



FLAME RETARDANT RESIN COMPOSITIONS CONTAINING
PHOSPHORAMIDES, AND METHOD FOR MAKING

This application is a continuation-in-part of copending application Serial No. 09/235,680, filed January 22, 1999.

BACKGROUND OF THE INVENTION

The present invention relates to resin compositions comprising a phosphoramidate compound having a glass transition temperature of at least about 0°C, preferably of at least about 10°C, and most preferably of at least about 20°C. The invention also relates to methods to make the resin compositions and articles made from the resin compositions.

Compounds containing phosphorus have been used in resin compositions for a variety of reasons. For example, various phosphites have been utilized to enhance the melt stability and/or color stability of resin compositions. Alternatively, various organic phosphate esters have been utilized in resin compositions to improve the flame resistance properties of the compositions and/or to enhance the melt flow characteristics of the compositions. Certain water soluble phosphoramides have also been used in the textile industry as flame retardant finishes for fabrics.

As part consolidation and weight reduction continues to evolve in many industries, the physical property demands placed upon resin manufacturers are increasing. Key industries increasing the demands include the electronics and computer industries, especially for computer housings, computer monitor housings, and printer housings. One increasing demand is for materials that possess higher heat resistance while preferably substantially retaining other key physical properties. Another increasing demand is for materials that are rated in the Underwriter's Laboratory UL-94 test protocol

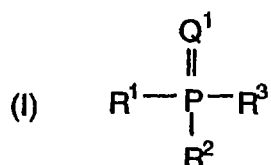


as V-0, V-1, or V-2. It is therefore apparent that new resin compositions that meet these and other demands continue to be sought.

SUMMARY OF THE INVENTION

This invention provides a resin composition comprising:

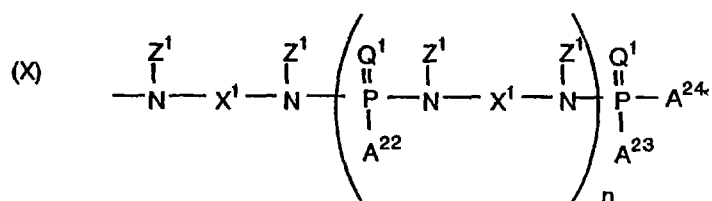
- a) a thermoplastic resin, and
- b) at least one phosphoramidate having a glass transition point of at least 0°C selected from the group consisting of:
 - i) a phosphoramidate having the formula:



wherein:

Q1 is oxygen or sulfur;

R1 is of the formula X:



wherein

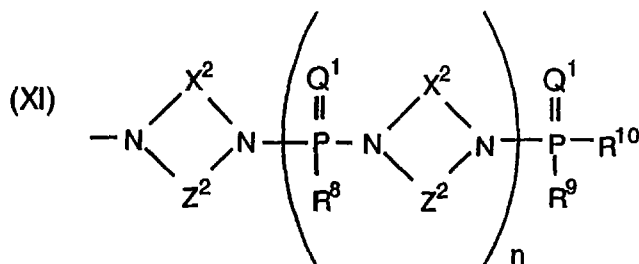
each of A22-24 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

each Z1 is an alkyl radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

each X1 is an alkylidene radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

or

R1 is of the formula XI:



wherein

each X2 is alkylidene, aryl, or alkaryl;

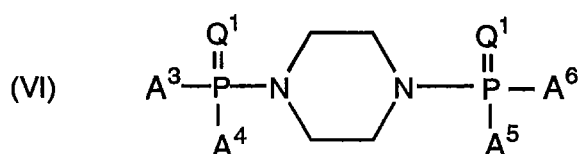
each Z2 is alkylidene;

each of R8, R9, and R10 is independently an alkyloxy residue, an aryloxy residue, an aryloxy residue containing at least one alkyl substitution, or an amine residue;

n is from 0 to about 5; and

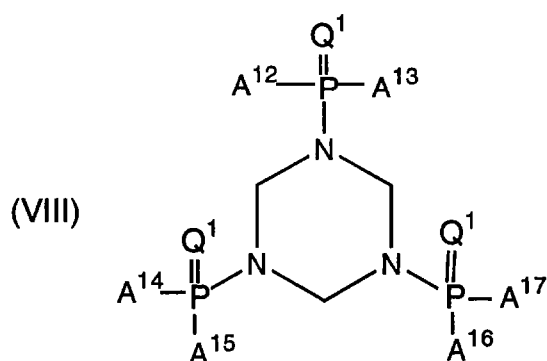
R2 and R3 are each independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

(ii) a phosphoramidate of the formula VI:



wherein each Q1 is independently oxygen or sulfur and each A moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethylphenoxy moiety;

(iii) a phosphoramidate of the formula VIII :

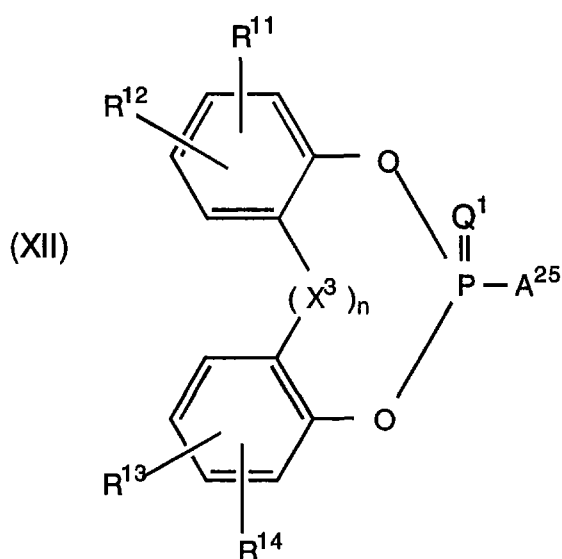


wherein

each Q1 is independently oxygen or sulfur and

each of A12-17 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution or an amine residue;

(iv) a phosphoramidate of the formula XII :



wherein Q1 is oxygen or sulfur;

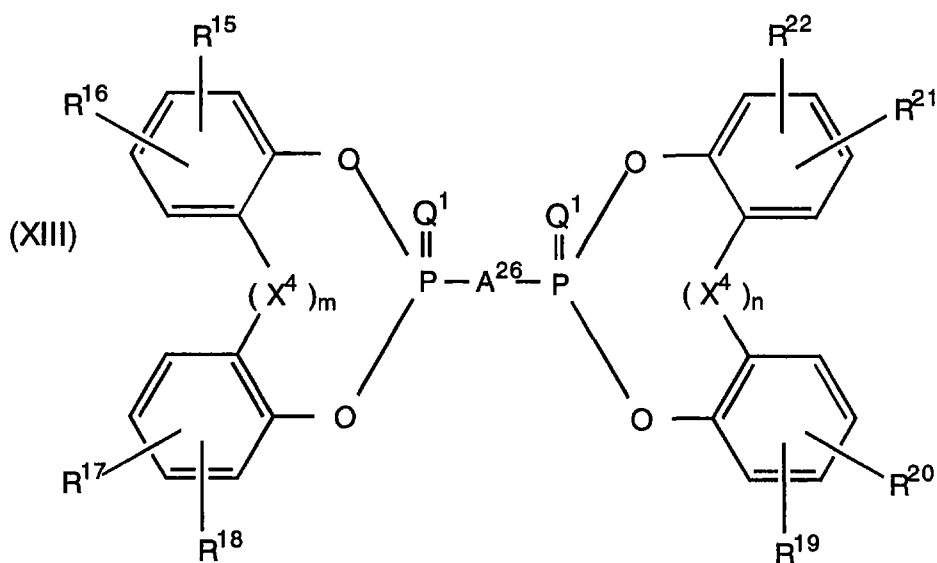
each of R11-14 is independently a hydrogen or an alkyl radical;

X3 is a alkylidene radical;

n is 0 or 1; and

A25 is a group derived from a primary or secondary amine having the same or different radicals that can be aliphatic, alicyclic, aromatic, or alkaryl, or A25 is a group derived from a heterocyclic amine, or A25 is a hydrazine compound; and

(v) a bis(cyclic) phosphoramidate of the formula XIII:

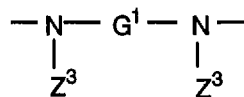


wherein each Q1 independently is oxygen or sulfur;

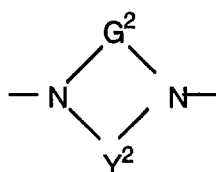
each of R15-22 is independently a hydrogen or an alkyl radical;

X4 is an alkylidene radical; m and n are each independently 0 or 1; and

A26 is



wherein G1 is sulfur, an alkylidene radical, aryl radical, or alkaryl radical; and each Z3 is independently an alkyl radical or an aryl radical; or wherein A26 is



wherein G2 is alkylidene, aryl, or alkaryl, and Y2 is alkylidene; and

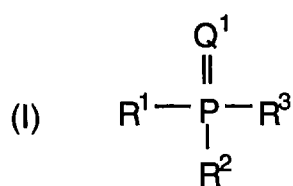
c) at least one adjunct flame retardant compound.

This invention further provides a resin composition consisting essentially of:

a) a thermoplastic resin, and

b) at least one phosphoramidate having a glass transition point of at least 0°C selected from the group consisting of:

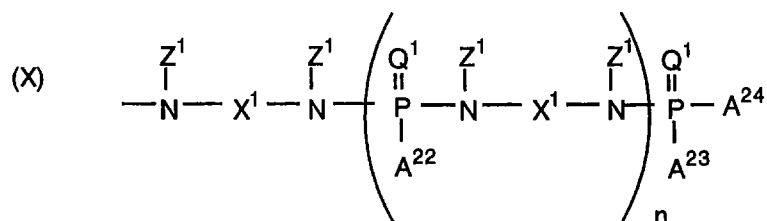
i) a phosphoramidate having the formula:



wherein:

Q1 is oxygen or sulfur;

R1 is of the formula X:



wherein

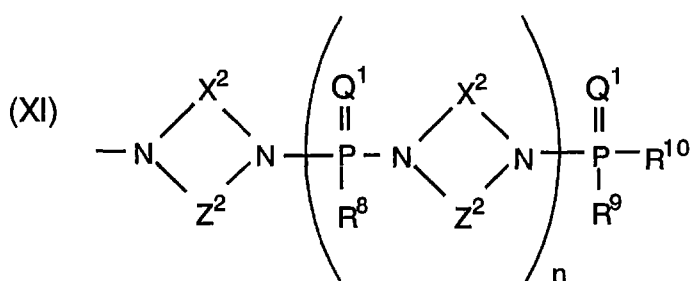
each of A22-24 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

each Z1 is an alkyl radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

each X1 is an alkylidene radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

or

R1 is of the formula XI:



wherein

each X2 is alkylidene, aryl, or alkaryl;

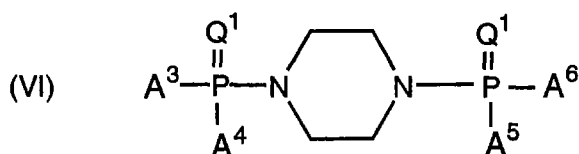
each Z2 is alkylidene;

each of R8, R9, and R10 is independently an alkyloxy residue, an aryloxy residue, an aryloxy residue containing at least one alkyl substitution, or an amine residue;

n is from 0 to about 5; and

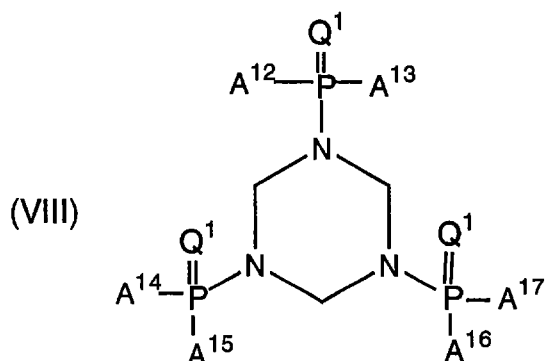
R2 and R3 are each independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

(ii) a phosphoramidate of the formula VI:



wherein each Q1 is independently oxygen or sulfur and each A moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethylphenoxy moiety;

(iii) a phosphoramidate of the formula VIII :

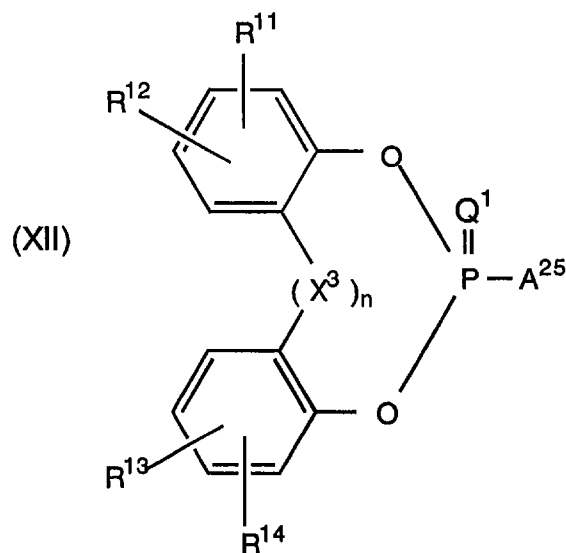


wherein

each Q1 is independently oxygen or sulfur and

each of A12-17 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution or an amine residue;

(iv) a phosphoramidate of the formula XII :



wherein Q1 is oxygen or sulfur;

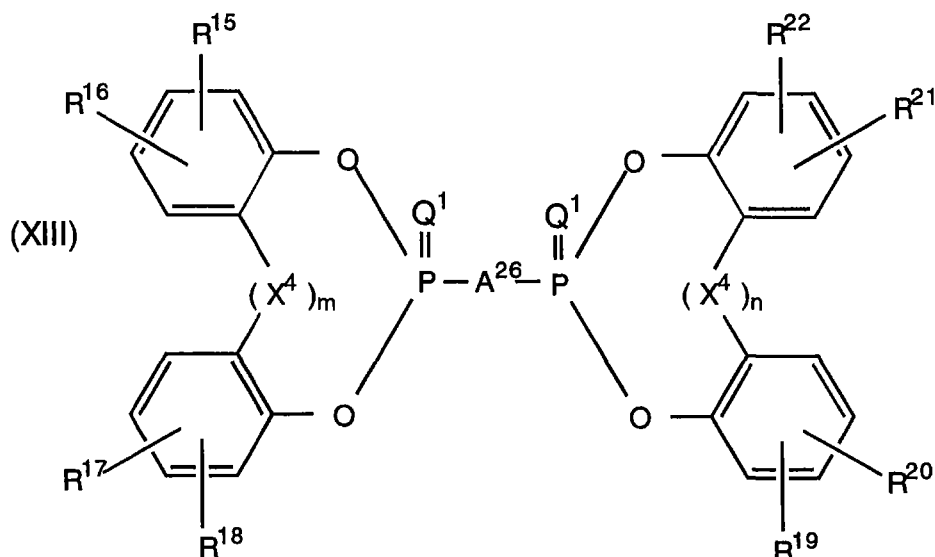
each of R11-14 is independently a hydrogen or an alkyl radical;

X3 is a alkylidene radical;

n is 0 or 1; and

A25 is a group derived from a primary or secondary amine having the same or different radicals that can be aliphatic, alicyclic, aromatic, or alkaryl, or A25 is a group derived from a heterocyclic amine, or A25 is a hydrazine compound; and

(v) a bis(cyclic) phosphoramidate of the formula XIII:

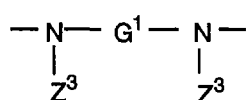


wherein each Q1 independently is oxygen or sulfur;

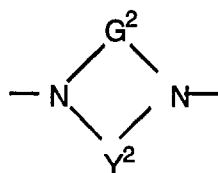
each of R15-22 is independently a hydrogen or an alkyl radical;

X4 is an alkylidene radical; m and n are each independently 0 or 1; and

A26 is



wherein G1 is sulfur, an alkylidene radical, aryl radical, or alkaryl radical; and each Z3 is independently an alkyl radical or an aryl radical; or wherein A26 is



wherein G2 is alkylidene, aryl, or alkaryl, and Y2 is alkylidene; and

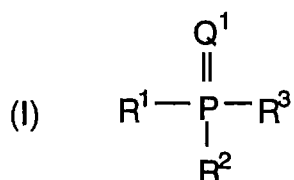
c) at least one adjunct flame retardant compound.

This invention also provides a method to increase the heat distortion temperature of a flame resistant composition containing an amount of at least one phosphoramidate and at least one adjunct flame retardant effective to render the composition a flame rating of at least V-2 in the Underwriter's Laboratory UL-94 protocol when measured on a test specimen of about 0.125 inch by about 0.5 inch by about 5 inch dimensions, wherein the method comprises combining a resin composition comprising:

a) a thermoplastic resin, and

b) at least one phosphoramidate having a glass transition point of at least 0°C selected from the group consisting of:

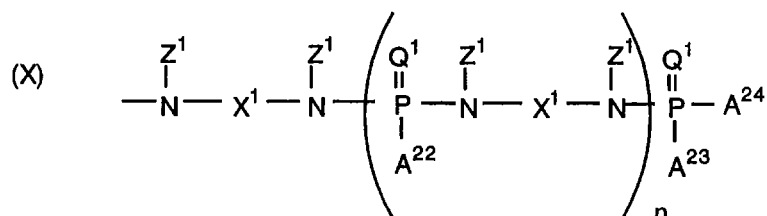
i) a phosphoramidate having the formula:



wherein:

Q1 is oxygen or sulfur;

R1 is of the formula X:



wherein

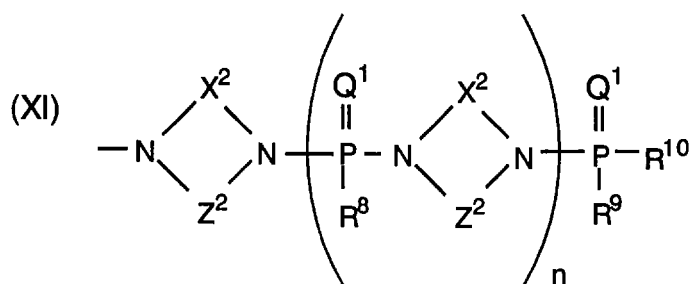
each of A22-24 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

each Z1 is an alkyl radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

each X1 is an alkylidene radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

or

R1 is of the formula XI:



wherein

each X² is alkylidene, aryl, or alkaryl;

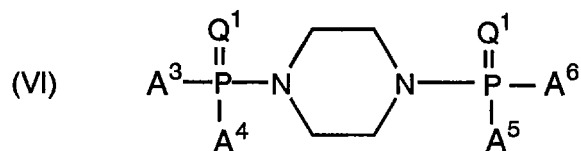
each Z² is alkylidene;

each of R⁸, R⁹, and R¹⁰ is independently an alkyloxy residue, an aryloxy residue, an aryloxy residue containing at least one alkyl substitution, or an amine residue;

n is from 0 to about 5; and

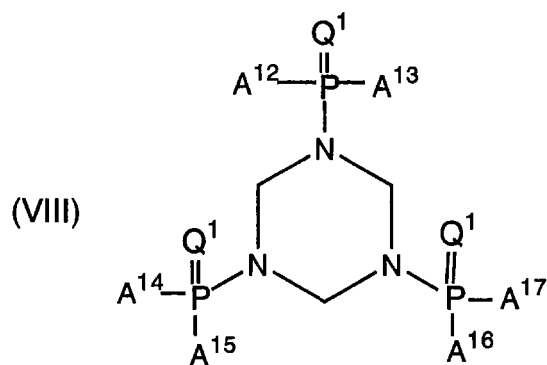
R² and R³ are each independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

(ii) a phosphoramidate of the formula VI:



wherein each Q¹ is independently oxygen or sulfur and each A moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethylphenoxy moiety;

(iii) a phosphoramidate of the formula VIII :

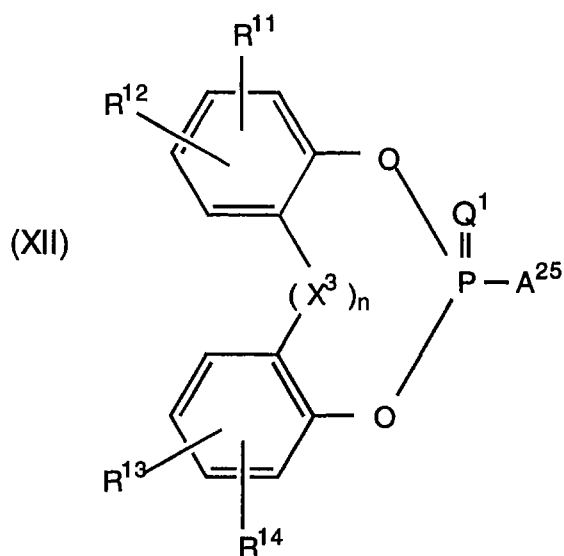


wherein

each Q1 is independently oxygen or sulfur and

each of A12-17 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution or an amine residue;

(iv) a phosphoramidate of the formula XII :



wherein Q1 is oxygen or sulfur;

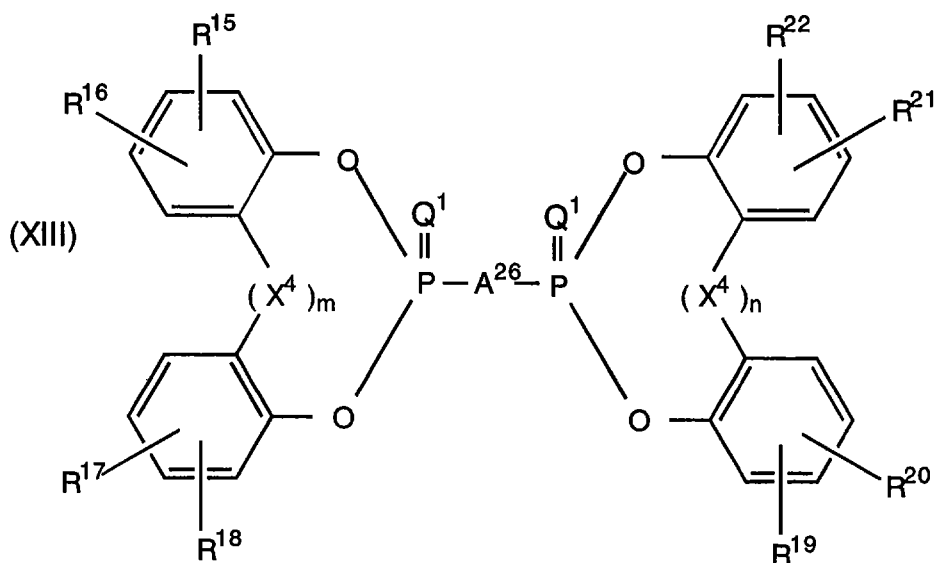
each of R11-14 is independently a hydrogen or an alkyl radical;

X3 is a alkylidene radical;

n is 0 or 1; and

A25 is a group derived from a primary or secondary amine having the same or different radicals that can be aliphatic, alicyclic, aromatic, or alkaryl, or A25 is a group derived from a heterocyclic amine, or A25 is a hydrazine compound; and

(v) a bis(cyclic) phosphoramidate of the formula XIII:

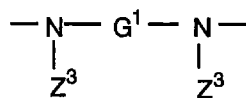


wherein each Q1 independently is oxygen or sulfur;

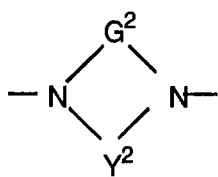
each of R15-22 is independently a hydrogen or an alkyl radical;

X4 is an alkylidene radical; m and n are each independently 0 or 1; and

A26 is



wherein G1 is sulfur, an alkylidene radical, aryl radical, or alkaryl radical; and each Z3 is independently an alkyl radical or an aryl radical; or wherein A26 is



wherein G2 is alkylidene, aryl, or alkaryl, and Y2 is alkylidene; and

c) at least one adjunct flame retardant compound.

The present invention also provides articles made from the resin compositions. Furthermore, the present invention provides methods to make resin compositions having improved heat and/or processability over compositions known in the art.

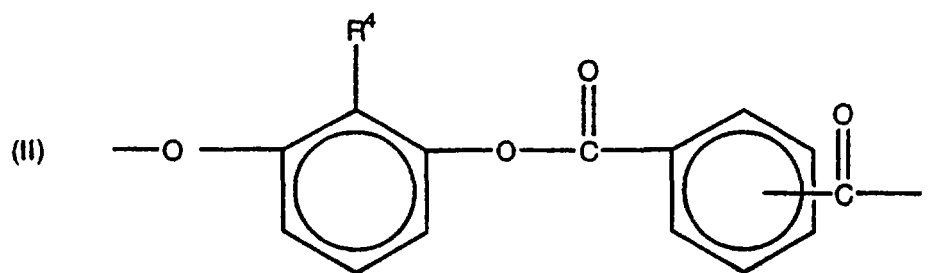
DETAILED DESCRIPTION OF THE INVENTION

The major constituent of the compositions of the invention is at least one thermoplastic polymer. Both addition and condensation polymers are

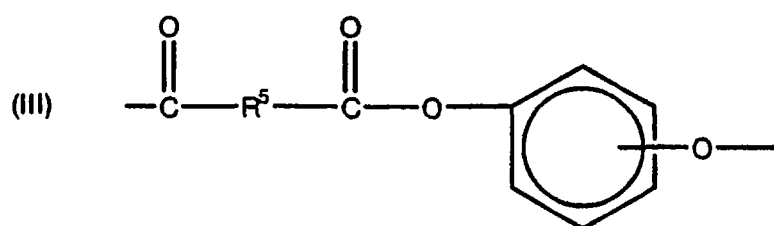
included. Illustrative, non-limiting examples of thermoplastic polymers are olefin polymers such as polyethylene and polypropylene; diene polymers such as polybutadiene and polyisoprene; polymers of ethylenically unsaturated carboxylic acids and their functional derivatives, including acrylic polymers such as poly(alkyl acrylates), poly(alkyl methacrylates), polyacrylamides, polyacrylonitrile and polyacrylic acid; alkenylaromatic polymers such as polystyrene, poly-alpha-methylstyrene, polyvinyltoluene, rubber-modified polystyrenes, and the like; polyamides such as nylon-6 and nylon-66; polyesters; polycarbonates; and polyarylene ethers.

Both thermoplastic and thermoplastic elastomeric polyesters are suitable for use in the present invention. Illustrative, non-limiting examples of thermoplastic polyesters include poly(ethylene terephthalate), poly(1,4-butylene terephthalate), poly(1,3-propylene terephthalate), polycyclohexanedimethanol terephthalate, polycyclohexanedimethanol-co-ethylene terephthalate, polyethylene naphthalate, polybutylene naphthalate, and polyarylates. Illustrative, non-limiting examples of thermoplastic elastomeric polyesters (commonly known as TPE) include polyetheresters such as poly(alkylene terephthalate)s (particularly poly[ethylene terephthalate] and poly[butylene terephthalate]) containing soft-block segments of poly(alkylene oxide), particularly segments of poly(ethylene oxide) and poly(butylene oxide); and polyesteramides such as those synthesized by the condensation of an aromatic diisocyanate with dicarboxylic acids and a carboxylic acid-terminated polyester or polyether prepolymer.

Suitable polyarylates include, but are not limited to, the polyphthalate esters of 2,2-bis(4-hydroxyphenyl)propane (commonly known as bisphenol A), and polyesters consisting of structural units of the formula II :



wherein R₄ is hydrogen or C1-4 alkyl, optionally in combination with structural units of the formula III :

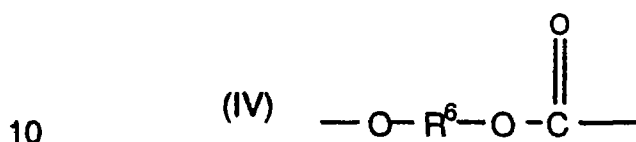


- 5 wherein R₅ is a divalent C₄-12 aliphatic, alicyclic or mixed aliphatic-alicyclic radical. The latter polyesters are prepared by the reaction of a 1,3-dihydroxy-benzene with at least one aromatic dicarboxylic acid chloride under alkaline conditions. Structural units of formula II contain a 1,3-dihydroxybenzene moiety which may be substituted with halogen, usually chlorine or bromine, or preferably with C1-4 alkyl; e.g., methyl, ethyl, isopropyl, propyl, butyl. Said alkyl groups are preferably primary or secondary groups, with methyl being more preferred, and are most often located in the ortho position to both oxygen atoms although other positions are also contemplated. The most preferred moieties are resorcinol moieties, in which R₄ is hydrogen. Said 1,3-dihydroxybenzene moieties are linked to aromatic dicarboxylic acid moieties which may be monocyclic moieties, e.g., isophthalate or terephthalate, or polycyclic moieties, e.g., naphthalenedicarboxylate. Preferably, the aromatic dicarboxylic acid moieties are isophthalate and/or terephthalate: either or both of said moieties may be present. For the most part, both are present in a molar ratio of isophthalate to terephthalate in the range of about 0.25-4.0:1, preferably about 0.8-2.5:1.
- 10
- 15
- 20

In the optional soft block units of formula II, resorcinol or alkylresorcinol moieties are again present in ester-forming combination with R5 which is a divalent C4-12 aliphatic, alicyclic or mixed aliphatic-alicyclic radical. It is preferably aliphatic and especially C8-12 straight chain aliphatic.

5 A particularly preferred arylate polymer containing soft block units is one consisting of resorcinol isophthalate and resorcinol sebacate units in a molar ratio between 8.5:1.5 and 9.5:0.5.

Polycarbonates useful in the compositions of the invention include those comprising structural units of the formula IV:



wherein at least about 60 percent of the total number of R6 groups are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. More preferably, R6 is an aromatic organic radical and still more preferably a radical of the formula V:



wherein each A1 and A2 is a monocyclic divalent aryl radical and Y1 is a bridging radical in which one or two atoms, separate A1 from A2. The preferred embodiment is one in which one atom separates A1 from A2. Illustrative non-limiting examples of radicals of this type are -O-, -S-, -S(O)- or -S(O2)-, -C(O)-, methylene, cyclohexyl-methylene, 2-[2.2.1]-bicycloheptylidene, ethylidene, isopropylidene, neopentylidene, cyclohexylidene, 3,3,5-trimethylcyclohexylidene, cyclopentadecylidene, cyclododecylidene, and adamantylidene. The bridging radical Y1 is most often a hydrocarbon group and particularly a saturated group such as methylene, cyclohexylidene,

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25 3,3,5-trimethylcyclohexylidene, or isopropylidene.

Preferred polycarbonates are derived from dihydric phenols in which only one atom separates A1 and A2. Some illustrative, non-limiting examples of dihydric phenols include the dihydroxy-substituted aromatic hydrocarbons disclosed by name or formula (generic or specific) in U.S. Patent 4,217,438, which is incorporated herein by reference. Some preferred examples of dihydric phenols include 2,2-bis(4-hydroxyphenyl)propane (commonly known as bisphenol A); 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol; 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane; 2,4'-dihydroxydiphenylmethane; bis(2-hydroxyphenyl)methane; bis(4-hydroxyphenyl)methane; bis(4-hydroxy-5-nitrophenyl)methane; bis(4-hydroxy-2,6-dimethyl-3-methoxyphenyl)methane; 1,1-bis(4-hydroxyphenyl)ethane; 1,1-bis(4-hydroxy-2-chlorophenyl)ethane; 2,2-bis(3-phenyl-4-hydroxyphenyl)propane; bis(4-hydroxyphenyl)-cyclohexylmethane; 2,2-bis(4-hydroxyphenyl)-1-phenylpropane; resorcinol; C1-3 alkyl-substituted resorcinols, and 6,6'-dihydroxy-3,3,3',3'-tetramethyl-1,1'-spirobiindane.

The most preferred polycarbonates are bisphenol A polycarbonates, in which each of A1 and A2 is p-phenylene and Y1 is isopropylidene. Preferably, the weight average molecular weight of the initial polycarbonate ranges from about 5,000 to about 100,000; more preferably from about 10,000 to about 65,000, still more preferably from about 16,000 to about 40,000, and most preferably from about 20,000 to about 36,000. Suitable polycarbonates may be made using any process known in the art, including interfacial, solution, solid-state, or melt processes.

In one embodiment the present invention comprises a composition containing at least one polycarbonate. In another embodiment the invention comprises compositions containing two different polycarbonates. Both homopolycarbonates derived from a single dihydroxy compound monomer and copolycarbonates derived from more than one dihydroxy compound monomer are encompassed. In a preferred embodiment compositions

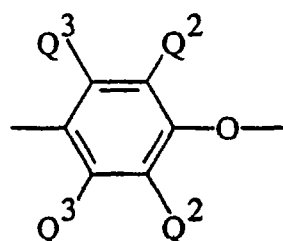
comprise a bisphenol A homopolycarbonate and a copolycarbonate comprising bisphenol A monomer units and 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol monomer units. Preferably, the copolycarbonate comprises 5-65 mole %, more preferably 15-60 mole %, and most preferably 30-55 mole % of 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol with the remaining dihydroxy monomer being bisphenol A. The weight ratio of bisphenol A polycarbonate to copolycarbonate comprising bisphenol A monomer units and 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol monomer units in compositions of the present invention is preferably between 95:5 and 70:30 and more preferably between 85:15 and 75:25.

Also suitable for use in the present invention are polyestercarbonates. The polyestercarbonates may generally be termed copolyesters containing carbonate groups, carboxylate groups, and aromatic carbocyclic groups in the polymer chain, in which at least some of the carboxylate groups and at least some of the carbonate groups are bonded directly to ring carbon atoms of the aromatic carbocyclic groups. These polyestercarbonates are, in general, prepared by reacting at least dihydric phenol, at least one difunctional carboxylic acid or reactive derivative of the acid such as the acid dihalide, and a carbonate precursor. Suitable dihydric phenols include, but are not limited to, those named or referred to hereinabove. Some illustrative, non-limiting examples of suitable aromatic dicarboxylic acids include phthalic acid, isophthalic acid, terephthalic acid, homophthalic acid, o-, m-, and p-phenylenediacetic acid; and the polynuclear aromatic acids such as diphenic acid, 1,4-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, and the like. These acids may be used either individually, or as a mixture of two or more different acids in the preparation of suitable polyestercarbonates.

The polyestercarbonates which find use in the instant invention and the methods for their preparation are well known in the art as disclosed in, for example, U.S. Pat. Nos. 3,030,331; 3,169,121; 3,207,814; 4,194,038; 4,156,069;

4,238,596; 4,238,597; 4,487,896; 4,506,065, and in copending application Ser. No. 09/181,902, filed Oct. 29, 1998, and assigned to the same assignee as the instant application, all of which are hereby incorporated by reference. Among the properties characterizing these polymers is a relatively high distortion
 5 temperature under load (DTUL) as well as a relatively high impact strength as measured by a notched Izod test protocol.

The polyarylene ethers are most often polyphenylene ethers having structural units of the formula:



10 wherein each Q² is independently halogen, primary or secondary lower alkyl, phenyl, haloalkyl, aminoalkyl, hydrocarbonoxy, or halohydrocarbonoxy wherein at least two carbon atoms separate the halogen and oxygen atoms, and each Q³ is independently hydrogen, halogen, primary or secondary lower alkyl, phenyl, haloalkyl, hydrocarbonoxy or
 15 halohydrocarbonoxy as defined for Q².

Both homopolymer and copolymer polyphenylene ethers are included. The preferred homopolymers are those containing 2,6-dimethyl-1,4-phenylene ether units. Suitable copolymers include random copolymers containing such units in combination with, for example, 2,3,6-trimethyl-1,4-phenylene ether units. Also included are polyphenylene ethers containing
 20 moieties prepared by grafting onto the polyphenylene ether in known manner such materials as vinyl monomers or polymers such as polystyrenes and elastomers, as well as coupled polyphenylene ethers in which coupling agents such as low molecular weight polycarbonates, quinones, heterocycles

and formals undergo reaction in known manner with the hydroxy groups of two polyphenylene ether chains to produce a higher molecular weight polymer.

5 The polyphenylene ethers generally have an intrinsic viscosity greater than about 0.1, most often in the range of about 0.2-0.6 and especially about 0.35-0.6 deciliters per gram (dl./g.), as measured in chloroform at 25°C.

10 The polyphenylene ethers are typically prepared by the oxidative coupling of at least one monohydroxyaromatic compound such as 2,6-xyleneol or 2,3,6-trimethylphenol. Catalyst systems are generally employed for such coupling; they typically contain at least one heavy metal compound such as a copper, manganese or cobalt compound, usually in combination with various other materials.

15 Particularly useful polyphenylene ethers for many purposes are those which comprise molecules having at least one aminoalkyl-containing end group. The aminoalkyl radical is covalently bound to a carbon atom located in an ortho position to a hydroxy group. Products containing such end groups may be obtained by incorporating an appropriate primary or secondary monoamine such as di-n-butylamine or dimethylamine as one of the constituents of the oxidative coupling reaction mixture. Also frequently
20 present are 4-hydroxybiphenyl end groups and/or biphenyl structural units, typically obtained from reaction mixtures in which a by-product diphenoquinone is present, especially in a copper-halide-secondary or tertiary amine system. A substantial proportion of the polymer molecules, typically constituting as much as about 90% by weight of the polymer, may contain at
25 least one of said aminoalkyl-containing and 4-hydroxy-biphenyl end groups. It will be apparent to those skilled in the art from the foregoing that the polyphenylene ethers contemplated for use in the invention include all those

presently known, irrespective of variations in structural units or ancillary chemical features.

Both homopolymer and copolymer thermoplastic polymers are included in the compositions of the present invention. Copolymers may include random, block or graft type. Thus, for example, suitable polystyrenes include homopolymers, such as amorphous polystyrene and syndiotactic polystyrene, and copolymers. The latter embraces high impact polystyrene (HIPS), a genus of rubber-modified polystyrenes comprising blends and grafts wherein the rubber is a polybutadiene or a rubbery copolymer of about 70-98% styrene and 2-30% diene monomer. Also included are ABS copolymers, which are typically grafts of styrene and acrylonitrile on a previously formed diene polymer backbone (e.g., polybutadiene or polyisoprene). Suitable ABS copolymers may be produced by any methods known in the art. Especially preferred ABS copolymers are typically produced by mass polymerization (often referred to as bulk ABS) or emulsion polymerization (often referred to as high rubber graft ABS).

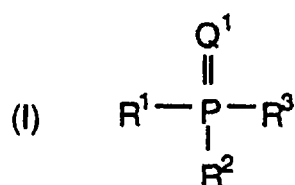
The preferred thermoplastic polymers for many purposes are polyesters, polycarbonates, polyphenylene ethers, polystyrene resin, high impact polystyrene resin (HIPS), and styrene-acrylonitrile copolymers (SAN), including ABS copolymers. These may be employed individually or as blends. Especially preferred blends include those of polyphenylene ether with at least one of HIPS, amorphous polystyrene, and syndiotactic polystyrene; and polycarbonate blends with at least one of ABS, SAN, and polyester.

In resinous compositions there is often an improvement in melt flow and/or other physical properties when one molecular weight grade of at least one resinous constituent is combined with a relatively lower molecular weight grade of similar resinous constituent. Illustrative, non-limiting examples include compositions containing polycarbonate, polyphenylene

ether, thermoplastic polyester, thermoplastic elastomeric polyester, or polyamide. For example, in a polycarbonate-containing blend there is often an improvement in melt flow when one molecular weight grade of polycarbonate is combined with a proportion of a relatively lower molecular weight grade of similar polycarbonate. Therefore, the present invention encompasses compositions comprising only one molecular weight grade of a particular resinous constituent and also compositions comprising two or more molecular weight grades of similar resinous constituent. When two or more molecular weight grades of similar resinous constituent are present, then the weight average molecular weight of the lowest molecular weight constituent is about 10% to about 95%, preferably about 40% to about 85%, and more preferably about 60% to about 80% of the weight average molecular weight of the highest molecular weight constituent. In one representative, non-limiting embodiment polycarbonate-containing blends include those comprising a polycarbonate with weight average molecular weight between about 28,000 and about 32,000 combined with a polycarbonate with weight average molecular weight between about 16,000 and about 26,000. When two or more molecular weight grades of similar resinous constituent are present, the weight ratios of the various molecular weight grades may range from about 1 to about 99 parts of one molecular weight grade and from about 99 to about 1 parts of any other molecular weight grades. A mixture of two molecular weight grades of a resinous constituent is often preferred, in which case the weight ratios of the two grades may range from about 99:1 to about 1:99, preferably from about 80:20 to about 20:80, and more preferably from about 70:30 to about 50:50. Since not all manufacturing processes for making a particular resinous constituent are capable of making all molecular weight grades of that constituent, the present invention encompasses compositions comprising two or more molecular weight grades of similar resinous constituent in which each of the similar resins is made by a different manufacturing process. In one particular embodiment the instant invention

encompasses compositions comprising a polycarbonate made by an interfacial process in combination with a polycarbonate of different weight average molecular weight made by a melt process.

Another constituent of the resin compositions of the invention is at least one phosphoramidate having a glass transition point of at least about 0°C, preferably of at least about 10°C, and most preferably of at least about 20°C, of the formula I:



wherein Q1 is oxygen or sulfur; R1 is an amine residue, and R2 and R3 are each independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl or halogen substitution, or mixture thereof; or an amine residue.

It should be noted that in the descriptions herein, the words "radical" and "residue" are used interchangeably, and are both intended to designate an organic moiety. For example, alkyl radical and alkyl residue are both intended to designate an alkyl moiety. The term "alkyl" as used in the various embodiments of the present invention is intended to designate both normal alkyl, branched alkyl, aralkyl, and cycloalkyl radicals. Normal and branched alkyl radicals are preferably those containing from 1 to about 12 carbon atoms, and include as illustrative non-limiting examples methyl, ethyl, propyl, isopropyl, butyl, tertiary-butyl, pentyl, neopentyl, and hexyl. Cycloalkyl radicals represented are preferably those containing from 3 to about 12 ring carbon atoms. Some illustrative non-limiting examples of these cycloalkyl radicals include cyclobutyl, cyclopentyl, cyclohexyl, methylcyclohexyl, and cycloheptyl. Preferred aralkyl radicals are those

containing from 7 to about 14 carbon atoms; these include, but are not limited to, benzyl, phenylbutyl, phenylpropyl, and phenylethyl. Aryl radicals used in the various embodiments of the present invention are preferably those containing from 6 to 12 ring carbon atoms. Some illustrative non-limiting
5 examples of these aryl radicals include phenyl, biphenyl, and naphthyl. The preferred halogen radicals used in the various embodiments of the present invention are chlorine and bromine.

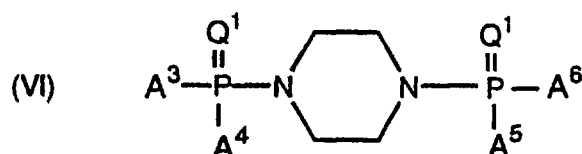
The compositions may contain essentially a single phosphoramidate or a mixture of two or more different types of phosphoramidates. Compositions
10 containing essentially a single phosphoramidate are preferred.

When a phosphoramidate having a glass transition point of at least about 0°C is used as a source of phosphorus in resin compositions, it was unexpectedly found that a higher heat deflection temperature of test specimens made from the resin composition could be obtained as compared
15 to compositions containing an organophosphate known in the art for enhancing the processability and/or flame resistance characteristics of the composition.

Although the invention is not dependent upon mechanism, it is believed that selection of each of R1, R2, and R3 residues that result in
20 restricted rotation of the bonds connected to the phosphorus provide an increased glass transition point in comparison to similar phosphoramidates with residues having a lesser degree of restriction. Residues having bulky substituents such as, for example, aryloxy residues containing at least one halogen, or preferably at least one alkyl substitution, result in
25 phosphoramidates having a higher glass transition point than similar phosphoramidates without the substitution on the aryloxy residue. Likewise, residues wherein at least two of the R1, R2, and R3 residues are interconnected, such as a neopentyl residue for the combination of the R2 and

R3 residues, can lead to desired phosphoramides having a glass transition point of at least about 0°C.

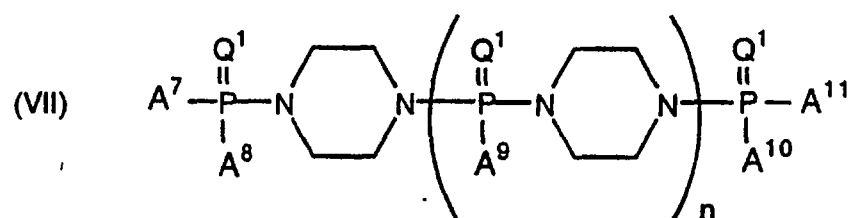
In a preferred embodiment, the phosphoramide comprises a phosphoramide having a glass transition temperature of at least about 0°C, preferably of at least about 10°C, and most preferably of at least about 20°C, of the formula VI:



wherein each Q1 is independently oxygen or sulfur; and each of A3-6 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl or halogen substitution, or mixture thereof; or an amine residue. In an especially preferred embodiment of the invention, each Q1 is oxygen, and each A3-6 moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethyl-phenoxy moiety. These phosphoramides are piperazine-type phosphoramides. In the above formula wherein each Q1 is oxygen, and each A3-6 moiety is a 2,6-dimethylphenoxy moiety, the glass transition temperature of the phosphoramide is about 62°C and the melting point is about 192°C. Conversely, in the above formula wherein each Q1 is oxygen, and each A3-6 moiety is phenoxy, the glass transition temperature of the phosphoramide is about 0°C and the melting point is about 188°C. It was unexpected that the glass transition temperature would be so high (i.e. about 62°C) for the phosphoramide of formula VI where each Q1 is oxygen, and wherein each of A3-6 is a 2,6-dimethylphenoxy moiety as compared to the corresponding phosphoramide of formula VI wherein each Q1 is oxygen, and each of A3-6 is a phenoxy moiety (i.e. about 0°C), especially since the melting points for the phosphoramides differ by only about 4°C. For comparison, the glass

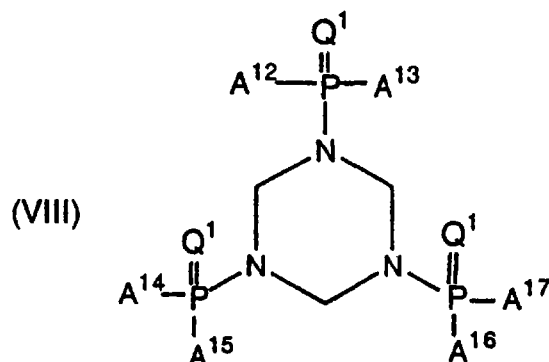
transition temperature of tetraphenyl resorcinol diphosphate is about -38°C . It is also possible to make phosphoramides with intermediate glass transition temperatures by using a mixture of various substituted and non-substituted aryl moieties within the phosphoramide.

- 5 In another preferred embodiment, the phosphoramide comprises a phosphoramide having a glass transition temperature of at least about 0°C , preferably of at least about 10°C , and most preferably of at least about 20°C , of the formula VII:



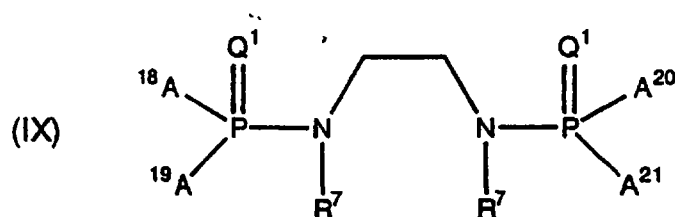
- 10 wherein each Q1 is independently oxygen or sulfur; and each of A7-11 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl or halogen substitution, or mixture thereof; or an amine residue; and n is from 0 to about 5. In a more preferred embodiment, each Q1 is oxygen, and each A7-11 moiety is independently phenoxy, 2,6-dimethylphenoxy, or 2,4,6-trimethylphenoxy, and n is from 0 to about 5.
- 15

- In another embodiment of the invention the phosphoramide comprises a phosphoramide having a glass transition temperature of at least about 0°C , preferably of at least about 10°C , and most preferably of at least about 20°C , of the formula VIII :
- 20



wherein each Q¹ is independently oxygen or sulfur; and each of A¹²-
 17 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an
 aryloxy or arylthio residue containing at least one alkyl or halogen
 5 substitution, or mixture thereof; or an amine residue. In a more preferred
 embodiment, each Q¹ is oxygen, and each A¹²-17 moiety is independently
 phenoxy, 2,6-dimethylphenoxy, or 2,4,6-trimethyl-phenoxy.

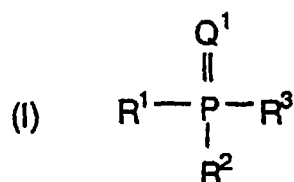
In another embodiment of the invention the phosphoramidate comprises
 a phosphoramidate having a glass transition temperature of at least about 0°C,
 10 preferably, of at least about 10°C, and most preferably of at least about 20°C,
 of the formula IX:



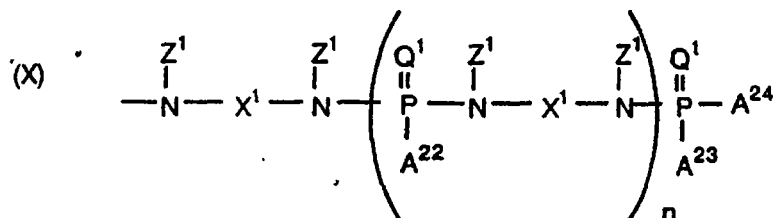
wherein each Q¹ is independently oxygen or sulfur; each of A¹⁸-21 is
 independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an
 15 aryloxy or arylthio residue containing at least one alkyl or halogen
 substitution, or mixture thereof; or an amine residue; and each R⁷ is an alkyl
 radical, or both R⁷ radicals taken together are an alkylidene or alkyl-
 substituted alkylidene radical. In a preferred embodiment, each Q¹ is oxygen;
 both R⁷ radicals taken together are an unsubstituted (CH₂)_m alkylidene

radical, wherein m is 2 to 10; and each A18-21 moiety is independently phenoxy, 2,6-dimethylphenoxy, or 2,4,6-trimethylphenoxy. In a more preferred embodiment, each Q1 is oxygen; each R7 is methyl; and each A18-21 moiety is independently phenoxy, 2,6-dimethylphenoxy, or 2,4,6-trimethylphenoxy.

In another embodiment of the invention, the phosphoramidate comprises a phosphoramidate having a glass transition point of at least about 0°C, preferably of at least about 10°C, and most preferably of at least about 20°C, of the formula I:



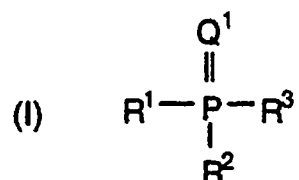
wherein Q1 is oxygen or sulfur, and R1 is of the formula X:



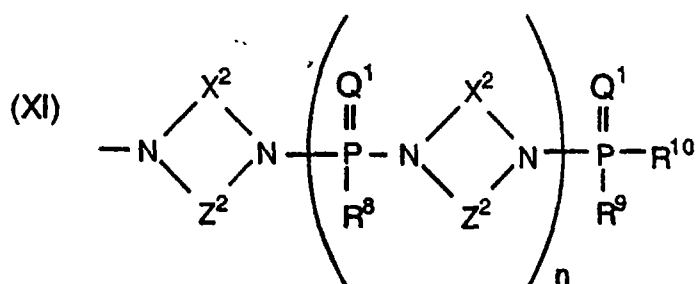
wherein each Q1 is independently oxygen or sulfur; each of A22-24 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl or halogen substitution, or mixture thereof; or an amine residue; each Z1 is an alkyl radical, aromatic radical, or aromatic radical containing at least one alkyl or halogen substitution or mixture thereof; each X1 is an alkylidene radical, aromatic radical, or aromatic radical containing at least one alkyl or halogen substitution or mixture thereof; n is from 0 to about 5; and R2 and R3 are each independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an

aryloxy or arylthio residue containing at least one alkyl or halogen substitution, or mixture thereof; or an amine residue. In a preferred embodiment, each Q1 is oxygen; each A22-24 moiety is independently phenoxy, 2,6-dimethylphenoxy, or 2,4,6-trimethylphenoxy; each Z1 is methyl or benzyl; each X1 is an alkylidene radical containing 2-24 carbon atoms; n is from 0 to about 5; and R2 and R3 are each independently phenoxy, 2,6-dimethylphenoxy, or 2,4,6-trimethylphenoxy.

In another embodiment of the invention, the phosphoramidate comprises a phosphoramidate having a glass transition point of at least about 0°C, preferably of at least about 10°C, and most preferably of at least about 20°C, of the formula I:



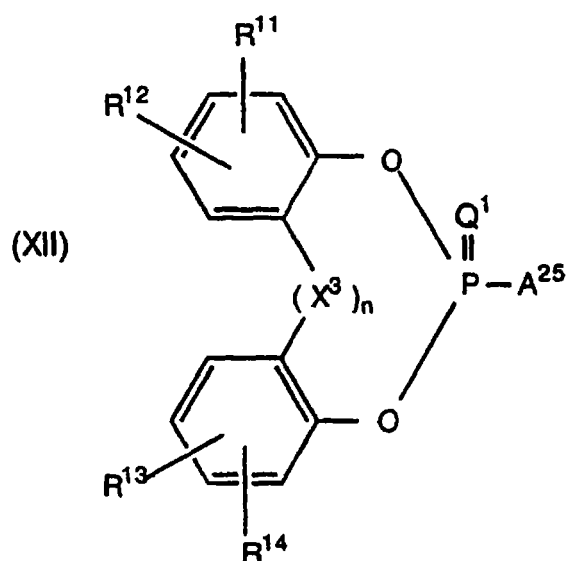
wherein Q1 is oxygen or sulfur; and R1 is of the formula XI:



wherein each Q1 is independently oxygen or sulfur; each X2 is an alkylidene or alkyl-substituted alkylidene residue, aryl residue, or alkaryl residue; each Z2 is an alkylidene or alkyl-substituted alkylidene residue; each of R8, R9, and R10 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl or halogen substitution, or mixture thereof; or an amine residue; n is from 0 to

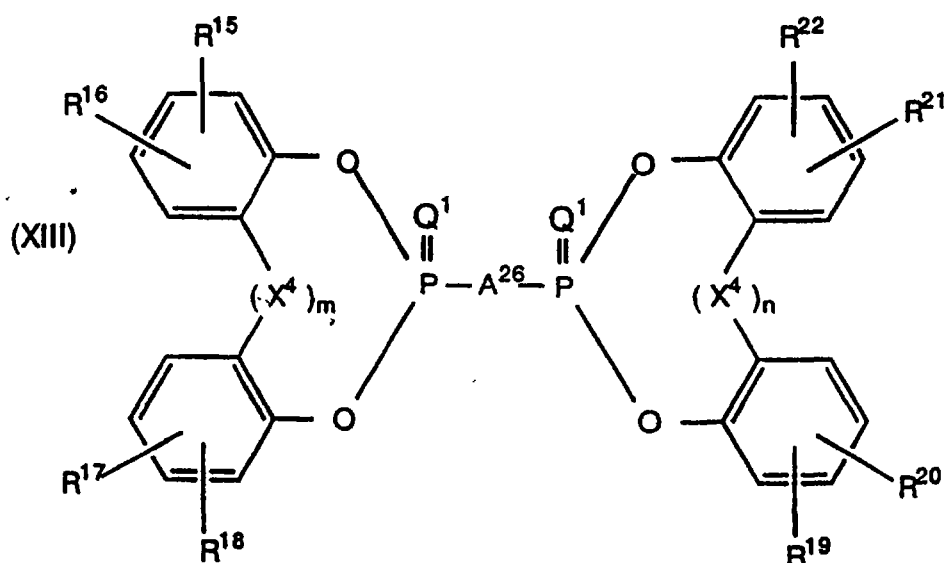
about 5; and R2 and R3 are each independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl or halogen substitution, or mixture thereof; or an amine residue. In a preferred embodiment, each Q1 is oxygen; each X2 is an alkylidene or alkyl-substituted alkylidene residue; each Z2 is an alkylidene or alkyl-substituted alkylidene residue; each of R2, R3, R8, R9, and R10 is independently phenoxy, 2,6-dimethylphenoxy, or 2,4,6-trimethylphenoxy; and n is from 0 to about 5. In a more preferred embodiment, each Q1 is oxygen; each X2 and Z2 is independently an unsubstituted alkylidene residue of the form (CH₂)_m, wherein m is 2 to 10; each of R2, R3, R8, R9, and R10 is independently phenoxy, 2,6-dimethylphenoxy, or 2,4,6-trimethyl-phenoxy; and n is from 0 to about 5. In an especially preferred embodiment, the phosphoramidate is derived from piperazine (i.e. X2 and Z2 are each -CH₂-CH₂-).

In another preferred embodiment, the phosphoramidate comprises a cyclic phosphoramidate having a glass transition point of at least about 0°C, preferably of at least about 10°C, and most preferably of at least about 20°C of the formula XII :

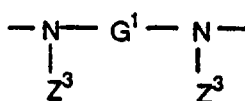


wherein each of R11-14 is independently a hydrogen or an alkyl radical, X3 is an alkylidene radical, Q1 is oxygen or sulfur, and A25 is a group derived from a primary or secondary amine having the same or different radicals that can be aliphatic, alicyclic, aromatic, or alkaryl, or A25 is a group
 5 derived from a heterocyclic amine, or A25 is a hydrazine compound. Preferably Q1 is oxygen. It should be noted that when n is 0, then the two aryl rings are linked together at that site (i.e. where X3 is absent) by a single bond in the positions ortho,ortho' to the phosphoryl bonds.

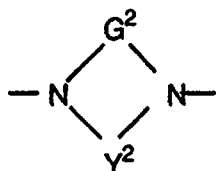
In another preferred embodiment, the phosphoramidate comprises a
 10 bis(cyclic) phosphoramidate having a glass transition point of at least about 0°C, preferably of at least about 10°C, and most preferably of at least about 20°C of the formula XIII:



wherein Q1 is oxygen or sulfur; each of R15-22 is independently a
 15 hydrogen or an alkyl radical; X4 is an alkylidene radical; m and n are each independently 0 or 1; and A26 is



wherein G1 is sulfur, an alkylidene radical, alkyl-substituted alkylidene radical, aryl radical, or alkaryl radical, and each Z3 is independently an alkyl radical, an aryl radical, or an aryl radical containing at least one alkyl or halogen substitution, or mixture thereof; or wherein A26 is



5

wherein G2 is alkylidene, aryl, or alkaryl, and Y2 is alkylidene or alkyl-substituted alkylidene. Preferred phosphoramides are those wherein Q1 is oxygen, A26 is a residue of piperazine, and the phosphoramide has a plane of symmetry through A26. Highly preferred phosphoramides include those wherein Q1 is oxygen; A26 is a residue of piperazine; the phosphoramide has a plane of symmetry through A26; at least one R substituent on each aryl ring is a methyl adjacent to the oxygen substituent; n and m are each 1; and X4 is CHR23 wherein R23 is a hydrogen or an alkyl residue of from about 1 to about 6 carbon atoms. It should be noted that when either or both of m or n is 0, then the two aryl rings are linked together at that site (i.e. where X4 is absent) by a single bond in the positions ortho,ortho' to the phosphoryl bonds.

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Phosphoramides of useful molecular structure are preferably prepared by the reaction of a corresponding amine such as, for example, piperazine or N,N'-dimethylethylenediamine with a diaryl chlorophosphate of the formula (aryl-O)₂POCl in the presence of a tertiary amine. This method of preparation is described in Talley, J. Chem. Eng. Data, 33, 221-222 (1988) and leads to specific phosphoramide compounds without repeating units. Alternatively, phosphoramides may be prepared by the reaction of the corresponding amine with P(O)Cl₃ in the presence of a tertiary amine, with the desired hydroxyl- or thiohydroxy-containing compound added simultaneously or subsequently

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to the addition of the amine. Addition of a diamine or triamine to $P(O)Cl_3$ with simultaneous or subsequent addition of the hydroxyl or thiohydroxy-containing compound is believed to lead to repeating units of phosphoramidate, often of 1 to about 5 phosphoramidate linkages per compound. Similarly, addition of a diamine or triamine to a monosubstituted phosphoryl- or thiophosphoryl dichloride with simultaneous or subsequent addition of hydroxyl- or thiohydroxy-containing compound is also believed to lead to repeating units of phosphoramidate. $P(S)Cl_3$ may be substituted for $P(O)Cl_3$ in the above preparations to provide suitable phosphoramidates.

Another constituent of the resin compositions of the invention is at least one adjunct flame retardant compound. An adjunct flame retardant compound may be an organic or inorganic, polymeric or non-polymeric compound. In certain preferred embodiments an adjunct flame retardant is one which may promote char formation in at least one resinous constituent, for example in polycarbonate when polycarbonate is a blend constituent.

In one embodiment of the present invention the adjunct flame retardant comprises at least one polymeric or non-polymeric organic phosphorus species selected from the group consisting of phosphate esters, thiophosphate esters, phosphonate esters, thiophosphonate esters, phosphinate esters, thiophosphinate esters, phosphines, including triphenylphosphine, phosphine oxides, including triphenylphosphine oxide and tris(2-cyanoethyl)phosphine oxide, thiophosphine oxides, and phosphonium salts. Preferred organic phosphorus species are non-polymeric phosphate esters including, for example, alkyl phosphate esters, aryl phosphate esters, resorcinol-based phosphate esters, and bisphenol-based phosphate esters. Illustrative, non-limiting examples of such phosphorus species include triphenylphosphate, tricresylphosphate, resorcinol bis(diphenyl-phosphate), bisphenol A bis(diphenyl-phosphate), and other aromatic phosphate esters known in the art.

In another embodiment of the present invention the adjunct flame retardant comprises at least one polymeric or non-polymeric inorganic phosphorus salt with anions selected from the group consisting of phosphates, thiophosphates, phosphonates, thiophosphonates, phosphinates, thiophosphinates, pyrophosphates, and metaphosphates. The cations in these inorganic phosphorus salts comprise at least one cation selected from the group consisting of ammonium, alkyl-substituted ammonium, aryl-substituted ammonium, and mixed alkyl-aryl-substituted ammonium; alkali metal, lithium, sodium, potassium; alkaline earth metal, magnesium, calcium, barium; transition metal, zirconium, hafnium, iron, zinc; lanthanide metal, lanthanum; boron; aluminum; and tin. Preferred inorganic phosphorus species are non-polymeric phosphate salts including, for example, alkali metal phosphates, boron phosphate, aluminum phosphate, and zinc phosphate.

In another embodiment of the present invention the adjunct flame retardant comprises at least one polymeric or non-polymeric sulfur species selected from the group consisting of sulfonate salts, sulfinic acid salts, sulfones, sulfoxides, and sulfides. Illustrative, non-limiting examples of such polymeric or non-polymeric sulfur species include polyarylene sulfide, polyarylene sulfide-sulfones, and salts of sulfonated aromatic compounds. Preferred sulfur species are polyphenylene sulfide, polyphenylsulfone, sodium para-toluene sulfonate, potassium diphenylsulfone-3-sulfonate, and Reimer's salts, including potassium perfluorobutane sulfonate.

In another embodiment of the present invention the adjunct flame retardant comprises at least one polymeric or non-polymeric boron-containing species. Illustrative, non-limiting examples of such species include zinc borate, boron phosphate, borax, and boric acid. Zinc borate is a particularly preferred boron-containing species.

In yet another embodiment of the present invention the adjunct flame retardant comprises at least one polymeric or non-polymeric antimony salt selected from the group consisting of oxides, halides, sulfides, sulfonates, phosphates, phosphonates, and carboxylates. Illustrative, non-limiting
5 examples of such polymeric or non-polymeric antimony salts include antimony oxide, antimony trichloride, and antimony potassium tartrate. A particularly preferred antimony salt is antimony oxide.

In yet another embodiment of the present invention the adjunct flame retardant comprises at least one polymeric or non-polymeric silicone
10 compound. Polymeric silicone compounds are often preferred. In one embodiment of the present invention particularly preferred polysiloxanes are those containing a plurality of dimethylsiloxane units, and, optionally, a minor proportion of organic groups, including but not limited to, at least one of vinyl, hydrogen, epoxy, amine, phenyl, and the like. For certain
15 embodiments suitable polymeric silicone compounds include SF1706 and SF1708 available from General Electric Silicones. In another embodiment further preferred polysiloxanes are those which have first units of $\text{RSiO}_{1.0}$ and second units of $\text{RSiO}_{1.5}$ where R is a radical selected from the group consisting of saturated and aromatic ring hydrocarbon groups as disclosed in
20 European Patent Application 829,521, which is incorporated herein by reference.

In another embodiment of the present invention the adjunct flame retardant comprises at least one organoclay. Examples of compositions containing organoclays are disclosed in copending, commonly owned
25 application Serial No. 09/032,533, filed February 27, 1998.

As used herein, "organoclay" means a layered clay, usually a silicate clay, derived from a layered mineral and in which organic moieties have been incorporated, ordinarily by ion exchange and especially cation exchange with

organic ions and/or onium compounds. Illustrative organic ions are mono- and polyammonium cations such as trimethyldodecylammonium and N,N'-didodecylimidazolium.

5 Illustrative layered minerals are the kaolinites and the montmorillonites. It is also possible to employ minerals of the illite group, including hydromicas, phengite, brammallite, glaucomite, cejadonite and the like. Often, the preferred layered minerals include those often referred to as 2:1 layered silicate minerals, including muscovite, vermiculite, saponite, hectorite and montmorillonite, the latter often being most preferred. The
10 layered minerals may be synthetically produced, but most often they are naturally occurring and commercially available. A detailed description of suitable layered minerals can be found in US Patent 5,530,052, the disclosure of which is incorporated by reference herein.

Suitable specific commercially available or easily prepared organoclays
15 which are illustrative of those which may be employed include Claytone HY, a montmorillonite which has been cation exchanged with dimethyldi(hydrogenated tallow)ammonium ion, and Claytone APA, a montmorillonite which has been cation exchanged with methylbenzyldi(hydrogenated tallow)ammonium ion, both available from
20 Southern Clay Products; and montmorillonite which has been cation exchanged with such ions as dodecylammonium, trimethyldodecylammonium, N,N'-didodecylimidazolium, N,N'-ditetradecylbenzimidazolium or methylbis(hydroxyethyl)-(hydrogenated tallow) ammonium.

25 In one embodiment of the invention the combination of adjunct flame retardant and at least one phosphoramidate having a glass transition point of at least about 0°C results in a flame retardant composition having a UL-94 rating of V-2, V-1, or V-0. In another embodiment of the invention the presence of

certain amounts of adjunct flame retardant permits the use of a lesser amount of at least one phosphoramidate having a glass transition point of at least about 0°C without substantial loss in flame retardant properties of the composition. Without substantial loss in flame retardant properties of the composition means that the UL-94 rating for the composition does not become worse in the presence of phosphoramidate/adjunct flame retardant combination compared to that rating observed in the absence of adjunct flame retardant. A UL-94 rating becomes worse, for example, when it increases from V-0 to either V-1 or V-2, or when it increases from V-1 to V-2. In yet another embodiment of the invention the flame retardant properties of the composition become better in the presence of phosphoramidate/adjunct flame retardant combination compared to those observed in the absence of adjunct flame retardant. Better flame retardant properties mean that either the flame out time (defined hereinafter below) for the composition decreases and/or that the UL-94 rating for the composition improves, for example, from V-2 to either V-1 or V-0, or from V-1 to V-0. In still another embodiment of the invention a synergistic effect on composition properties, particularly flame retardant properties, is observed in the presence of the phosphoramidate/adjunct flame retardant combination compared to that observed in the presence of at least one phosphoramidate or adjunct flame retardant alone.

The resinous compositions of this invention may contain a flame retarding amount and/or processability enhancing amount of the combination of at least one phosphoramidate and adjunct flame retardant. Flame retardancy is preferably measured according to the Underwriters' Laboratory UL-94 protocol. A flame retarding amount is an amount effective to render the composition at least a V-2 rating, preferably at least a V-1 rating, and most preferably a V-0 rating after testing in the UL-94 protocol when measured on a test specimen of about 0.03 to about 0.125 inch in thickness by

about 0.5 inch by about 5 inch, preferably about 0.125 inch in thickness by about 0.5 inch by about 5 inch, more preferably about 0.06 inch in thickness by about 0.5 inch by about 5 inch, and most preferably about 0.03 inch in thickness by about 0.5 inch by about 5 inch dimensions. Enhanced
5 processability can be determined, for example, as a reduction in extruder torque during compounding, reduced pressure in injection molding, reduced viscosity, and/or decreased cycle time.

Typically, a flame retarding amount of the combination of at least one phosphoramidate and at least one adjunct flame retardant in the compositions
10 of the invention is in the range of about 0.008-5 parts, preferably about 0.1-2.5 parts, of phosphorus per 100 parts of resinous materials (phr), all percentages herein being by weight. The total amount of phosphoramidate and adjunct flame retardant is most often in the range of about 0.1-50 phr, preferably about 0.5-35 phr, and more preferably about 1-25 phr.

15 In one embodiment of the present invention halogen-containing flame retardants or other halogen-containing species may also be present in the compositions as adjunct flame retardants. In many resinous compositions, the combination of a halogen-containing flame retardant and at least one phosphoramidate (or mixture of phosphoramidate with another adjunct flame
20 retardant), particularly including a phosphoramidate having a glass transition point of at least about 0°C, provides both suitable flame retardant properties and unexpectedly improved high temperature properties (such as measured, for example, by HDT or Tg of a resinous phase). Illustrative, non-limiting examples of halogen-containing flame retardants or halogen-containing
25 species include brominated flame retardants and phosphoramidates containing halogenated aromatic substituents. Due to environmental regulations chlorine-free and bromine-free compositions may be preferred for certain applications. Therefore, in a preferred embodiment the present invention includes compositions comprising a thermoplastic resin, at least one

phosphoramidate having a glass transition point of at least about 0°C, and an adjunct flame retardant, said compositions being essentially free of chlorine and bromine. In this context essentially free means that no chlorine- or bromine-containing species has been added to the compositions in their formulation. In another of its embodiments the present invention includes articles obtained from said chlorine-free or bromine-free compositions.

The compositions of the invention may also contain other conventional additives including stabilizers, inhibitors, plasticizers, fillers, mold release agents, and anti-drip agents. Anti-drip agents are illustrated by tetrafluoroethylene polymers or copolymers, including mixtures with such other polymers as polystyrene-co-acrylonitrile (sometimes referred to herein as styrene-acrylonitrile copolymer).

A principal characteristic of preferred compositions of the invention is their improved high temperature properties. These are demonstrated by the fact that the decrease in glass transition temperature (T_g) exhibited as a result of the incorporation of a phosphoramidate in the composition is substantially less than the corresponding decrease exhibited in blends containing, for example, phosphate esters such as bis(diaryl phosphates) of dihydroxyaromatic compounds. This is evident when a phosphoramidate is compared to the organic phosphate ester in amounts suitable to provide enhanced flame resistance when measured, for example, in the UL-94 test procedure. In the case of phase-separated blends such as polycarbonate-ABS blends, the decrease in T_g is noted in the polycarbonate phase.

Experience has shown that the flame retarding properties of a phosphorus-based compound included in a resinous composition are generally proportional to the amount of phosphorus in the composition rather than to the amount of the compound itself. Thus, equal weights of two additives having different molecular weights but the same flame retarding

properties may produce different UL-94 results, but amounts of the two additives which contribute the same proportion of phosphorus to the resinous composition will produce the same UL-94 results. On the other hand, other physical properties such as high temperature resistance are dependent on the amount of the compound itself and relatively independent of the phosphorus proportion therein. For this reason, the dependence of flame retarding and high temperature resistance of compositions containing two phosphorus-based compounds may not follow the same pattern.

It has been shown, however, with respect to the preferred phosphoramides employed according to the present invention that their superior properties of flame retardance and high temperature resistance are consistent. Thus, for example, proportions of resorcinol bis(di-2,6-xylyl phosphate) effective to confer a suitable flame-out time on certain resinous compositions are similar to those produced by a typical bis(2,6-xylyl)-phosphoramide at an essentially equivalent level of phosphorus, but the bisphosphoramide has a substantially lower tendency to decrease heat deflection temperature (HDT) despite the slightly greater amount of the bulk additive.

It should be clear that the present invention also affords methods to increase the heat distortion temperature of flame resistant compositions containing an amount of at least one phosphoramide and at least one adjunct flame retardant effective to render the composition a flame rating of at least V-2, preferably of at least V-1, most preferably V-0, in the UL-94 protocol, wherein the method comprises combining at least one thermoplastic resin, at least one phosphoramide having a glass transition point of at least about 0°C, preferably of at least about 10°C, and most preferably of at least about 20°C; and at least one adjunct flame retardant. In a preferred embodiment the invention also affords methods to increase the heat distortion temperature of chlorine-free and bromine-free, flame resistant compositions as described in

the previous sentence. The method may be used to increase the heat distortion temperature of compositions comprising essentially a single phosphoramidate or a mixture of two or more different types of phosphoramidate; and those comprising essentially a single adjunct flame retardant, or a mixture of two or more different types of adjunct flame retardant. Compositions containing essentially a single phosphoramidate and a single adjunct flame retardant are often preferred. Useful thermoplastic resins have been described herein. Especially preferred thermoplastic resins are polycarbonate, most especially bisphenol A- based polycarbonate, and blends of polycarbonate, especially polycarbonate-SAN-ABS blends, and polycarbonate-ABS blends, in which the amount of ABS may typically vary from about 1 to about 45 wt. %. An especially preferred phosphoramidate is N,N'-bis-[di-(2,6-xylyl)-phosphoryl]-piperazine. It should also be clear that the present invention includes compositions made by the methods as well as articles made from the compositions.

Preparation methods for the compositions of the invention are typical of those employed for resinous blends. They may include such steps as dry blending followed by melt processing, the latter operation frequently being performed under continuous conditions as by extrusion. Following melt processing, the compositions are molded into test specimens by conventional means such as injection molding.

The addition of at least one phosphoramidate and at least one adjunct flame retardant to the compositions of the present invention may be by mixing all of the blend components together prior to melt processing. Alternatively, either one of, or both of at least one phosphoramidate and at least one adjunct flame retardant may be combined with at least one resinous blend component as a concentrate in a prior processing step. Such concentrates are often made by melt processing. The concentrate may then be combined with the remaining blend components.

The various embodiments of the invention are inclusive of simple blends comprising at least one thermoplastic resin and at least one phosphoramidate and at least one adjunct flame retardant, and also of compositions in which one or more of said materials has undergone chemical reaction, either by itself or in combination with another blend component. When proportions are specified, they apply to the originally incorporated materials rather than those remaining after any such reaction.

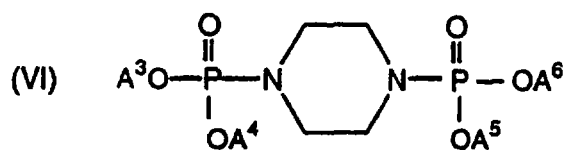
In another of its embodiments the present invention comprises articles of manufacture made from the instantly disclosed compositions. Such articles may be transparent, translucent, or opaque depending upon the blend composition. Said articles can be made by any convenient means known in the art. Typical means include, but are not limited to, injection molding, thermoforming, blow molding, and calendering. Especially preferred articles include indirect and direct wound deflection yokes for all cathode ray tube applications including television and computer monitors, slit type deflection yokes, mold coil deflection yokes, television backplates, docking stations, pedestals, bezels, pallets, electronic equipment such as switches, switch housings, plugs, plug housings, electrical connectors, connecting devices, sockets; housings for electronic equipment such as television cabinets, computer housings, including desk-top computers, portable computers, laptop computers, palm-held computers; monitor housings, printer housings, keyboards, FAX machine housings, copier housings, telephone housings, mobile phone housings, radio sender and/or receiver housings, lights and lighting fixtures, battery chargers, battery housings, antenna housings, transformers, modems, cartridges, network interface devices, circuit breakers, meter housings, panels for wet and dry appliances such as dishwashers, clothes washers, clothes dryers, refrigerators; heating and ventilation enclosures, fans, air conditioner housings, cladding and seating for indoor

and outdoor application such as public transportation including trains, subways, buses; automotive electrical components.

The invention is illustrated by the following examples. All parts and percentages are by weight. Intrinsic viscosity was determined in chloroform at 25°C. HDT values were determined at 264 psi (1820 kPa) according to ASTM procedure D648.

EXAMPLE 1

Blends of various amounts of a bisphenol A homopolycarbonate, 6.5 parts of a commercially available high rubber graft ABS copolymer and 9 parts of a commercially available SAN copolymer were prepared under identical conditions by blending in a Henschel mixer followed by extrusion on a twin screw extruder and were molded into test specimens. The blends also contained conventional additives including 0.4 part of polytetrafluoroethylene dispersed within styrene-acrylonitrile copolymer as an anti-drip agent, which were not considered in determining proportions, and various amounts of the following phosphoryl-based flame retardant additives: N,N'-bis-[di-(2,6-xylyl)phosphoryl]piperazine (XPP), a compound according to formula VI:



wherein each A moiety is a 2,6-dimethylphenyl residue; N,N'-bis(neopentylendioxy phosphoryl)piperazine (NPP), a compound of similar structure but wherein each pair of A moieties on each phosphorus atom (e.g. the A3 and A4 pair) is a bridging neopentyl residue; N,N'-bis(diphenyl phosphoryl)piperazine (PPP), a compound of similar structure but wherein each A moiety is a phenyl residue; and resorcinol bis(diphenyl phosphate)

(RDP) and bisphenol A bis(diphenyl phosphate) (BPADP), two conventional phosphate esters. The FOT (total flameout times for first and second ignitions for 5 bars of 0.125 inch thickness) and Tg of the polycarbonate phase of each test specimen was determined and the results are given in Table I.

TABLE I

Sample	Base	1	2	3	4	5
Polycarbonate, parts	81.3	72.2	76.9	73.9	73.6	71.6
FR, identity	none	XPP	NPP	PPP	RDP	BPADP
FR, phr	0	12.4	6.9	10.4	10.7	13.2
FR, phr P	0	1.16	1.11		0.97	1.02
FR, %P	0	1.02	1.01	1.04	1.03	1.04
FOT, sec	burns	19.4	84	--	20.3	27.3
Tg, °C	147	131	149	121	111	112

- 5 It is apparent that the compositions of this invention had an significantly reduced FOT and a Tg that differed from that of polycarbonate (147°C) in a base composition not containing a phosphoramidate or phosphate ester by an acceptable increment. Sample 2 had a Tg essentially equal within experimental error to that of the polycarbonate in the base composition but
- 10 the FOT was appreciably higher than that obtained with XPP. Sample 3 utilizing PPP had a significantly lower Tg than that of XPP and NPP, yet exhibited similar FOT as obtained with XPP. It was unexpected that XPP-containing compositions (e.g., sample 1) would exhibit such superior FOT as compared to NPP-containing compositions (e.g., sample 2), and such a large
- 15 increase in polycarbonate Tg as compared to PPP-containing compositions (e.g., sample 3). Samples 4 and 5, employing conventional flame retardants

(FR), had unacceptably low Tg's for many commercial applications. The variations in FR content in terms of phr of total FR and of phosphorus are not considered significant from the standpoint of properties.

EXAMPLE 2

In the same base composition used for Example 1, a composition was made containing 4.5 parts RDP and 5.7 XPP. The resultant composition has a flame out time of 17 seconds and the polycarbonate had a Tg of 127°C. The glass transition temperature is higher for this composition that would be expected based upon the results obtained in samples 1 and 4.

EXAMPLE 3

Blends of 62 parts of a commercially available poly(2,6-dimethyl-1,4-phenylene ether) and 38 parts of a commercially available HIPS were prepared and molded under identical conditions similar to those of Example 1. The blends also contained conventional additives including 0.21 part of a polytetrafluoroethylene/styrene-acrylonitrile copolymer as an anti-drip agent, which were not considered in determining proportions, and 20.5 phr of XPP, RDP and BPADP as phosphoryl-based flame retardant additives. The FOT (total flameout times for first and second ignitions for 5 bars of 0.06 inch thickness) and heat deflection temperature (HDT) of each test specimen was determined and the results are given in Table II.

TABLE II

Sample	6	7	8
FR, identity	XPP	RDP	BPADP
FR, phr P	1.92	1.85	1.58
FOT, sec	24	21	37
HDT, °C	223.9	177.9	190.5

Again, it is apparent that the composition of the invention (Sample 6) had acceptable FR properties and a significantly higher HDT than the compositions containing conventional FR additives, indicating superior high temperature properties.

EXAMPLE 4

5 A blend of 40 parts of a commercially available poly(2,6-dimethyl-1,4-phenylene ether) and 60 parts of a commercially available HIPS were prepared and molded under conditions similar to those of Example 3, using N,N'-bis[di-(2,6-xylyl)phosphoryl]piperazine (XPP) as the flame retardant material in essentially the same proportion. The observed FOT was 34
10 seconds.

EXAMPLE 5

A commercially available HIPS, optionally containing poly(2,6-dimethyl-1,4-phenylene ether) and / or a polystyrene-polybutadiene-polystyrene elastomer, were prepared and molded under conditions similar to those of Example 1, using N,N'-bis[di-(2,6-xylyl)phosphoryl]piperazine
15 (XPP) as the flame retardant material. The compositions and flame out times (FOT, as defined above for Table 1) are provided in Table III.

TABLE III

Sample	Base	9	10	11	12	13
HIPS, parts	100	90	70	65	72	78.5
PPE, parts	0	0	0	25	7	3.5
Rubber, parts	0	0	0	0	2	3.5
XPP, parts	0	10	30	10	19	14
FOT, sec	burns	320	135	400	215	315
HDT, °C, 264 psi	86	74	68	79	71	73

As seen by the above data, phosphoramides as described herein are effective in reducing the flame out time of HIPS, optionally in the presence of PPE and /or rubber. It was unexpected that the flame out times would be so dramatically improved, i.e. decreased, with the addition of the phosphoramide to render the material V-2 under UL-94 classification. It was also unexpected that the HDT would be so high for the compositions containing the phosphoramide.

EXAMPLE 6

Blends of 90 parts of a commercially available bisphenol A polycarbonate were prepared containing 10 parts of either RDP or XPP. The blends also contained conventional additives, including a UV screener and an antioxidant, which were not considered in determining proportions. The compositions were extruded and molded into transparent specimens. Optical properties (according to ASTM 1003-61), including % transmission, yellowness index, and haze, and the Tg of the polycarbonate phase were determined for test specimens of each blend. The results are given in Table IV along with results for a comparable composition containing essentially 100% of the same polycarbonate and no added flame retardant.

TABLE IV

Sample	Base	14	15
Polycarbonate	100	90	90
RDP	0	10	0
XPP	0	0	10
Tg, °C	149	111	131
Transmission, %	90.1	88.3	89.5
Haze	0.7	3.3	0.7
Yellowness index	2.24	3.18	4.16

The above data show that the composition containing XPP has the same % transmission and haze as a specimen of essentially pure polycarbonate, and an acceptable yellowness index. Compared to the base sample, the decrease in polycarbonate Tg is only 18°C for the specimen containing XPP compared to 38°C for the specimen containing RDP.

EXAMPLE 7

A blend of 26.5 parts of a first bisphenol A homopoly-carbonate, 61.8 parts of a second bisphenol A homopolycarbonate with weight average molecular weight about 71% of that of the first bisphenol A homopolycarbonate, 4 parts of a commercially available bulk ABS copolymer, and 5 parts XPP was prepared by blending in a Henschel mixer followed by extrusion on a twin screw extruder and molded into test specimens. The blend also contained 2.75 parts conventional additives including titanium dioxide and polytetrafluoro-ethylene dispersed within styrene-acrylonitrile copolymer as an anti-drip agent. Measurement of the Melt Volume Rate (260°C and 5 kilograms applied weight) for the blend gave a value of 24.9 cubic centimeters per 10 minutes. The blend showed a melt viscosity at 280°C of 390 Pascal-seconds (Pa-s) at a shear rate of 100 sec⁻¹, 220 Pa-s at a shear rate of 1500 sec⁻¹, and 72 Pa-s at a shear rate of 10000 sec⁻¹. The observed FOT (total flameout times for first and second ignitions for 5 bars of 0.06 inch thickness) was 21.5 seconds. A Ball Pressure Test run on test specimens at 125°C according to test protocol IEC 695-10-2 (1995-08) gave puncture diameter of 1.6 millimeters (mm). Typically, a value of less than 2 mm is desirable for most applications.

EXAMPLE 8

A blend of 64.3 parts bisphenol A homopolycarbonate, 16 parts of a copolycarbonate comprising 45 mole % bisphenol A and 55 mole % 4,4'-(3,3,5-

trimethylcyclohexylidene)diphenol (APEC 9371 obtained from Bayer Corp.); 4 parts of a commercially available high rubber graft ABS copolymer; 6 parts of a commercially available SAN copolymer, and 9 parts XPP was prepared by blending in a Henschel mixer followed by extrusion on a twin screw extruder and molded into test specimens. The blend also contained 0.7 parts of conventional additives including polytetrafluoroethylene dispersed within styrene-acrylonitrile copolymer as an anti-drip agent. The blend showed a glass transition temperature of 139°C. The observed FOT (total flameout times for first and second ignitions for 5 bars of 0.06 inch thickness) was 24 seconds.

EXAMPLE 9

The same composition of Example 8 was prepared except that 16 parts of a copolycarbonate comprising 65 mole % bisphenol A and 35 mole % 4,4'-(3,3,5-trimethylcyclo-hexylidene)diphenol (APEC 9351 obtained from Bayer Corp.) was used. The blend showed a glass transition temperature of 140°C. The observed FOT (total flameout times for first and second ignitions for 5 bars of 0.06 inch thickness) was 21 seconds.

EXAMPLE 10

A blend of 58.8 parts bisphenol A homopolycarbonate, 25 parts of a copolycarbonate comprising 65 mole % bisphenol A and 35 mole % 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol (APEC 9351 obtained from Bayer Corp.); 4 parts of a commercially available high rubber graft ABS copolymer; 2 parts of a commercially available SAN copolymer, 0.5 parts CLAYTONE HY, and 9 parts XPP was prepared by blending in a Henschel mixer followed by extrusion on a twin screw extruder and molded into test specimens. The blend also contained 0.7 parts of conventional additives including polytetrafluoroethylene dispersed within styrene-acrylonitrile copolymer as an anti-drip agent. The blend showed a glass transition temperature of 140°C.

The observed FOT (total flameout times for first and second ignitions for 5 bars of 0.06 inch thickness) was 19 seconds.

EXAMPLES 11-25

Blends of 88 parts of a commercially available bisphenol A homopolycarbonate, 6 parts of a commercially available high rubber graft
5 ABS copolymer and 4.5 parts of a commercially available SAN copolymer were prepared under conditions similar to those used for Example 1. The blends also contained conventional additives, including 0.5 part of polytetrafluoroethylene dispersed within styrene-acrylonitrile copolymer as an anti-drip agent, which were not considered in determining proportions.
10 The blends also contained various amounts (in phr) of XPP and adjunct flame retardants. The compositions, flame out times (FOT, as defined above for Table I), and UL-94 ratings are provided in Table V.

Table V

Material, phr	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
XPP	10.4	8.1	8.1	8.2	8.3	8.1	8.1	8.2	8.1	8.1	8.1	8.1	8.2	8.3	8.5
antimony oxide	0	0	0.5	1.1	2.2	0	0	0	0	0	0	0	0	0	0
boron phosphate	0	0	0	0	0	0.27	0.55	1.1	0	0	0	0	0	0	0
OrganoclayHY	0	0	0	0	0	0	0	0	0.27	0.55	0	0	0	0	0
Organoclay APA	0	0	0	0	0	0	0	0	0	0	0.27	0.55	0	0	0
PPS*	0	0	0	0	0	0	0	0	0	0	0	0	1.1	2.2	4.6
FOT, sec.	30	70	20	4	109	30	42	35	7	35	15	27	24	53	67
UL 94 rating	V-0	V-1	V-0	V-0	V-2	V-0	V-1	V-1	V-0	V-1	V-0	V-1	V-0	V-1	V-1

- PPS = polyphenylene sulfide

Samples 11 and 12 are control sample containing two different
15 amounts of XPP and no adjunct flame retardant. It can be seen that the UL-94 rating changes from V-0 to V-1 when a lower amount of XPP is used in control sample 12. The samples containing adjunct flame retardant demonstrate that compositions with acceptable UL-94 ratings can be made

by the method of the invention. Compositions containing certain amounts of adjunct flame retardant have UL-94 rating that is as good as the rating for the control sample 11 although they contain only as much XPP as control sample 12.

EXAMPLES 26-32

5 Blends of 25 parts of a bisphenol A polycarbonate with weight average molecular weight about 30,000 and 75 parts of a bisphenol A polycarbonate with lower weight average molecular weight were prepared. The blends contained various amounts of XPP, and of potassium diphenylsulfone-3-sulfonate (referred to as "KSS") as adjunct flame retardant. The blends also
10 contained conventional additives which were not considered in determining proportions. The compositions were extruded and molded into transparent specimens. The total flame out times for first and second ignitions for 5 bars of each sample were determined using bars of both of 0.060 inch thickness and of 0.125 inch thickness. Optical properties, including yellowness index
15 (according to ASTM D1925) and haze (according to ASTM 1003), were determined for test specimens of each blend. The results are given in Table VI along with results for a control composition (sample 24) containing the same polycarbonate mixture and a commercially available brominated polycarbonate flame retardant (PC-B).

TABLE VI

Material, phr	26	27	28	29	30	31	32
PC-B	0.5	0	0	0	0	0	0
KSS	0.25	0.15	0.05	0.05	0.25	0.05	0.15
XPP	0	0.5	0.1	0.9	0.9	0.1	0.5
FOT-a, sec.	19	26	36	64	61	25	35
FOT-b, sec.	24	34	56	83	31	48	53
Yellowness Index	2	2.5	2.3	2.8	3.4	1.8	2
Haze	1	0.6	0.7	0.5	1	0.5	0.5

FOT-a = measured on 0.125 inch thickness test bars

FOT-b = measured on 0.060 inch thickness test bars

The data show that samples with acceptable FOT values can be made by the method of the invention. Samples containing XPP and adjunct flame retardant demonstrate optical properties comparable to those for a similar blend containing only a commercially available brominated flame retardant.

EXAMPLES 33-41

Blends of a commercially available bisphenol A homopolycarbonate, a commercially available high rubber graft ABS copolymer and a commercially available SAN copolymer were prepared under conditions similar to those used for Example 1. The blends also contained 0.7 part of conventional additives, including polytetrafluoroethylene dispersed within styrene-acrylonitrile copolymer as an anti-drip agent, which were not considered in determining proportions. The blends also contained various amounts (in phr) of XPP, CLAYTONE HY, and a commercially available polyphenylsulfone (RADEL R available from Amoco Chemical Co.) as adjunct flame retardants. The compositions, flame out times (FOT, as defined above for Table I), UL-94 ratings, and Limiting Oxygen Indices are provided in Table VII.

TABLE VII

Material	33	34	35	36	37	38	39	40	41
PC	77.8	70.3	77.8	73.8	65.8	73.8	77.8	77.8	79.3
ABS	4	8	4	4	8	4	4	8	7
SAN	6	2	2	6	6	6	2	6	2
XPP	9	9	5	5.5	9	5.5	5	5	9
Organoclay HY	0.5	0	0.5	0	0.5	0	0.5	0.5	0
PPSO*	2	10	10	10	10	10	10	2	2
FOT, sec.	14	30	30	70	53	52	43	240	24
UL 94 rating	V-0	V-0	V-0	V-1	V-1	V-1	V-1	--	V-0
LOI	34	--	35.9	--	--	--	--	30	--

* polyphenylsulfone

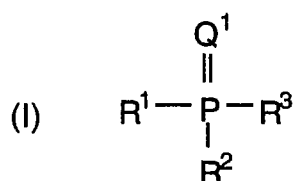
CLAIMS:

1. A resin composition comprising:

a) a thermoplastic resin, and

b) at least one phosphoramidate having a glass transition point of at least 0°C selected from the group consisting of:

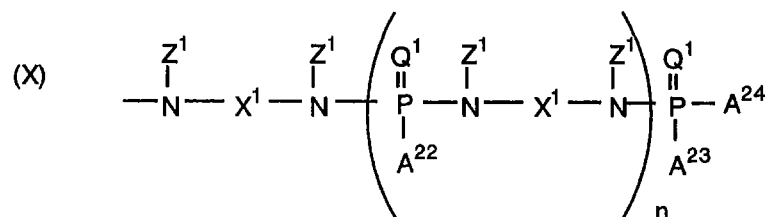
i) a phosphoramidate having the formula:



wherein:

Q1 is oxygen or sulfur;

R1 is of the formula X:



wherein

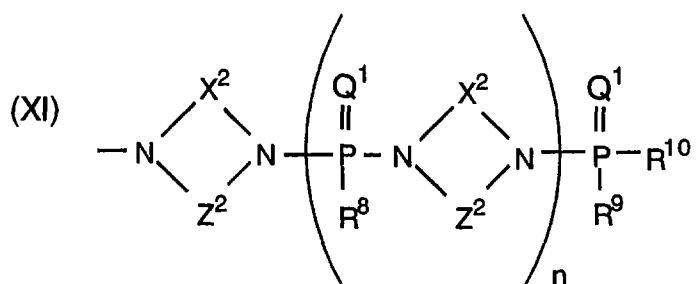
each of A²²⁻²⁴ is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

each Z¹ is an alkyl radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

each X¹ is an alkylidene radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

or

R1 is of the formula XI:



wherein

each X2 is alkylidene, aryl, or alkaryl;

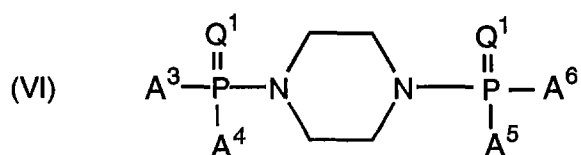
each Z2 is alkylidene;

each of R8, R9, and R10 is independently an alkyloxy residue, an aryloxy residue, an aryloxy residue containing at least one alkyl substitution, or an amine residue;

n is from 0 to about 5; and

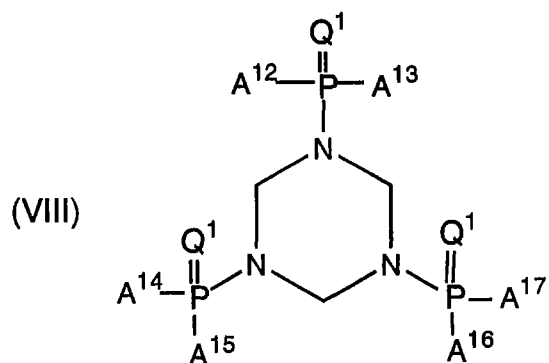
R2 and R3 are each independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

(ii) a phosphoramidate of the formula VI:



wherein each Q1 is independently oxygen or sulfur and each A moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethylphenoxy moiety;

(iii) a phosphoramidate of the formula VIII :

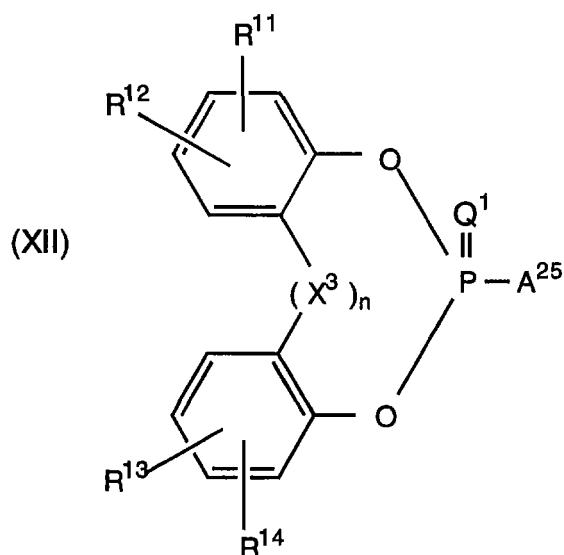


wherein

each Q1 is independently oxygen or sulfur and

each of A12-17 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution or an amine residue;

(iv) a phosphoramidate of the formula XII :



wherein Q1 is oxygen or sulfur;

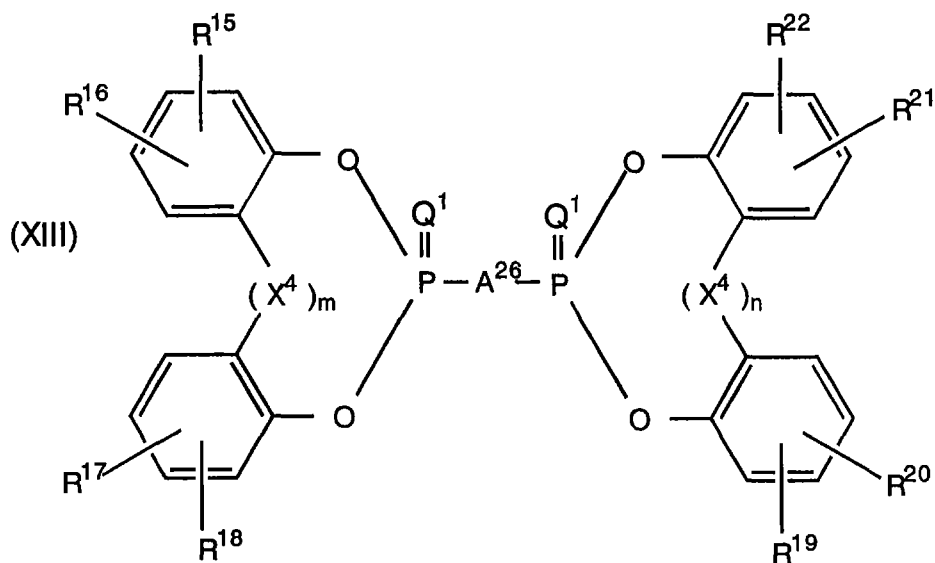
each of R11-14 is independently a hydrogen or an alkyl radical;

X3 is a alkylidene radical;

n is 0 or 1; and

A25 is a group derived from a primary or secondary amine having the same or different radicals that can be aliphatic, alicyclic, aromatic, or alkaryl, or A25 is a group derived from a heterocyclic amine, or A25 is a hydrazine compound; and

(v) a bis(cyclic) phosphoramidate of the formula XIII:

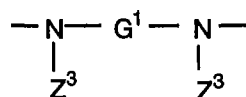


wherein each Q1 independently is oxygen or sulfur;

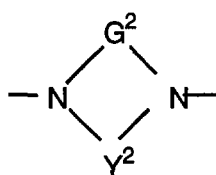
each of R15-22 is independently a hydrogen or an alkyl radical;

X4 is an alkylidene radical; m and n are each independently 0 or 1; and

A26 is



wherein G1 is sulfur, an alkylidene radical, aryl radical, or alkaryl radical; and each Z3 is independently an alkyl radical or an aryl radical; or wherein A26 is



wherein G2 is alkylidene, aryl, or alkaryl, and Y2 is alkylidene; and

c) at least one adjunct flame retardant compound.

2. The composition of claim 1 wherein at least one phosphoramidate has a glass transition point of at least about 10°C.

3. The composition of claim 1 wherein all of the phosphoramidate of component b) has a glass transition point of at least about 10°C.

4. The composition of claim 1 wherein at least one phosphoramidate has a glass transition point of at least about 20°C.

5. The composition of claim 1 wherein all of the phosphoramidate of component b) has a glass transition point of at least about 20°C.

6. The composition of claim 1 wherein the thermoplastic resin is selected from the group consisting of (i) polycarbonate resins and blends containing at least one polycarbonate resin, (ii) polyphenylene ether resins and blends containing at least one polyphenylene ether resin, (iii) polystyrene resin and blends containing polystyrene resin, (iv) styrene-containing copolymer resin and blends containing styrene-containing copolymer resin; (v) styrene-containing graft copolymer resin and blends containing styrene-containing graft copolymer resin; and (vi) high impact polystyrene resin and blends containing high impact polystyrene resin.

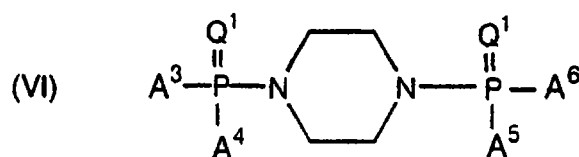
7. The composition of claim 1 wherein the thermoplastic resin is selected from the group consisting of high impact polystyrene resin, syndiotactic polystyrene, polyphenylene ether / high impact polystyrene resin blends, polyphenylene ether / syndiotactic polystyrene resin blends, polycarbonate-SAN blends, polycarbonate-ABS blends, polycarbonate-SAN-ABS blends, and polycarbonate-polyester blends.

8. The composition of claim 1 wherein the thermoplastic resin is at least one of polycarbonates, polyphenylene ethers, high impact polystyrenes, syndiotactic polystyrenes, acrylonitrile-butadiene-styrene copolymers, and styrene-acrylonitrile copolymers.

9. The composition of claim 1 wherein the thermoplastic resin comprises at least one polycarbonate and ABS.

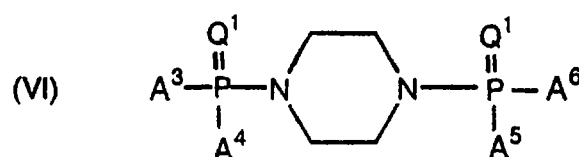
10. The composition of claim 9 wherein the at least one polycarbonate comprises bisphenol A polycarbonate and a copolycarbonate of bisphenol A and 4,4'-(3,3,5-trimethylcyclo-hexylidene)diphenol.

11. The composition of claim 9 wherein the at least one phosphoramidate comprises a phosphoramidate of the formula VI :



wherein each Q1 is independently oxygen or sulfur; and each A moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethylphenoxy moiety.

12. The composition of claim 9 wherein the at least one
5 phosphoramidate comprises a phosphoramidate of the formula VI :

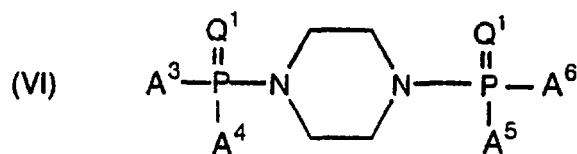


wherein each Q1 is oxygen; and each A moiety is a 2,6-dimethylphenoxy moiety.

13. The composition of claim 1 wherein the thermoplastic resin
10 comprises polyphenylene ether and high impact polystyrene resin.

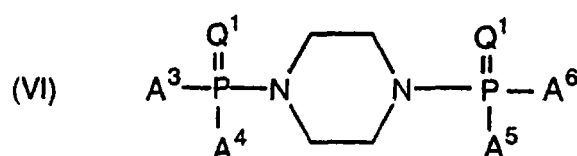
14. The composition of claim 1 wherein the adjunct flame retardant
comprises at least one polymeric or non-polymeric member selected from the
group consisting of phosphate esters, thiophosphate esters, phosphonate
esters, thiophosphonate esters, phosphinate esters, thiophosphinate esters,
15 phosphines, phosphine oxides, thiophosphine oxides, phosphonium salts;
phosphate salts, thiophosphate salts, phosphonate salts, thiophosphonate
salts, phosphinate salts, thiophosphinate salts, pyrophosphate salts,
metaphosphate salts; sulfonate salts, sulfinates, sulfones, sulfoxides,
sulfides; borates; antimony salts; siloxanes; and organoclays.

- 20 15. The composition of claim 14 wherein the at least one
phosphoramidate comprises a phosphoramidate of the formula VI :



wherein each Q1 is independently oxygen or sulfur; and each A moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethylphenoxy moiety.

16. The composition of claim 14 wherein the at least one
5 phosphoramidate comprises a phosphoramidate of the formula VI :



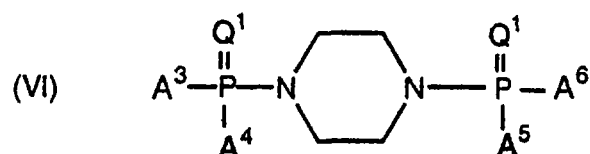
wherein each Q1 is oxygen; and each A moiety is a 2,6-dimethylphenoxy moiety.

17. The composition of claim 1 wherein the adjunct flame retardant
10 comprises at least one polymeric or non-polymeric member selected from the group consisting of phosphate esters, phosphate salts, sulfonate salts, sulfones, sulfides, borates, antimony salts; siloxanes; and organoclays.

18. The composition of claim 1 wherein the adjunct flame retardant
15 comprises at least one member selected from the group consisting of resorcinol bis(diphenylphosphate), bisphenol A bis(diphenylphosphate), triphenylphosphate, tricresylphosphate, boron phosphate, potassium diphenylsulfone-3-sulfonate, potassium perfluorobutane sulfonate, polyphenylene sulfide, polyphenylsulfone, zinc borate, antimony oxide; polysiloxanes; and organoclays.

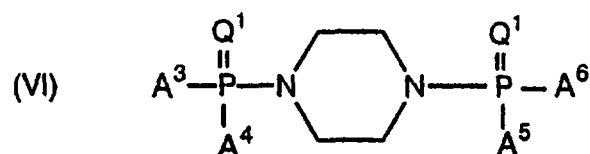
19. The composition of claim 18 wherein the combination of
20 phosphoramidate and adjunct flame retardant is present in an amount effective to render the resin composition a flame rating of V-0, V-1, or V-2 in the Underwriter's Laboratory UL-94 protocol when measured on a test specimen of about 0.125 inch by about 0.5 inch by about 5 inch dimensions.

20. The composition of claim 1 wherein at least one phosphoramidate comprises a phosphoramidate of the formula VI:



5 wherein each Q1 is independently oxygen or sulfur; and each A moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethylphenoxy moiety.

21. The composition of claim 1 wherein at least one phosphoramidate comprises a phosphoramidate of the formula VI:



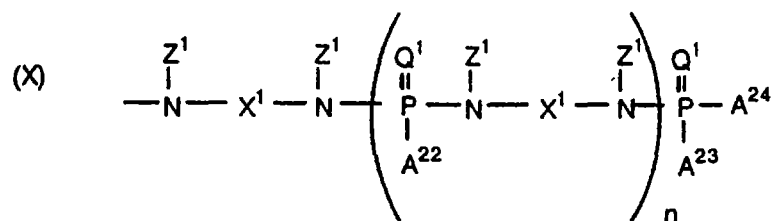
10 wherein each Q1 is oxygen; and each A moiety is a 2,6-dimethylphenoxy moiety.

22. The composition of claim 1 wherein at least one phosphoramidate is present in an amount effective to render the resin composition a flame rating of V-0, V-1, or V-2 in the Underwriter's Laboratory UL-94 protocol when measured on a test specimen of about 0.125 inch by about 0.5 inch by about 5 inch dimensions.

23. The composition of claim 1 wherein the total amount of phosphorus per 100 parts of resinous materials is in the range of about 0.008-3 parts by weight.

20 24. The composition of claim 1 which is essentially free of chlorine and bromine.

25. The composition of claim 1 wherein R1 is of the formula X :



wherein

each Q1 is independently oxygen or sulfur;

each of A22-24 is independently an alkyloxy, alkylthio, aryloxy, or
5 arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl
substitution; or an amine residue;

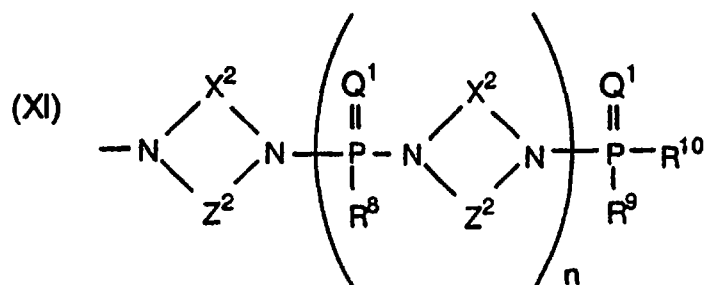
each Z1 is an alkyl radical, aromatic radical, or aromatic radical
containing at least one alkyl substitution;

each X1 is an alkylidene radical, aromatic radical, or aromatic radical
10 containing at least one alkyl substitution;

n is from 0 to about 5; and

R2 and R3 are each independently an alkyloxy, alkylthio, aryloxy, or
arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl
substitution; or an amine residue.

15 26. The composition of claim 1 wherein R1 is of the formula XI :



wherein

each Q1 is independently oxygen or sulfur;

each X2 is alkylidene, aryl, or alkaryl;

each Z2 is alkylidene;

each of R8, R9, and R10 is independently an alkyloxy residue, an
 5 aryloxy residue, an aryloxy residue containing at least one alkyl substitution,
 or an amine residue; and

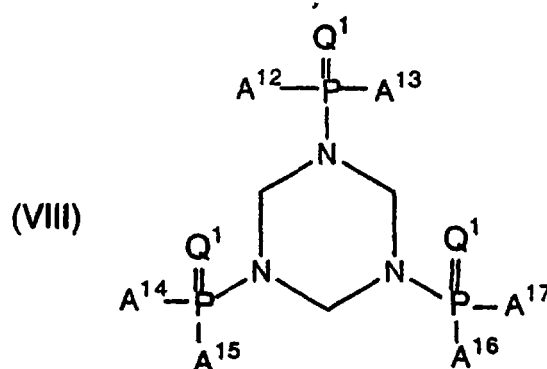
n is from 0 to about 5; and

R2 and R3 are each independently an alkyloxy, alkylthio, aryloxy, or
 10 arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl
 substitution; or an amine residue.

27. A resin composition comprising the following and any reaction
 products thereof:

a) a thermoplastic resin

b) at least one phosphoramidate having a glass transition point of at
 15 least about 0°C of the formula VIII :



wherein

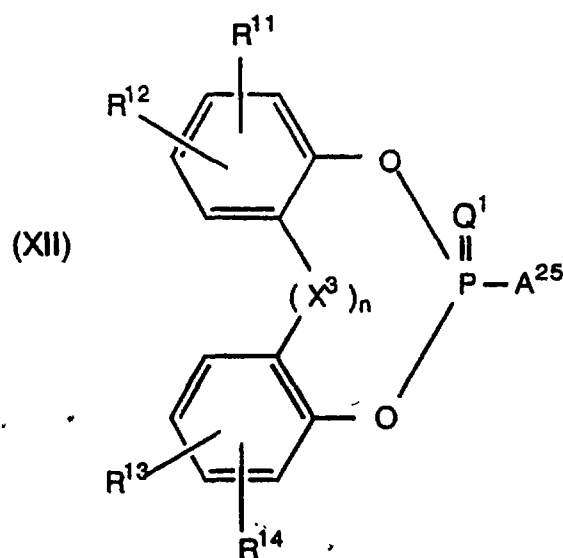
each Q1 is independently oxygen or sulfur; and

each of A12-17 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue.

28. A resin composition comprising the following and any reaction products thereof:

a) a thermoplastic resin and

b) at least one cyclic phosphoramidate having a glass transition point of at least about 0°C of the formula XII :



wherein Q1 is oxygen or sulfur;

each of R11-14 is independently a hydrogen or an alkyl radical;

X3 is a alkylidene radical;

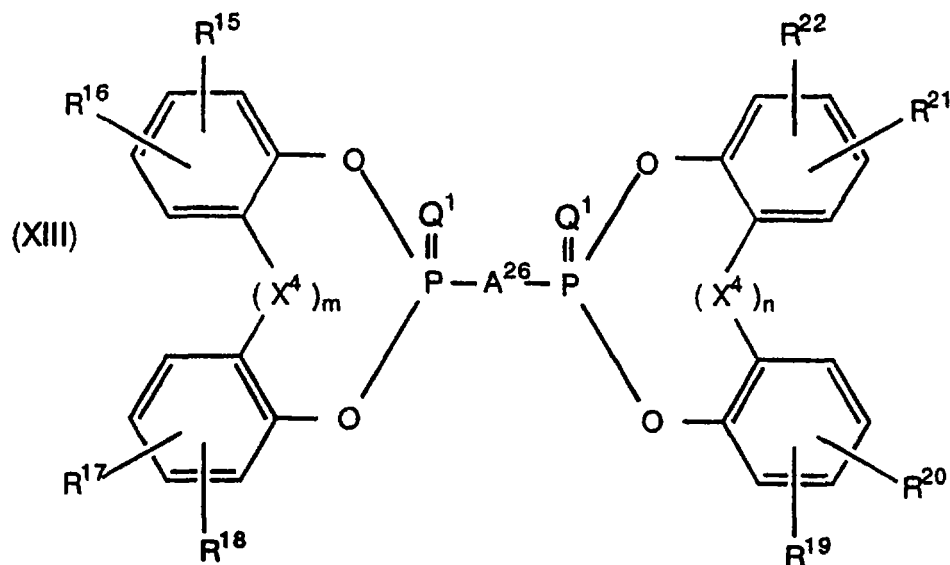
n is 0 or 1; and

A25 is a group derived from a primary or secondary amine having the same or different radicals that can be aliphatic, alicyclic, aromatic, or alkaryl, or A25 is a group derived from a heterocyclic amine, or A25 is a hydrazine compound.

29. A resin composition comprising the following and any reaction products thereof:

a) a thermoplastic resin

b) at least one bis(cyclic) phosphoramidate having a glass transition point of at least about 0°C of the formula XIII :



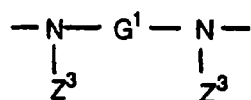
wherein each Q1 independently is oxygen or sulfur;

each of R15-22 is independently a hydrogen or an alkyl radical;

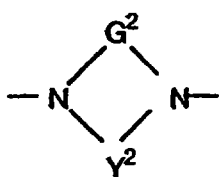
X4 is an alkylidene radical; m and n are each independently 0 or 1;

10 and

A26 is

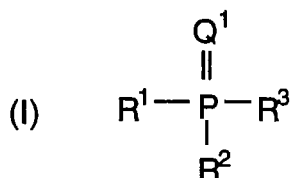


wherein G1 is sulfur, an alkylidene radical, aryl radical, or alkaryl radical; and each Z3 is independently an alkyl radical or an aryl radical; or
15 wherein A26 is



wherein G² is alkylidene, aryl, or alkaryl, and Y² is alkylidene.

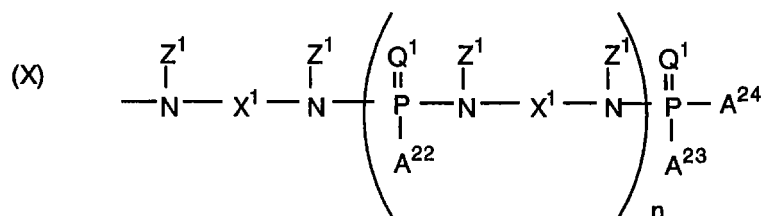
30. A resin composition consisting essentially of:
- a) a thermoplastic resin, and
 - b) at least one phosphoramidate having a glass transition point of at least 0°C selected from the group consisting of:
 - i) a phosphoramidate having the formula:



wherein:

Q¹ is oxygen or sulfur;

R¹ is of the formula X:



wherein

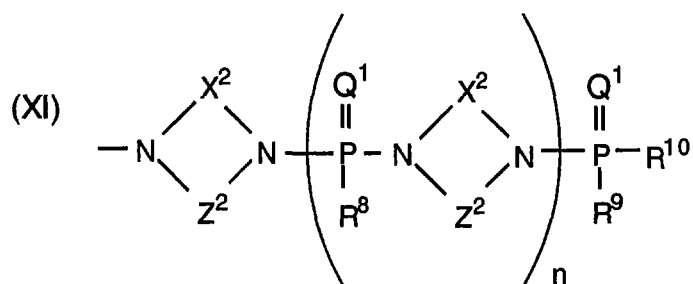
each of A²²⁻²⁴ is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

each Z¹ is an alkyl radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

each X¹ is an alkylidene radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

or

R¹ is of the formula XI:



wherein

each X² is alkylidene, aryl, or alkaryl;

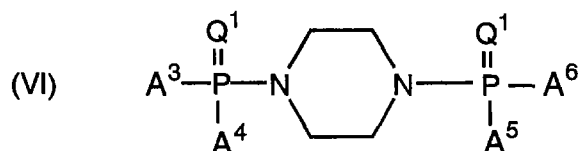
each Z² is alkylidene;

each of R⁸, R⁹, and R¹⁰ is independently an alkyloxy residue, an aryloxy residue, an aryloxy residue containing at least one alkyl substitution, or an amine residue;

n is from 0 to about 5; and

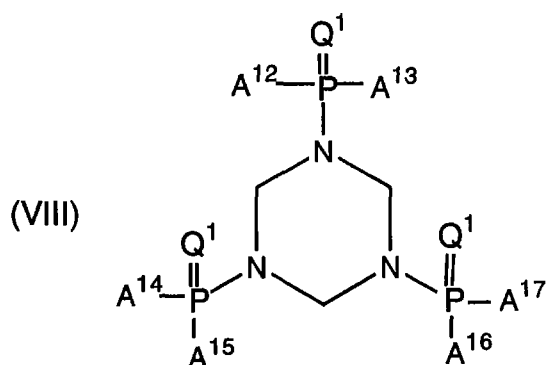
R² and R³ are each independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

(ii) a phosphoramidate of the formula VI:



wherein each Q¹ is independently oxygen or sulfur and each A moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethylphenoxy moiety;

(iii) a phosphoramidate of the formula VIII :

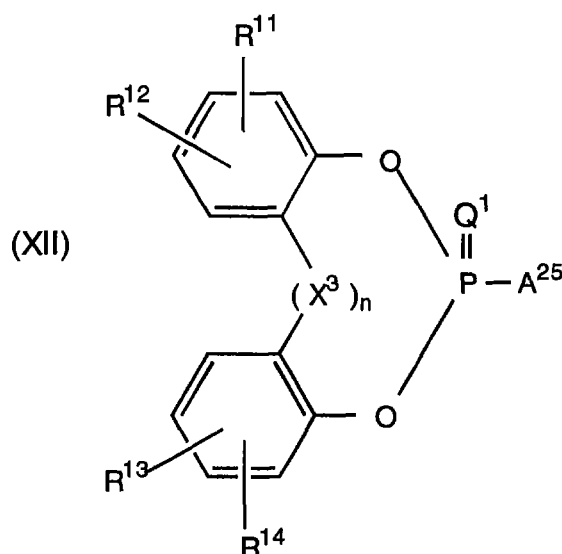


wherein

each Q1 is independently oxygen or sulfur and

each of A12-17 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution or an amine residue;

(iv) a phosphoramidate of the formula XII :



wherein Q1 is oxygen or sulfur;

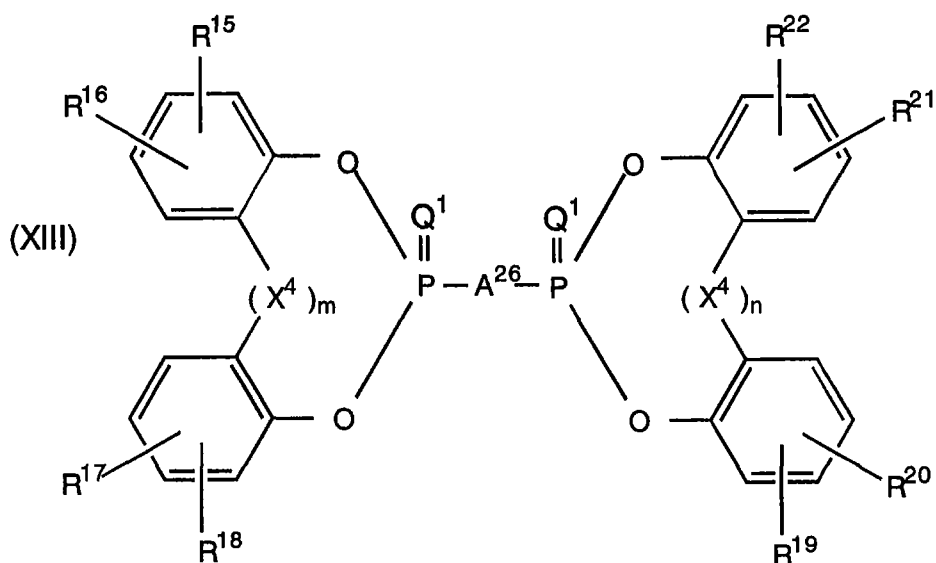
each of R11-14 is independently a hydrogen or an alkyl radical;

X3 is a alkylidene radical;

n is 0 or 1; and

A25 is a group derived from a primary or secondary amine having the same or different radicals that can be aliphatic, alicyclic, aromatic, or alkaryl, or A25 is a group derived from a heterocyclic amine, or A25 is a hydrazine compound; and

(v) a bis(cyclic) phosphoramidate of the formula XIII:

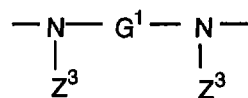


wherein each Q1 independently is oxygen or sulfur;

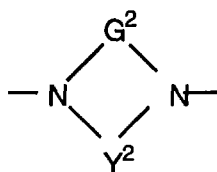
each of R15-22 is independently a hydrogen or an alkyl radical;

X4 is an alkylidene radical; m and n are each independently 0 or 1; and

A26 is



wherein G1 is sulfur, an alkylidene radical, aryl radical, or alkaryl radical; and each Z3 is independently an alkyl radical or an aryl radical; or wherein A26 is



wherein G2 is alkylidene, aryl, or alkaryl, and Y2 is alkylidene; and

c) at least one adjunct flame retardant compound.

31. An article made from the composition of claim 1.

32. The article of claim 31 which is a deflection yoke for cathode ray tube, deflection yoke for television, slit type deflection yoke, mold coil deflection yoke, television backplate, docking station, pedestal, bezel, pallet, switch, switch housing, plug, plug housing, electrical connector, connecting device, socket, television housing, computer housing, desk-top computer

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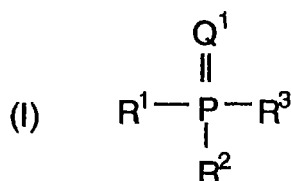
housing, portable computer housing, lap-top computer housing, palm-held computer housing; monitor housing, printer housing, keyboard, FAX machine housing, copier housing, telephone housing, mobile phone housing, radio sender housing, radio receiver housing, light fixture, battery charger housing, battery housing, automotive electrical component, antenna housing, transformer housing, modem, cartridge, network interface device housing, circuit breaker housing, meter housing, panel for wet or dry appliance, dishwasher panel, clothes washer panel, clothes dryer panel, refrigerator panel; heating or ventilation enclosure, fan, air conditioner housing, cladding or seating for public transportation; or cladding or seating for trains, subways, or buses.

33. A method to increase the heat distortion temperature of a flame resistant composition containing an amount of at least one phosphoramidate and at least one adjunct flame retardant effective to render the composition a flame rating of at least V-2 in the Underwriter's Laboratory UL-94 protocol when measured on a test specimen of about 0.125 inch by about 0.5 inch by about 5 inch dimensions, wherein the method comprises combining

a) a thermoplastic resin, and

b) at least one phosphoramidate having a glass transition point of at least 0°C selected from the group consisting of:

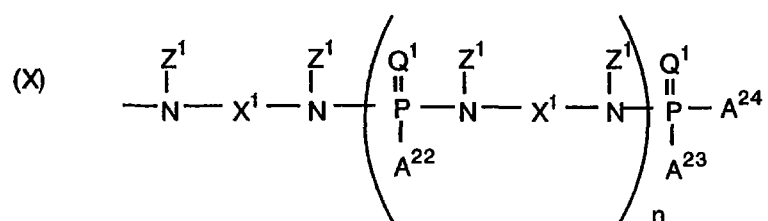
i) a phosphoramidate having the formula:



wherein:

Q1 is oxygen or sulfur;

R1 is of the formula X:



wherein

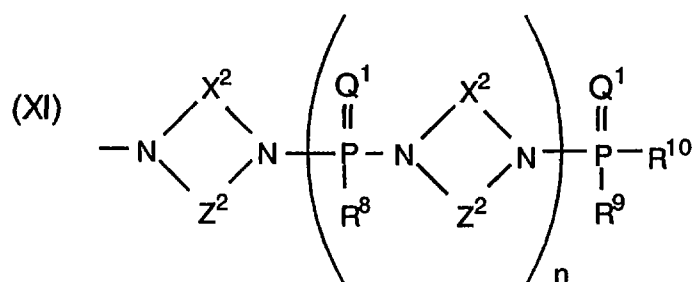
each of A²²⁻²⁴ is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

each Z¹ is an alkyl radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

each X¹ is an alkylidene radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

or

R¹ is of the formula XI:



wherein

each X2 is alkylidene, aryl, or alkaryl;

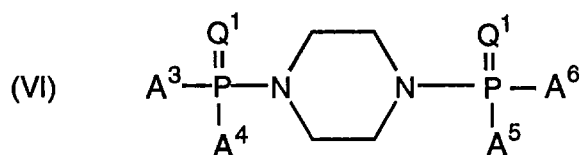
each Z2 is alkylidene;

each of R8, R9, and R10 is independently an alkyloxy residue, an aryloxy residue, an aryloxy residue containing at least one alkyl substitution, or an amine residue;

n is from 0 to about 5; and

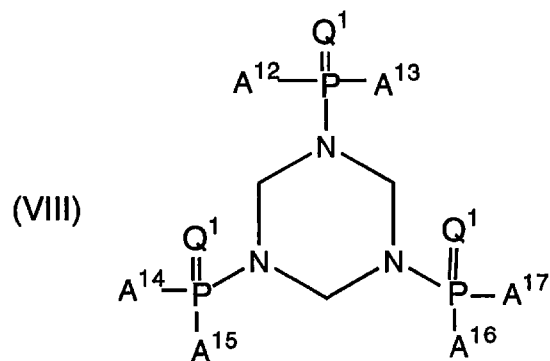
R2 and R3 are each independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

(ii) a phosphoramidate of the formula VI:



wherein each Q1 is independently oxygen or sulfur and each A moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethylphenoxy moiety;

(iii) a phosphoramidate of the formula VIII :

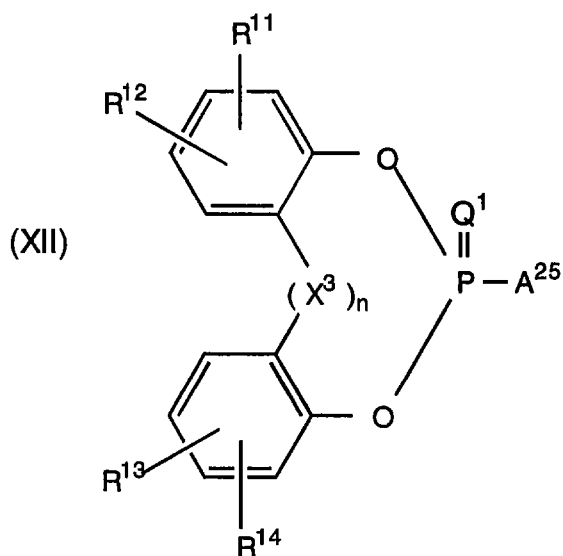


wherein

each Q1 is independently oxygen or sulfur and

each of A12-17 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution or an amine residue;

(iv) a phosphoramidate of the formula XII :



wherein Q1 is oxygen or sulfur;

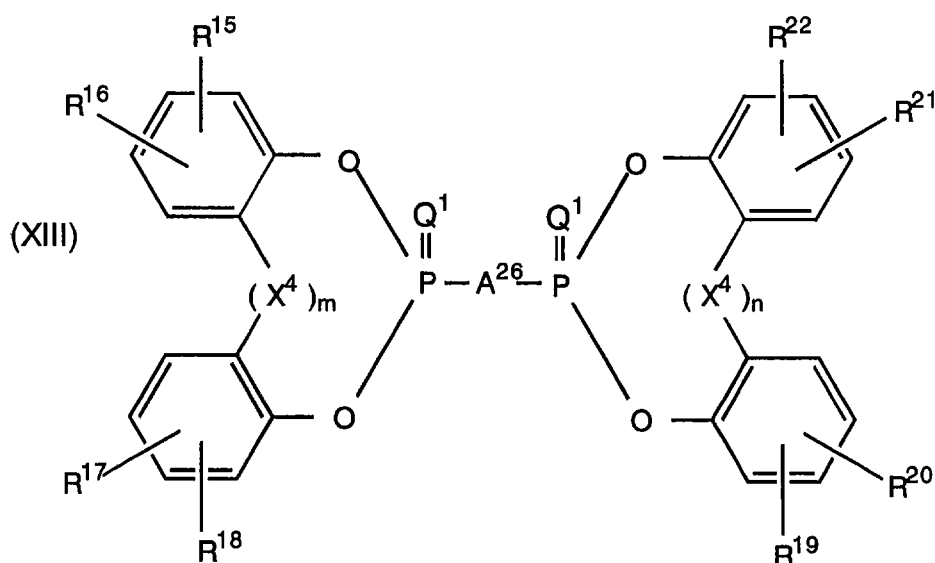
each of R11-14 is independently a hydrogen or an alkyl radical;

X3 is a alkylidene radical;

n is 0 or 1; and

A25 is a group derived from a primary or secondary amine having the same or different radicals that can be aliphatic, alicyclic, aromatic, or alkaryl, or A25 is a group derived from a heterocyclic amine, or A25 is a hydrazine compound; and

(v) a bis(cyclic) phosphoramidate of the formula XIII:

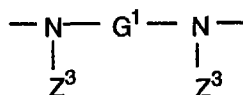


wherein each Q1 independently is oxygen or sulfur;

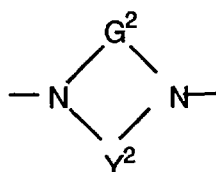
each of R15-22 is independently a hydrogen or an alkyl radical;

X4 is an alkylidene radical; m and n are each independently 0 or 1; and

A26 is



wherein G1 is sulfur, an alkylidene radical, aryl radical, or alkaryl radical; and each Z3 is independently an alkyl radical or an aryl radical; or wherein A26 is



wherein G2 is alkylidene, aryl, or alkaryl, and Y2 is alkylidene; and

c) at least one adjunct flame retardant compound.

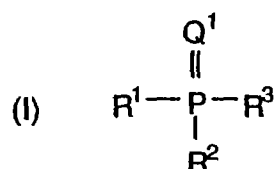
34. The method of claim 33 wherein at least one phosphoramidate has a glass transition point of at least about 10°C.

35. The method of claim 33 wherein the phosphoramidate has a glass transition point of at least about 10°C.

36. The method of claim 33 wherein at least one phosphoramidate has a glass transition point of at least about 20°C.

37 . The method of claim 33 wherein the phosphoramidate has a glass transition point of at least about 20°C.

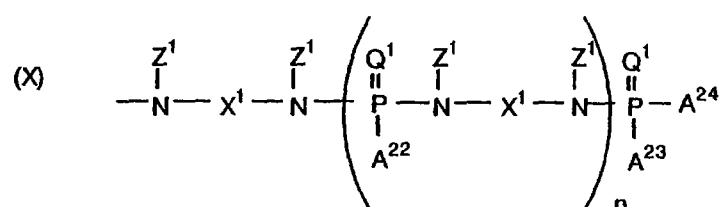
38 . The method of claim 33 wherein the at least one phosphoramidate comprises (i) a phosphoramidate having the formula



wherein:

Q1 is oxygen or sulfur;

R1 is of the formula X:



wherein

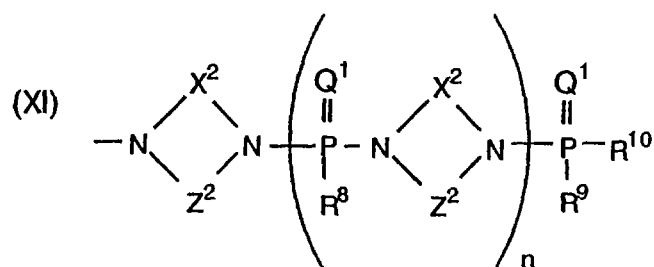
each of A22-24 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

each Z1 is an alkyl radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

each X1 is an alkylidene radical, aromatic radical, or aromatic radical containing at least one alkyl substitution;

or

R1 is of the formula XI:



wherein

each X2 is alkylidene, aryl, or alkaryl;

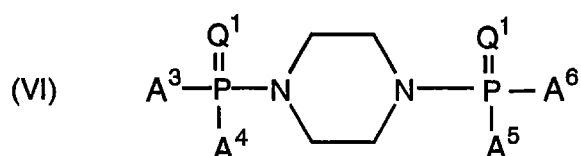
each Z2 is alkylidene;

each of R8, R9, and R10 is independently an alkyloxy residue, an aryloxy residue, an aryloxy residue containing at least one alkyl substitution, or an amine residue;

n is from 0 to about 5; and

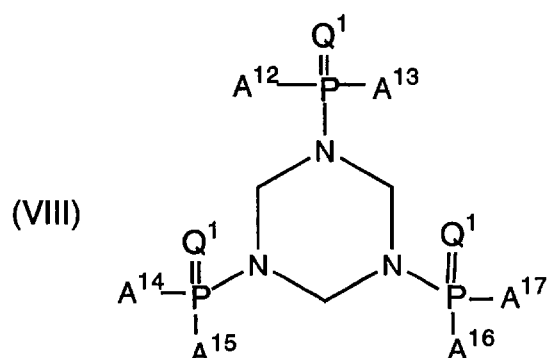
R2 and R3 are each independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution; or an amine residue;

(ii) a phosphoramidate of the formula VI:



wherein each Q1 is independently oxygen or sulfur and each A moiety is a 2,6-dimethylphenoxy moiety or a 2,4,6-trimethylphenoxy moiety;

(iii) a phosphoramidate of the formula VIII :

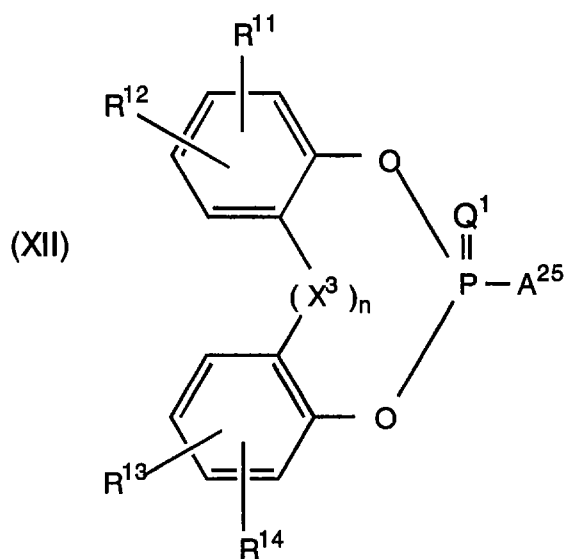


wherein

each Q1 is independently oxygen or sulfur and

each of A12-17 is independently an alkyloxy, alkylthio, aryloxy, or arylthio residue, or an aryloxy or arylthio residue containing at least one alkyl substitution or an amine residue;

(iv) a phosphoramidate of the formula XII :



wherein Q1 is oxygen or sulfur;

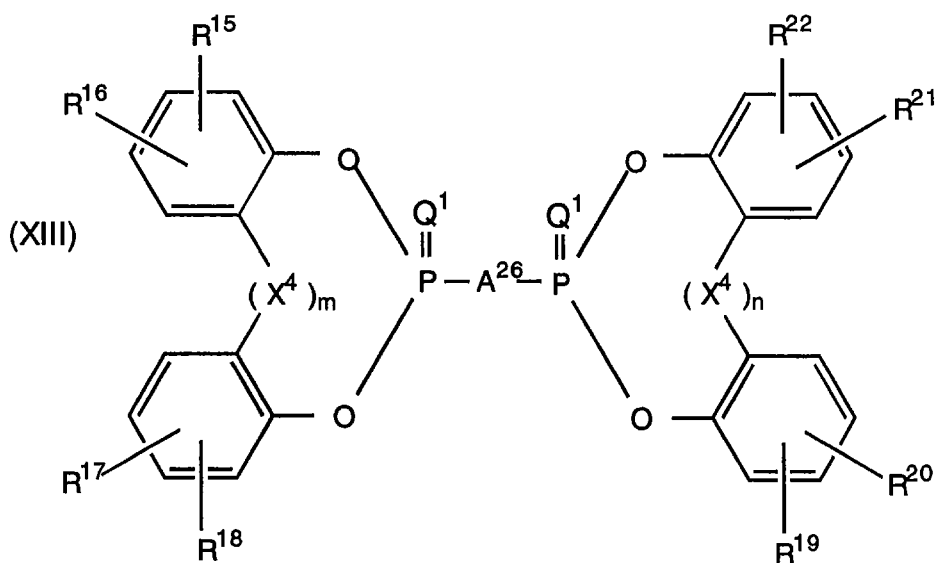
each of R11-14 is independently a hydrogen or an alkyl radical;

X3 is a alkylidene radical;

n is 0 or 1; and

A25 is a group derived from a primary or secondary amine having the same or different radicals that can be aliphatic, alicyclic, aromatic, or alkaryl, or A25 is a group derived from a heterocyclic amine, or A25 is a hydrazine compound; and

(v) a bis(cyclic) phosphoramidate of the formula XIII:

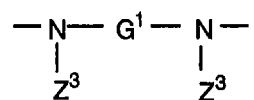


wherein each Q1 independently is oxygen or sulfur;

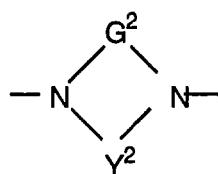
each of R15-22 is independently a hydrogen or an alkyl radical;

X4 is an alkylidene radical; m and n are each independently 0 or 1; and

A26 is



wherein G1 is sulfur, an alkylidene radical, aryl radical, or alkaryl radical; and each Z3 is independently an alkyl radical or an aryl radical; or wherein A26 is



wherein G2 is alkylidene, aryl, or alkaryl, and Y2 is alkylidene; and

c) at least one adjunct flame retardant compound.

39. The method of claim 33 wherein the thermoplastic resin is selected from the group consisting of (i) polycarbonate resins and blends containing at least one polycarbonate resin, (ii) polyphenylene ether resins and blends containing at least one polyphenylene ether resin, (iii) polystyrene resin and blends containing polystyrene resin, (iv) styrene-containing copolymer resin and blends containing styrene-containing copolymer resin; (v) styrene-containing graft copolymer resin and blends containing styrene-containing graft copolymer resin; and (vi) high impact polystyrene resin and blends containing high impact polystyrene resin.

40. The method of claim 33 wherein the thermoplastic resin is a polycarbonate resin or a blend containing at least one polycarbonate resin.

41. The method of claim 33 wherein the thermoplastic resin comprises at least one polycarbonate and ABS.

42. The method of claim 41 wherein the at least one polycarbonate comprises bisphenol A polycarbonate and a copolycarbonate of bisphenol A and 4,4'-(3,3,5-trimethylcyclo-hexylidene)diphenol.

43 . The method of claim 33 wherein the adjunct flame retardant comprises at least one polymeric or non-polymeric member selected from the group consisting of phosphate esters, thiophosphate esters, phosphonate esters, thiophosphonate esters, phosphinate esters, thiophosphinate esters, phosphines, phosphine oxides, thiophosphine oxides, phosphonium salts; phosphate salts, thiophosphate salts, phosphonate salts, thiophosphonate salts, phosphinate salts, thiophosphinate salts, pyrophosphate salts, metaphosphate salts; sulfonate salts, sulfinatate salts, sulfones, sulfoxides, sulfides; borates; antimony salts; siloxanes; and organoclays.

44 . The method of claim 33 wherein the adjunct flame retardant comprises at least one polymeric or non-polymeric member selected from the group consisting of phosphate esters, phosphate salts, sulfonate salts, sulfides, sulfones, borates, antimony salts; siloxanes; and organoclays.

45 . The method of claim 33 wherein the adjunct flame retardant comprises at least one member selected from the group consisting of resorcinol bis(diphenylphosphate), bisphenol A bis(diphenylphosphate), triphenylphosphate, tricresylphosphate, boron phosphate, potassium diphenylsulfone-3-sulfonate, potassium perfluorobutane sulfonate, polyphenylene sulfide, polyphenylsulfone, zinc borate, antimony oxide; polysiloxanes; and organoclays.

46 . The method of claim 33 in which the composition is essentially free of chlorine and bromine.

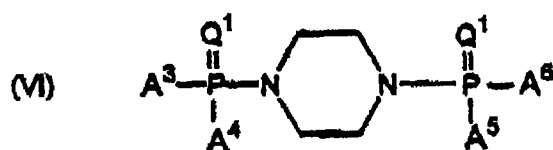
47 . The flame resistant composition of claim 46.

48 . The flame resistant composition of claim 33.

49. A resin composition comprising the following and any reaction products thereof:

(a) at least one thermoplastic resin selected from the group consisting of (i) polycarbonate resins and blends containing at least one polycarbonate resin, (ii) polyphenylene ether resins and blends containing at least one polyphenylene ether resin, (iii) polystyrene resin and blends containing polystyrene resin, (iv) styrene-containing copolymer resin and blends containing styrene-containing copolymer resin; (v) styrene-containing graft copolymer resin and blends containing styrene-containing graft copolymer resin.; and (vi) high impact polystyrene resin and blends containing high impact polystyrene resin, and

(b) a phosphoramidate having a glass transition point of at least about 20°C of the formula VI:



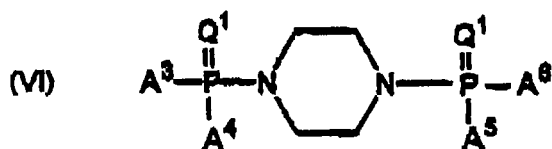
wherein each Q¹ is oxygen; and each A moiety is a 2,6-dimethylphenoxy moiety, and

(c) at least one polymeric or non-polymeric adjunct flame retardant compound selected from the group consisting of phosphate esters, phosphate salts, phosphonate esters, phosphonate salts, phosphinate esters, phosphinate salts, phosphines, phosphonium salts; phosphine oxides, pyrophosphate salts, metaphosphate salts, sulfonate salts, sulfinates, sulfones, sulfoxides, sulfides; borates; resorcinol bis(diphenylphosphate), bisphenol A bis(diphenylphosphate), triphenylphosphate, tricresylphosphate, boron phosphate, potassium diphenylsulfone-3-sulfonate, potassium perfluorobutane sulfonate, polyphenylene sulfide, polyphenylsulfone, and zinc borate.

50. A method to increase the heat distortion temperature of a flame resistant composition containing an amount of at least one phosphoramidate and at least one adjunct flame retardant effective to render the composition a flame rating of at least V-2 in the Underwriter's Laboratory UL-94 protocol when measured on a test specimen of about 0.125 inch by about 0.5 inch by about 5 inch dimensions, wherein the method comprises combining

(a) at least one thermoplastic resin selected from the group consisting of i) polycarbonate resins and blends containing at least one polycarbonate resin, (ii) polyphenylene ether resins and blends containing at least one polyphenylene ether resin, (iii) polystyrene resin and blends containing polystyrene resin, (iv) styrene-containing copolymer resin and blends containing styrene-containing copolymer resin; (v) styrene-containing graft copolymer resin and blends containing styrene-containing graft copolymer resin; and (vi) high impact polystyrene resin and blends containing high impact polystyrene resin, and

(b) a phosphoramidate having a glass transition point of at least about 20°C of the formula VI:



wherein each Q¹ is oxygen; and each A moiety is a 2,6-dimethylphenoxy moiety, and

(c) at least one polymeric or non-polymeric adjunct flame retardant compound selected from the group consisting of phosphate esters, phosphate salts, phosphonate esters, phosphonate salts, phosphinate esters, phosphinate salts, phosphines, phosphonium salts; phosphine oxides, pyrophosphate salts, metaphosphate salts; sulfonate salts, sulfinates, sulfones, sulfoxides, sulfides; borates; resorcinol bis(diphenylphosphate) bisphenol A bis(diphenylphosphate), triphenylphosphate, tricresylphosphate, boron phosphate, potassium diphenylsulfone-3sulfonate, potassium perfluorobutane sulfonate, polyphenylene sulfide, polyphenylsulfone, and zinc borate.