocyanurate, ethylene glycol dimethacrylate and divinyl benzene. Any polyunsaturated monomer may be used in practicing this invention. 90

The polyunsaturated materials and polychlorinated aromatic hydrocarbons can be either compounded into a thermosetting composition, such as a molding compound, in place of part of the conventional thermosetting polymer or can be prereacted to form a kind of gel polymer by mixing about 3 to 100 2 mols of the polychlorinated aromatic compounds with 2 to 3 mols of polyethylenically-unsaturated monomer and subjecting the mixture to a free radical initiator, by incorporating 1 to 5% by weight, preferably about 1.5 to 3% by weight of a peroxide catalyst in such a composition. 105

The preferred ratio of chlorinated aromatic compound to polyethylenicallyunsaturated monomer, when making the prereacted materials, is 1 mol of polychlorinated aromatic compound to each mol of polyunsaturated monomer. The free radical initiation should take place at a temperature of at least 130°C and below the boiling point of the monomer. 115 The reaction is exothermic and the temperature attained during the exothermic reaction period of a 100 g mass should be between about 200 and about 250°C under adiabatic conditions. Generally the reaction mixture must reach a temperature of at least 130°C for 2 to 5 minutes to initiate the exothermic reaction. Preferably the polychlorinated aromatic hydrocarbon and the polyethylenically unsaturated monomer are selected so that a hard, grindable reaction product is produced. Fillers may be incorporated in the prereaction mixture provided that the filler does not cause initiation of the reaction at less than 130°C or inhibit reaction above 130°C. Inert fillers 120 130

can comprise up to 60% by weight of the total mixture.

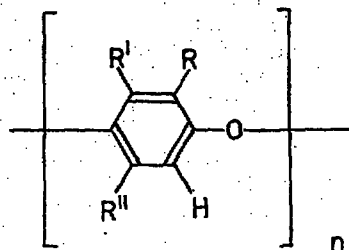
Typical polychlorinated aromatic hydrocarbons used in the practice of this invention are chlorinated biphenyls and terphenyls which are known to be so stable and chemically inactive that they are used, for example, as plasticizers and heat exchange fluids. Diallyl phthalate resins and unsaturated polyester resins, which are typical of the polyethylenically unsaturated materials used in practicing this invention, when cured, are known to be plasticized by chlorinated biphenyls and terphenyls. For example, ordinary molded diallyl phthalate polymer articles containing chlorinated biphenyls do not have the characteristic "hot hardness" of diallyl phthalate molded articles; when removed from a hot mold, the molded articles containing a chlorinated biphenyl are soft, like hot rubber, and harden only on cooling. Physical mixtures of highly chlorinated biphenyls (some with melting points above 150°C) and an allylic 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 polychlorinated aromatic compound. It is therefore quite surprising that when at least one mol of a polyethylenically unsaturated monomer is present for every 3 mols of the polychlorinated aromatic compound, these polychlorinated aromatic hydrocarbons can be incorporated into a diallyl phthalate prepolymer or unsaturated polyester resin molding compositions which can be cured into articles that are essentially not plasticized by the polychlorinated aromatic compound.

The polychlorinated aromatic hydrocarbon and polyethylenically unsaturated materials do not have to be prereacted. These materials may be incorporated into thermosetting resin 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 unsaturated monomer for every three mols of polychlorinated 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 electrical and mechanical properties and are flame resistant. The polychlorinated aromatics have little or no plasticizing effect upon the cured thermoset compositions and there is substantially no loss of thermoset properties.

Polychlorinated aromatic hydrocarbons are commercially available and represent a low cost chlorine source for making flame retardant thermoset resin compositions. Surprisingly, compared to the more expensive flame retardant compositions made with polyester or

diallyl phthalate resins and diallyl chloroendate, the compositions of this invention have somewhat improved electrical properties. These novel compositions can be used with ordinary flame retardant additives and synergists used in flame retardant resin compositions, such as antimony trioxide and hydrated alumina.

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 for each part of polyphenylene ether polymer. Typical polyphenylene ether polymers 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 halo-hydrocarbon 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 halo-hydrocarbonoxy 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 are the same as R and, in addition, halogen. All of the polyphenylene ether polymers currently available have been found to be useful in practicing 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 practicing this invention ("Noryl" is a Trade Mark). As far as is known, all known polyphenylene ether polymers are useful in practicing this invention.

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 polychlorinated aro-

matic 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 homopolymers. 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 practicing this invention.

A wide variety of water-insoluble, inert fillers may be used in preparing the molding 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-polychlorinated aromatic compound may be used in these molding compositions. Up to 400 parts by weight of fiber-glass may be present.

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.

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 polychlorinated 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 varied 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.

There are two convenient ways to add the polychlorinated aromatic hydrocarbons to the polyethylenically unsaturated polymerizable materials. The preferred method of addition is to add the polychlorinated 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 polychlorinated aromatic hydrocarbon may be added after it has been prereacted 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 polychlorinated aromatic compound in preparation of the molding compound can be done by simply adding a polyethylenically unsaturated monomer and a polychlorinated 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 polychlorinated aromatic compound.

The polyethylenically unsaturated polymerizable materials and polychlorinated hydrocarbons have been prereacted to form solid reaction products by heating together a mixture of about 3 to 2 mols of polychlorinated 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

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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 polychlorinated aromatic compound was varied over ratios from 3 to 2 mols of monomer per 2 to 3 mols of polychlorinated aromatic compound. These products, due to their high chlorine 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 chlorine it is advisable to incorporate antimony oxide along with the chlorine 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% chlorine, based on the weight of the total organic content of the molding compound or laminate for high levels of flame resistance. However, less chlorine is required where low levels of flame resistance can be tolerated.

Where low pressure, long flow laminating, impregnating and molding compositions are desired, the polychlorinated 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 polychlorinated 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 as 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 or a polyphenylene ether polymer, a polychlorinated aromatic compound, a catalyst, and other modifying ingredient 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 aug-

mented 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.

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 such as diallyl orthophthalate, a polychlorinated aromatic hydrocarbon, a polyphenylene ether polymer, and where desired, a polymer containing carbon to carbon unsaturation such as an allylic prepolymer or a 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. 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 it suitable for application to the mat or fabric with conventional, commercial saturating or impregnating equipment.

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 suffices. Prepregs are generally most 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 chloride, trichloroethylene, perchlorethylene and mixtures thereof and other solvents known to be useful in preparing allylic prepregs.

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, 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 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 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 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 laminates can be prepared by coating copper foil with a composition of this invention containing a polyphenylene ether polymer and then baking the coated copper foil at 100° to 170°C for 2 to 30 minutes. The baked resin coated foil is then placed on resin impregnated fibrous materials such as glass cloth which has been impregnated with the novel resin 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, 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 in 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 polychlorinated aromatic compound containing at least 50% by weight combined chlorine 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 polychlorinated aromatic compound 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.

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 coated copper 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-I-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 precoating the foil. Compositions containing a polychlorinated aromatic hydrocarbon apparently "wet" metal surfaces better than similar compositions without the polychlorinated 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 heated for 2 to 30 minutes at 100° to 170°C, and then subjected to mold encapsulation at a temperature of at least 130°C, usually for at least 5 minutes, 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 Examples.

A.	Flexural Strength*	ASTM D—790
B.	Modulus of Elasticity in Flexure (Flex. Mod.)	„ D—790
C.	Tensile Strength	„ D—638
D.	Izod Impact	„ D—256
E.	Compressive Strength (Comp. Str.)	„ D—695
F.	Deflection Temperature	„ D—648
G.	Water Absorption	„ D—570 (a)
H.	Specific Gravity	„ D—792
I.	Dielectric Constant (D.C.)	„ D—150
J.	Dissipation Factor** (D.F.)	„ D—150
K.	Volume and Surface Resistivity	„ D—257
L.	Flame Resistance (Burning and Ignition Tests Method 1 and 2)	„ D—229
M.	Hardness	„ D—785
N.	Hardness (Rockwell)	„ D—785
O.	Interlaminar Shear Strength	„ D—2733

*The flexural strengths at 150°C for the unfilled resin systems were obtained after 1/2 hour conditioning at 150°C. Each individual specimen was held to 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.

**The wet test is conducted on samples which were conditioned by immersing the samples for 24 hours at 23°C in distilled water, removing the samples, blotting them dry and then testing the samples as soon as practical according to the test method.

In the Examples all parts and percentages are by weight unless otherwise specified

Example 1

5 A series of samples were prepared which were simply mixtures of a chlorinated terphenyl containing 6% chlorine or a chlorinated biphenyl containing 68% chlorine with different monomers and 2% by weight of dicumyl peroxide based on the total weight of the chlorinated aromatic compound and monomer. The samples were placed in a paper cup and a thermocouple connected to a recording thermocouple bridge was inserted in each of the samples. The samples were placed in an oven maintained at a temperature of 160°C.

Various concentrations of the chlorinated aromatics with various monomer concentrations were prepared. Some of the samples tested were subjected to a 16 hour acetone soxhlet extraction at the reflux temperature of acetone. The composition details, the reaction initiating temperature, the reaction peak exotherm temperature, the reaction time to peak exotherm, and the results of the reaction are contained in Table I.

Soxhlet extraction studies were made on some of the compositions. Mixtures of the unreacted chlorinated aromatics and the mono-

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mers yield clear solutions in chloroform and hot acetone. The chlorinated aromatics can only be partially extracted from the reaction product, and that fraction which is extracted is different from the original crystalline chlorinated aromatic in that it tends to be a resinous gum.

Example 2

Molding compositions were prepared from diallyl phthalate prepolymer and polychlorinated aromatic compound prereacted with monomer. The prereacted polychlorinated aromatic hydrocarbon and monomer reaction products were prepared in 3 1/2 lb. batches. Chlorinated biphenyls, containing 68% combined chlorine (Aroclor 1268 from Monsanto Chemical Company — "Aroclor" is a Trade Mark), and a diallyl phthalate monomer were heated together in a ratio of 62 parts of chlorinated biphenyls to 38 parts of diallyl phthalate monomer with 2 parts by weight of dicumyl peroxide per 100 parts of chlorinated biphenyls plus monomer. The reaction products were prepared in a one-gallon sigma blade mixer equipped with a steam jacket. The steam to the jacket was at 160°C and the internal temperature of the blade and side walls was about 120°C. Although accurate reaction time measurements could not be made, reasonably short reaction times of about 10 minutes were observed in preparing these reaction products. The reactants were highly fluid up to the point of gelation, from which point the reaction proceeded rapidly to a brittle stage breaking up thereafter into small lumps. The prereacted materials were ball milled for a two hour period in a 1 1/2 gallon jar mill to produce 1,000 g of ground product. Reaction products were prepared using diallyl phthalate and diallyl isophthalate monomer and are designated Reaction Product #1 and Reaction Product #2 respectively in Table II. The reaction products were mixed with diallyl phthalate prepolymer and diallyl isophthalate prepolymer along with some catalyst, monomer and fillers to make molding compositions. The composition details and physical properties of samples molded from the molding compositions are found in Table II. For comparison, the Table includes qualifying specifications for diallyl phthalate molding compounds for military use under MIL M-14F and MIL-19833. (The largest market for the diallyl phthalate molding compounds in the United States is for military applications).

Example 3

A portion of the diallyl phthalate monomer-chlorinated biphenyl reaction product, Reaction Product #1 of Example 2, was incorporated into a diallyl phthalate/unsaturated polyester copolymer molding composition. Test

specimens were molded from the composition for three minutes at 150°C at 2000 psi (pounds per square inch). The composition of the molding composition, the physical and electrical properties of the molded test specimens and the MIL-M-14F specification requirements for MAI 30 diallyl phthalate polyester molding compounds are shown in Table III.

Example 4

High pressure laminates containing diallyl phthalate polychlorinated aromatic compound reaction products were prepared using polychlorinated aromatic compound/diallyl phthalate reaction products made according to Example 2. Sixty parts of polychlorinated aromatic compound, a chlorinated terphenyl containing 60% by weight chlorine, was reacted with forty parts of diallyl phthalate monomer and 2 parts of dicumyl peroxide as described in Example 2, and is labelled Reaction Product #3 in Table IV. A similarly prepared reaction product, using 40 parts of diallyl isophthalate monomer in place of diallyl phthalate monomer, is labelled Reaction Product #4 in Table IV. A glass cloth laminate was prepared as follows: A "resin blend" of the polychlorinated aromatic diallyl phthalate reaction product with the corresponding diallyl phthalate prepolymer and a small amount of diallyl phthalate monomer and two parts of dicumyl peroxide catalyst per 100 parts of reactants as shown in Table IV was dispersed, in the amount of 100 parts by weight of the "resin blend", in 100 parts by weight of acetone. Woven glass cloth was impregnated with this dispersion and allowed to dry at least 48 hours in air at room temperature. The impregnated glass cloth, often termed prepreg, was cut into 12" by 12" squares and stacked 18 plies deep with the warp yarns parallel. The pre-impregnated lay-up was laminated in a flat bed press for 30 minutes at 80°C at contact pressure, 30 minutes at 120°C at 300 psi and 1 hour at 160°C at 300 psi. Two samples were prepared, one using diallyl phthalate monomer and prepolymer; another sample using diallyl isophthalate prepolymer and diallyl isophthalate monomer. The composition details of the resin mixture used to impregnate the glass fabric, the resin content of the prepreps from the resin systems and the physical properties of the cured laminates are found in Table IV.

Example 5

A molding compound was prepared directly from a mixture of a chlorinated terphenyl, containing 60% combined chlorine by weight, diallyl phthalate prepolymer and diallyl phthalate monomer. The following composition was compounded as an "SDG-F Type" flame resistant molding compound designed

to meet Military Specification MIL—M—14F.

		parts
5	Diallyl phthalate prepolymer (Dapon 35 — "Dapon" is a Trade Mark)	73
	Diallyl phthalate monomer	9
	Chlorinated terphenyl (60% combined chlorine)	18
	Chopped glass (1/4" strands)	90
10	Clay, hydrated	30
	Antimony oxide	15
	Calcium Stearate	1
	Tertiary Butyl Perbenzoate	3
	Acetone	160

- 15 The ingredients above were mixed together in a heavy duty mixer until the glass and the fillers were thoroughly wetted. The composition was spread on trays and the acetone was allowed to evaporate at room temperature.
- 20 The composition was then compounded on a two-roll rubber mill at a temperature of 80—90°C. The mill sheet was cooled and ground into a molding powder. Test pieces molded at 150°C at 2000 psi for a minimum of 1.5
- 25 minutes showed full cure as measured by development of "hot hardness" and resistance to boiling chloroform. The test data in Table VI shows the properties of the above molded compositions compared to the MIL—M—14F
- 30 specification requirements for diallyl phthalate molding compounds.

Example 6

- Wet lay-up ie vacuum bag laminates were prepared using a diallyl phthalate prepolymer, a diallyl phthalate monomer and chlorinated terphenyl (Aroclor 5460). The wet lay-up was prepared by making a liquid blend of the monomer, chlorinated terphenyl and diallyl phthalate resin and catalyst. The liquid polymerizable resin composition was poured onto
- 35 several layers of woven glass fabric. After impregnation, the laminates were placed in a vacuum bag and evacuated to remove air from the polymerizable liquid resin mixture. The
- 40 lay-up was laminated while maintaining the vacuum at pressures of 15 psi or less (in the very early stages of cure it was very difficult to maintain pressure on the polymerizable liquid). Full cure was obtained after about
- 45 15 minutes at 150°C as measured by hot hardness, hot strength, and solvent resistance in boiling acetone. This laminate construction was also cured in a vacuum bag by exposure to a 3 MEV (million electron volts) electron
- 50 beam in multiple passes of 5 megarads each until a room temperature Barcol hardness of 60 was developed. The polymerizable liquid details and the physical properties of the cured laminates are set forth in Table VI.
- 55

Example 7

A premixed molding composition containing a portion of the polyester resin described in Example 3 and a polychlorinated aromatic compound was prepared. The formulations listed in Table VII were mixed in a heavy duty mixer until the glass and fillers were thoroughly wetted with the polyester resin-monomer-chlorinated terphenyl mixture. The compositions of this invention were compared with similarly compounded conventional diallyl phthalate polyesters. The composition details and physical properties are set forth in Table VII. The test specimens were molded at 1000 psi at 150°C for three minutes.

Example 8

A low-pressure laminate containing diallyl isophthalate monomer and prepolymer, a chlorinated terphenyl and polyphenylene ether polymer was prepared in which the following formulation was used to saturate glass cloth from which the laminate was prepared.

	Parts by Weight	
Polyphenylene ether resin (General Electric Grade 691—111)	25	85
Chlorinated terphenyl containing 60% combined chlorine (Aroclor 5460)	15	
Diallyl isophthalate prepolymer (Dapon M)	30	90
Diallyl isophthalate monomer	30	
Dicumyl peroxide (recrystallized)	3	
Acetone	130	

The diallyl isophthalate prepolymer and polyphenylene ether polymer were ball-milled together until 70% of the product was —200 mesh (U.S. Standard Sieve Series 1940). The chlorinated terphenyl-diallyl phthalate monomer and dicumyl peroxide were dissolved in the acetone solvent and the ball-milled powder was added to this solution to make up a saturating mixture. Woven glass cloth, type 181, was impregnated with this mixture and allowed to dry at least 48 hours at room temperature. The dry impregnated glass cloth was cut into 12" by 12" squares, stacked 18 plies deep with the warp yarns parallel. The pre-impregnated lay-up was laminated in a flat bed press for 30 minutes at 80°C at contact pressure, 30 minutes at 120°C at 300 psi and 1 hour at 160°C at 300 psi. The laminated sample had a resin content of 44% and was found to be non-burning in ASTM Flammability Test D—229, Part 1.

The following physical properties were obtained on the laminated sample:

Laminate Physical and Electrical Properties

	Resin content	44%
	Specific Gravity	1.752
	Rockwell Hardness (M)	120
5	Compressive strength, psi	50,400
	Tensile strength, psi	43,700
	Flexural strength, psi @ 23°C	67,300
	Flexural strength, psi @ 200°C	13,700
	Flexural modulus @ 23°C, psi	3.0×10 ⁶
10	Flexural modulus @ 200°C, psi	1.3×10 ⁶
	Interlaminar shear strength, psi	3,530

Example 9

A vacuum bag laminate was prepared from a composition containing no polyunsaturated polymer. Thirty parts of polyphenylene ether polymer was ball-milled 1 hour together with 10 parts of trihydrate of aluminium oxide (Hydral 710 from Alcoa). The ball-milled materials were mixed with a solution containing 90 parts of diallyl isophthalate monomer, 17.5 parts of chlorinated terphenyl containing 60% by weight combined chlorine (Aroclor 5460) and 4.5 parts of dicumyl peroxide catalyst (DiCup R — "Dicup" is a Trade Mark) with stirring at 60–80°C. This mixture was used to saturate 12 plies of 181 glass cloth 12 inches square. The impregnated cloth was stacked 12 plies deep with the warp yarns parallel. The impregnated lay-up was placed in a vacuum bag which was then evacuated until essentially all of the air was removed. The lay-up was then laminated in a flat bed press, maintaining the vacuum, throughout the lamination, for 1 hour at 93°C, 1 hour at 121°C and 1 hour at 160°C. The cured laminate had good "hot" hardness when removed from the vacuum bag at about 150°C and when cooled was a tough flexible laminate.

Example 10

A copper-clad laminate was prepared by roller coating onto 1 oz. copper foil, (1 oz. per sq. ft.), a standard copper used in the preparation of printed circuit boards, the following coating composition:

	Ingredients	Parts by weight
50	Polyphenylene ether polymer (General Electric Company Grade 631—101)	60
	Diallyl isophthalate prepolymer (FMC Corporation, Dapon M)	10
	Diallyl isophthalate monomer	10
55	Chlorinated terphenyl, 60% chlorine (Aroclor 5460), Monsanto Chemical Corporation	20
	Dicumyl peroxide	5
	Chloroform	150
	Trichloroethylene	150

After solvent removal and baking for 5 minutes at 165°C, the average film thickness of the coating on the copper was 1.5 mil thick. An eighteen ply, low pressure, glass cloth, laminate was prepared for laminating as described in Example 8. The treated copper foil was placed on one side of the laminate, with the treated side of the foil facing the laminate, and the laminate was then cured as described in Example 8.

The bond and peel strength of the copper foil to the laminate base after laminating exceeded 10 lbs. per inch. This bond strength was essentially unchanged after immersion in a solder bath at 260°C for 2 minutes.

Example 11

A copper-clad glass cloth laminate was prepared using the following coating composition to saturate glass cloth as described in Example 8:

Three hundred and twenty parts (320) of polyphenylene ether polymer (General Electric Grade 691—111), 80 parts of diallyl isophthalate prepolymer (Dapon M) and 50 parts of hydrated alumina (Hydral 710) were ground together in a ceramic ball-mill until 70% of the mixture passed through a 200 mesh sieve (U.S. Standard Sieve Series, 1940). Forty-five (45) parts of this powdered mixture was added with agitation to a solution of 30 parts of diallyl phthalate monomer, 30 parts of chlorinated terphenyl (Aroclor 5460), ten parts of diallyl isophthalate prepolymer (Dapon M), and 5 parts of recrystallized dicumyl peroxide (Di—Cup R — Hercules Powder Company) in 100 parts of methyl ethyl ketone.

The saturated glass cloth was cut into 12" squares prepared for laminating as described in Example 8. A 12" square of one ounce (1 oz.) copper foil was placed on one side of the saturated glass cloth lay-up which was then laminated (cured) as described in Example 8 to produce a copper clad laminate. When laminated, the copper foil had a bond strength to the glass cloth base in excess of eight pounds per inch peel strength at 90°. This bond strength was maintained, and the laminate maintained its integrity, when immersed for two minutes in solder at 260°C.

Example 12

A silicon diode was coated by dipping the diode into the polymerizable coating composition of Example 10. Only about 1/8" of the metal leads (Covar) to the diode, nearest to the body of the diode, were coated thereby leaving part of the leads uncoated to facilitate soldering. The coated diode was baked in an air circulating oven at 170°C for 2 minutes to remove solvent and polymerize the coating. The resulting coating was between 1. and 2 mils thick.

The coated diode was then mold encapsulated using the following encapsulating composition:

5	Diallyl phthalate prepolymer (Dapon D — FMC Corp.)	45
	Glass, 1/4" chopped fibers	25
	Clay, calcined	30
	Calcium stearate	0.5
	Tertiary Butyl perbenzoate	1.5

- 10 The encapsulation was done by transfer molding at a ram pressure of 1000 psi at 160°C for a cure time of 3 minutes. The

encapsulated silicon diode showed no loss of electrical performance after 100 hours immersion in boiling water.

A second silicon diode was coated as described above. This second coated diode was mold encapsulated as described above using a bisphenol A diglycidyl ether type epoxy polymer encapsulating composition (Polyset 300 available from Morton Chemical Company). The wet electrical performance of the coated-encapsulated diode was improved as compared of a similar diode that was not coated prior to encapsulation with the epoxy encapsulating composition.

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TABLE I

Batch Reaction at 160°C, Monomer Study

	1	2	3	4	5	6	7	8	9	10	11	12
Chlorinated terphenyl, 60% chlorine	50	45	40	60	65	60	—	—	40	74	87	78
Chlorinated biphenyl, 68% chlorine	—	—	—	—	—	—	62	62	—	—	—	—
Diallyl phthalate	—	—	—	—	—	40	—	38	—	—	—	—
Diallyl isophthalate	50	55	60	40	35	—	38	—	—	—	—	—
Diallyl Chloroendate	—	—	—	—	—	—	—	—	60	—	—	—
Triallyl cyanurate	—	—	—	—	—	—	—	—	—	26	—	—
Triallyl phosphate	—	—	—	—	—	—	—	—	—	—	13	22
Diallyl maleate	—	—	—	—	—	—	—	—	—	—	—	—
Divinyl benzene (55%)	—	—	—	—	—	—	—	—	—	—	—	—
Dicumyl peroxide	2	2	2	2	2.5	2	2	2	2	2	2	2
Initiation Temp. °C	130	130	130	135	155	125	145	140	135	125	135	122
Peak Exotherm Temp. °C	223	211	227	218	273	222	225	216	205	245	248	230
Time to Exotherm, min.	3	5	7	4	5	3	3	3	3	4	4	3
16 hr. Acetone Soxhlet Extraction												
Nature of Solution:				×			×	×				
Clear												
Cloudy												
Nature of Dried Extract												
Powder				×			×					
Gum								×				

TABLE I (continued)

Batch Reaction at 160°C, Monomer Study

	13	14	C-1	Comparison		
				C-2	C-3	C-4
Chlorinated terphenyl 60% chlorine	70	70	100	—	—	50
Chlorinated biphenyl, 68% chlorine	—	—	—	—	100	—
Diallyl phthalate	—	—	—	80	—	50
Diallyl isophthalate	—	—	—	—	—	—
Diallyl chlorendate	—	—	—	—	—	—
Triallyl cyanurate	—	—	—	—	—	—
Triallyl phosphate	—	—	—	—	—	—
Diallyl maleate	—	—	—	—	—	—
Divinyl benzene (55%)	30	—	—	—	—	—
Ethylene glycol dimetha- crylate	—	30	—	—	—	—
Dicumyl peroxide	2	2	2	2	2	—
Initiation Temp. °C	125	115	none	110	none	none
Peak Exotherm Temp. °C	235	200	none	250	none	none
Time to Exotherm, min.	3	4	∞	5	∞	∞
16 hr. Acetone Soxhlet Extraction						
Nature of Solution						
Clear			×	×		
Cloudy					×	
Nature of Dried Extract						
Powder			×		×	
Gum				×		

TABLE II
Molding Compositions

Formulation	United States Military MIL M- 14F Specification Requirements for SDGF Molding Compounds		
Diallyl phthalate prepolymer	74		
Diallyl isophthalate prepolymer		70	
Diallyl phthalate monomer	3		
Diallyl isophthalate monomer		3	
Reaction Product #1 ⁽¹⁾	26		
Reaction Product #2 ⁽²⁾		30	
<i>tert</i> Butyl perbenzoate	3	3	
Calcium Stearate	2	2	
Antimony oxide	15	18	
Wollastonite	30	20	
Glass (1/4" strands)	90	100	
Properties			
Ignition time (sec.)	93	98	90 (min.)
Burning time (sec.)	78	76	90 (max.)
Heat Deflection Temp. °C	175	270	160 (min.)
Impact (ft. lbs.)	0.66	0.60	0.30 (min.)
Comp. Str. (psi)	24,620	26,500	16,000 (min.)
Flex. Str. (psi)	11,462	11,200	9,000 (min.)
Flex. Mod. (psi)	.70 × 10 ⁶	1.72 × 10 ⁶	—
Water absorption (%)	0.12	0.11	0.50 (max.)
Specific Gravity	1.902	1.897	—
D.C. 10 ³ /10 ⁶ ⁽³⁾	4.50/4.39	4.36/4.24	4.6/4.4 (max.)
" " (wet)	4.52/4.38	4.41/4.29	4.7/4.45 (max.)
D.F. 10 ³ /10 ⁶ ⁽⁴⁾	.005/.005	.005/.005	.009/.015 (max.)
" " (wet)	.006/.005	.006/.005	.013/.017 (max.)
Volume Resist. (ohm)	1.0 × 10 ¹²	0.8 × 10 ¹²	5 × 10 ⁹ (min.)
720 hr @ 70°C, 100% R.H.			

⁽¹⁾ 62/38 Reaction Product of chlorinated biphenyl with diallyl phthalate monomer.

⁽²⁾ 62/38 Reaction Product of chlorinated biphenyl with diallyl isophthalate monomer.

⁽³⁾ Dielectric constant.

⁽⁴⁾ Dissipation Factor.

TABLE III

Diallyl Phthalate Polyester Molding Compositions

Formulation		United States Military MIL M-14F Specification Requirements for MAI- 30 (Polyester) Molding Compounds	
Diallyl phthalate monomer	35		
Uncut isophthalate polyester resin, reactive type,	35 ⁽¹⁾		
Reaction Product #1	30 ⁽²⁾		
Glass (1.4" strands)	57		
Hydrated alumina	48		
Wollastonite	48		
Antimony oxide	18		
Calcium stearate	2		
<i>tert</i> -Butyl perbenzoate	2		
Physical Properties			
Comp. Str. (psi)	21,200	20,000 (min.)	
D.C. $10^3/10^6$	4.95/4.54	6.3/6.2 (max.)	
D.C. " (wet)	5.15/4.63	6.4/6.6 (max.)	
D.F. $10^3/10^6$	.010/.009	.015/.012 (max.)	
D.F. " (wet)	.012/.011	.017/.015 (max.)	
Flex. Str. (psi)	16,700	14,000 (min.)	
Flex. Mod. (psi)	2.0×10^6	—	
Heat Deflection Temp. °C	272	200 (min.)	
Impact (ft. lbs.)	4.37	3.0 (min.)	
Water Absorption (%)	0.17	0.5 (max.)	
Ignition time (sec.)	105	100 (min.)	
Burning time (sec.)	17	75 (max.)	
Rockwell Hardness (M)	108	—	
Specific Gravity	1.93	—	
Vol. Resistivity (ohm. cm.)	1.2×10^{15}	—	
Surface Resistivity (ohm.)	2.8×10^{15}	—	

⁽¹⁾ Equimolar amounts of maleic anhydride and isophthalic acid were heated together with a 10% excess of diethylene glycol. Water was removed azeotropically and the heating, at about 200°C, was continued until the acid number of the polyester resin fell below 6. Excess diethylene glycol was removed under vacuum and the polyester resin recovered.

⁽²⁾ 62/38 Reaction Product of chlorinated biphenyl with diallyl phthalate monomer from Example 2.

TABLE IV

High Pressure Diallyl Phthalate-Chlorinated
Terphenyl Laminates

Formulation		
Reaction Product #3	50	
Reaction Product #4		50
Diallyl phthalate prepolymer (Dapon 35)	45	
Diallyl isophthalate prepolymer (Dapon M)		45
Diallyl phthalate monomer	5	
Diallyl isophthalate monomer		5
Dicumyl peroxide	2	
Physical Properties		
Burning ¹ time (sec.)	12.7	32
Comp. Str. (psi)	49,500	44,900
Rockwell Hardness (M)	118	122
Flex. Str. (psi) R.T.	67,800	76,200
150°C	13,700	—
Flex. Mod. (psi) R.T.	2.43×10^6	2.92×10^6
150°C	0.97×10^6	—
Tensile strength (psi)	49,100	50,400
Specific Gravity	1.822	1.858
Shear Str. (psi)	4010	3400
Flex. Str. (psi)	67,900	72,700
Flex. Mod. (psi)	2.48×10^6	2.89×10^6
Flex. Str. (psi) after aging:		
	at 155°C	at 180°C
1 day	68,200	72,800
4 days	70,900	75,300
10 days	65,600	77,800
D.C. $10^3/10^6$ (2)	4.46/4.35	4.26/4.22
" " (wet)	4.52/4.38	4.27/4.18
D.F. $10^3/10^6$ (2)	.0055/.0059	.0039/.0042
" " (wet)	.0063/.0061	.0042/.0048
Vol. Resist. (ohm. cm.)	5.2×10^{15}	12.9×10^{15}
Surf. Resist. (ohm.)	1.3×10^{15}	1.19×10^{15}
Insulation Resist. (ohm)		
10 day cycle 72/70/100	1.25×10^{10}	6.3×10^{11}
72/25/100	5.60×10^{11}	3.6×10^{12}
100/70/100	8.3×10^9	1.9×10^{11}

¹ASTM D229, Part I.²Dielectric constant³Dissipation Factor⁴Sample conditioned 2 hours in boiling water.

TABLE V

Chlorinated Terphenyl Aroclor/Monomer/Dapon
SDG-F Compound

	Example 6	Comparison ⁽¹⁾
Ignition time (sec.)	97	90 (min.)
Burning time (sec.)	70	90 (max.)
Deflection Temp. °C	165	160 (max.)
Rockwell Hardness (M)	115	—
Impact (ft. lbs.)	0.58	0.30 (min.)
Flex. Str. (psi)	12,120	9000 (min.)
Flex. Mod. (psi)	1.72×10^8	—
Comp. Stre. (psi)	23,060	16,000 (min.)
Water Absorption (%)	0.08	—
Specific Gravity	1.880	0.30
D.C. $10^3/10^6$ ⁽²⁾	4.44/4.35	4.6/4.4 (max.)
" " (wet)	4.47/4.37	4.7/4.5 (max.)
D.F. $10^3/10^6$ ⁽³⁾	.0044/.0043	.009/.015 (max.)
" " (wet)	.0054/.0047	.013/.017 (max.)
Vol. Resist. (ohm. cm.)	6.76×10^{15}	—
Surf. Resist. (ohm.)	7.95×10^{15}	—
Vol. Resist. (ohm.) (720 hrs. 70°C @ 100% relative humidity)	1.97×10^{13}	5×10^9

(¹) United States Military MIL M—14F Specification requirement properties for glass filled flame resistant diallyl phthalate molding compounds.

(²) Dielectric constant.

(³) Dissipation Factor.

TABLE VI

Vacuum Bag Laminates

Formulation		
Diallyl phthalate prepolymer (Dapon 35)	50	
Diallyl isophthalate prepolymer (Dapon M)		50
Diallyl phthalate monomer	20	
Diallyl isophthalate monomer		20
Chlorinated terphenyl (60% chlorine)	30	30
Dicumyl peroxide	2	2
Burning time (Pt. I)	16 sec.	27 sec.
Specific Gravity	2.104	2.040
Percent resins	28.0	32.7
Rockwell Hardness (M)	117	121
Flex. Str. (psi) 25°C	94,000	101,700
" " 150°C	25,410	(260°C) 6,050 ⁽¹⁾
Flex. Mod. (psi) 25°C	4.08×10^6	3.86×10^6
" " 150°C	2.49×10^6	(260°C) 1.47×10^6 ⁽¹⁾
Comp. Str. (psi)	49,110	48,740
Tensile Str. (psi)	63,460	62,110
Shear Str. (psi)	3710	2040
Flex. Str. (H)	93,390	88,810
Flex. Mod. (H)	4.18×10^6	3.26×10^6
Flexural (psi) after aging:	at 155°C	at 180°C
1 day	101,900	95,400
4 days	97,600	98,870
10 days	93,900	88,580
D.C. $10^3/10^6$ ⁽²⁾	4.94/4.85	4.72/4.65
" " (wet)	5.00/4.84	4.81/4.65
D.F. $10^3/10^6$ ⁽³⁾	.0054/.0049	.0068/.0040
" " (wet)	.0088/.0057	.0091/.0048
Vol. Resistivity (ohm. cm.)	4.17×10^{15}	3.56×10^{15}
Surf. Resistivity (ohm.)	5.08×10^{14}	2.36×10^{14}

⁽¹⁾ Test run at 260°C.⁽²⁾ Dielectric constant.⁽³⁾ Dissipation Factor.⁽⁴⁾ Sample conditioned 2 hours in boiling water.

TABLE VII

Premix Molding Compositions

Formulation		
Polyester resin, Reactive isophthalate type ⁽¹⁾	50	41
Diallyl phthalate monomer	50	41
Chlorinated terphenyl (60% chlorine)	0	18
1/4" Chopped glass fibers	57	57
Wollastonite	55	55
Hydrated alumina (Hydral 710 "Hydral" is a Trade Mark)	55	55
tert-Butyl perbenzoate	2	2
Zinc stearate	1	1
Antimony oxide	18	18
Physical Properties		
Ignition time (sec.)	103	102
Burning time (sec.)	244	31
Deflect. Temp. °C	283	270
Rockwell Hardness (M)	102	103
Impact (ft. lbs.)	4.90	6.90
Specific Gravity	1.935	1.953
Water Absorption (%)	0.37	0.25
Comp. Str. (psi)	20,360	21,450
Flex. Str. (psi)	15,860	18,450
Flex. Mod. (psi)	2.0×10^6	2.01×10^6
D.C. $10^3/10^6$	5.56/4.85	5.11/4.66
" " (wet)	6.25/5.08	5.46/4.79
D.F. $10^3/10^6$	.023/.016	.014/.010
" " (wet)	.041/.025	.018/.016
Vol. Resistivity (ohm. cm.)	6.82×10^{14}	8.74×10^{14}
Surf. Resistivity (ohms.)	7.43×10^{15}	5.13×10^{15}

(¹) Reactive polyester resin from Example 3 made by reacting equimolar portions of maleic and isophthalic acids with a 10% excess of diethylene glycol.

WHAT WE CLAIM IS:—

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 polychlorinated aromatic compound containing at least 50% by weight combined chlorine 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 polychlorinated aromatic compound.

2. A composition as claimed in claim 1 in which the polychlorinated aromatic compound is used in the form of a reaction product prepared by heating 3 to 2 mols of polychlorinated aromatic hydrocarbon containing at least 50% by weight chlorine and having a molecular weight of at least 200 with 2 to 3 mols of the polyethylenically unsaturated monomer at a temperature of at least 130°C in the presence of a free radical initiator.
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



TABLE VII

Premix Molding Compositions

Formulation		
Polyester resin, Reactive isophthalate type ⁽¹⁾	50	41
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(¹) Reactive polyester resin from Example 3 made by reacting equimolar portions of maleic and isophthalic acids with a 10% excess of diethylene glycol.

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2. A composition as claimed in claim 1 in which the polychlorinated aromatic compound is used in the form of a reaction product prepared by heating 3 to 2 mols of polychlorinated aromatic hydrocarbon containing at least 50% by weight chlorine and having a molecular weight of at least 200 with 2 to 3 mols of the polyethylenically unsaturated monomer at a temperature of at least 130°C in the presence of a free radical initiator.

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 monomerpolymer-chlorinated aromatic hydrocarbon mixture to the thermoset state at elevated temperatures.

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

(1) 10 to 50 parts by weight of the polyethylenically unsaturated monomer;

(2) 5 to 30 parts by weight of the polychlorinated aromatic hydrocarbon containing at least 50% by weight chlorine and having a molecular weight of at least 200, the ratio of monomer to chlorinated hydrocarbon being at least 1:3 on a molar basis;

(3) 20 to 60 parts by weight of the polyphenylene ether polymer;

(4) 0—30 parts by weight of the polyethylenically unsaturated polymer; and

(5) 2—10 parts by weight per 100 parts of all of (1) plus (2) plus (3) plus (4) 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 polychlorinated aromatic compound is a chlorinated biphenyl, a chlorinated terphenyl, trichlorobenzene, or a chlorinated 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 polychlorinated 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, 2,5 - 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 % 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 an 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 of fiber-glass.

12. A composition as claimed in any of claims 1 to 11 which also comprises a fluid in which the composition is dispersed or dissolved.

13. A composition as claimed in claim 11 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 any of the foregoing Examples.

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 polychlorinated aromatic compound containing at least 50% by weight combined chloride 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 polychlorinated aromatic compound 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



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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.

23. A method as claimed in claim 21 or 22 which comprises laminating a copper foil sheet on one or both surfaces of said saturated fibrous sheet to form a copper clad laminate.

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.

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.

W. P. THOMPSON & CO.,
12 Church Street, Liverpool, L1 3AB.
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.