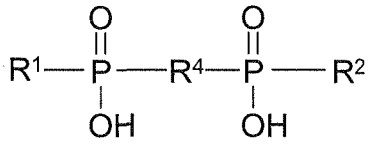
It is an object of the present invention to modify polymers for prepregs, printed circuit boards and laminates such that they are subject only to very low thermal expansion – if any at all – and dimensional stability is fulfilled.

In one aspect, there is provided a mixture of at least one diphosphinic acid of the formula (I)

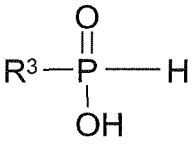


(I)

in which

R^4 is ethylene or butylene

with at least one alkylphosphinic acid of the formula (II)

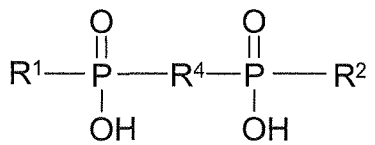


(II)

in which

R^1, R^2 and R^3 are the same or different, and are each ethyl, n-propyl, isopropyl, n-butyl, isobutyl and/or tert-butyl, and R^4 is ethylene or butylene; comprising 90 to 99.9% by weight of diphosphinic acid of the formula (I) and 10 to 0.1% by weight of alkylphosphinic acid of the formula (II).

In one ~~aspect~~embodiment, there is also provided mixtures of at least one diphosphinic acid of the formula (I)

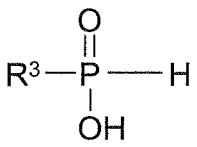


(I)

in which

R^4 is C_1-C_{18}-alkylene, C_2-C_{18}-alkenylene, C_6-C_{18}-arylene, C_7-C_{18}-alkylarylene

with at least one alkylphosphinic acid of the formula (II)



(II)

in which

R^1, R^2 and R^3 are the same or different, and are each ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, n-hexyl, isohexyl and/or phenyl, and R^4 is ethylene, butylene, hexylene or octylene.

In some embodiments, R^1, R^2 and R^3 are the same or different and are each methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, n-hexyl, isohexyl and/or phenyl, where R^1 and R^2 may also be H, and R^4 is ethylene, butylene, hexylene or octylene.

More preferably, R^1, R^2 and R^3 are the same or different and are each ethyl or butyl.

allantoin, glycoluril, cyanurates, cyanurate-epoxide compounds, urea cyanurate, dicyanamide, guanidine, guanidine phosphate and/or sulfate.

The mixtures preferably comprise 99 to 1% by weight of the mixture of diphosphinic acids of the formula (I) and alkylphosphinic acid of the formula (II) as claimed in at least one of claims 1 to 12 and 1 to 99% by weight of synergist.

Another aspect relates to a process for preparing the mixtures as disclosed herein, wherein a phosphinic acid source is reacted with an alkyne in a solvent, in the presence of an initiator to give a mixture of diphosphinic acids of the formula (I) and alkylphosphinic acid of the formula (II).

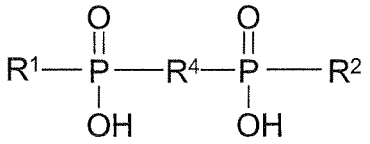
Preferably, the phosphinic acid source is ethylphosphinic acid and the alkyne is acetylene, methylacetylene, 1-butyne, 1-hexyne, 2-hexyne, 1-octyne, 4-octyne, 1-butyn-4-ol, 2-butyn-1-ol, 3-butyn-1-ol, 5-hexyn-1-ol, 1-octyn-3-ol, 1-pentyne, phenylacetylene, trimethylsilylacetylene and/or diphenylacetylene.

The initiator is preferably a free-radical initiator having a nitrogen-nitrogen or an oxygen-oxygen bond.

The free-radical initiator is preferably 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride, azobis(isobutyronitrile), 4,4'-azobis(4-cyanopentanoic acid) and/or 2,2'-azobis(2-methylbutyronitrile) or hydrogen peroxide, ammonium peroxodisulfate, potassium peroxodisulfate, dibenzoyl peroxide, di-tert-butyl peroxide, peracetic acid, diisobutyryl peroxide, cumene peroxyneodecanoate, tert-butyl peroxyneodecanoate, tert-butyl peroxypivalate, tert-amyl peroxypivalate, dipropyl peroxydicarbonate, dibutyl peroxydicarbonate, dimyristyl peroxydicarbonate, dilauroyl peroxide, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexylcarbonate, tert-butyl peroxyisobutyrate, 1,1-di(tert-butylperoxy)cyclohexane, tert-butyl peroxybenzoate, tert-butyl peroxyacetate, tert-butyl peroxydiethylacetate, tert-butyl peroxyisopropylcarbonate, 2,2-di(tert-

Claims

1. A mixture of at least one diphosphinic acid of the formula (I)

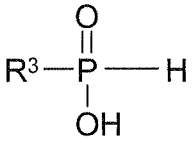


(I)

in which

R^4 is ~~C_1-C_{18}-alkylene, C_2-C_{18}-alkenylene, C_6-C_{18}-arylene, C_7-C_{18}-alkylarylene~~ethylene or butylene

with at least one alkylphosphinic acid of the formula (II)



(II)

in which

R^1, R^2 and R^3 are the same or different, and are each ethyl, n-propyl, isopropyl, n-butyl, isobutyl~~,~~ and/or tert-butyl~~, n-pentyl, isopentyl, n-hexyl, isohexyl and/or phenyl~~, and R^4 is ethylene~~,~~ or butylene~~, hexylene or octylene;~~.

~~2. The mixture as claimed in claim 1, which comprises 0.1 to 99.9% by weight of diphosphinic acid of the formula (I) and 99.9 to 0.1% by weight of alkylphosphinic acid of the formula (II).~~

~~3. The mixture as claimed in claims 1 or 2, which comprises 40 to 99.9% by weight of diphosphinic acid of the formula (I) and 60 to 0.1% by weight of alkylphosphinic acid of the formula (II).~~

~~4. The mixture as claimed in one or more of claims 1 to 3, which comprises 60 to 99.9% by weight of diphosphinic acid of the formula (I) and 40 to 0.1% by weight of alkylphosphinic acid of the formula (II).~~

~~5. The mixture as claimed in one or more of claims 1 to 4, which comprises 80 to 99.9% by weight of diphosphinic acid of the formula (I) and 20 to 0.1% by weight of alkylphosphinic acid of the formula (II).~~

~~6. The mixture as claimed in one or more of claims 1 to 5, which comprises~~ comprising 90 to 99.9% by weight of diphosphinic acid of the formula (I) and 10 to 0.1% by weight of alkylphosphinic acid of the formula (II).

~~7~~2. The mixture as claimed in ~~one or more of~~ claim~~s~~ 1 ~~to 6~~, which comprises 95 to 99.9% by weight of diphosphinic acid of the formula (I) and 5 to 0.1% by weight of alkylphosphinic acid of the formula (II).

~~8~~3. The mixture as claimed in one or more of claims 1 ~~to 7~~or 2, which comprises 98 to 99.9% by weight of diphosphinic acid of the formula (I) and 2 to 0.1% by weight of alkylphosphinic acid of the formula (II).

~~9~~4. The mixture as claimed in one or more of claims 1 to ~~8~~3, wherein the diphosphinic acid is ethylene-1,2-bis(ethylphosphinic acid), ethylene-1,2-bis(propylphosphinic acid), ethylene-1,2-bis(butylphosphinic acid), ~~ethylene-1,2-bis(pentylphosphinic acid), ethylene-1,2-bis(hexylphosphinic acid),~~ butane-1,2-bis(ethylphosphinic acid), butylene-1,2-bis(propylphosphinic acid)~~,~~ or butylene-1,2-bis(butylphosphinic acid), ~~butylene-1,2-bis(pentylphosphinic acid), butylene-1,2-bis(hexylphosphinic acid), hexylene-1,2-bis(ethylphosphinic acid), hexylene-1,2-bis(propylphosphinic acid), hexylene-1,2-bis(butylphosphinic acid), hexylene-1,2-bis(pentylphosphinic acid) or hexylene-1,2-bis(hexylphosphinic acid),~~ and the

alkylphosphinic acid is ethylphosphinic acid, propylphosphinic acid~~,~~ or butylphosphinic acid~~, pentylphosphinic acid or hexylphosphinic acid~~.

~~105~~. A mixture of ethylene-1,2-bis(ethylphosphinic acid) and ethylphosphinic acid, comprising 98 to 99.9% by weight of ethylene-1,2-bis(ethylphosphinic acid) and 0.1 to 2% by weight of ethylphosphinic acid.

~~116~~. The mixture as claimed in one or more of claims 1 to ~~105~~, which further comprises at least one synergist, the latter being melem, melam, melon, melamine borate, melamine cyanurate, melamine phosphate, dimelamine phosphate, pentamelamine triphosphate, trimelamine diphosphate, tetrakismelamine triphosphate, hexakismelamine pentaphosphate, melamine diphosphate, melamine tetraphosphate, melamine pyrophosphate, melamine polyphosphate, melam polyphosphate, melem polyphosphate and/or melon polyphosphate; aluminum compounds, magnesium compounds, tin compounds, antimony compounds, zinc compounds, silicon compounds, phosphorus compounds, carbodiimides, phosphazenes, piperazines, piperazine (pyro)phosphates, (poly)isocyanates and/or styrene-acrylic polymers; aluminum hydroxide, halloysites, sapphire products, boehmite, nanoboehmite; magnesium hydroxide; antimony oxides; tin oxides; zinc oxide, zinc hydroxide, zinc oxide hydrate, zinc carbonate, zinc stannate, zinc hydroxystannate, zinc silicate, zinc phosphate, zinc borophosphate, zinc borate and/or zinc molybdate; phosphinic acids and salts thereof, phosphonic acids and salts thereof and/or phosphine oxides; carbonylbiscaprolactam; nitrogen compounds from the group of oligomeric esters of tris(hydroxyethyl) isocyanurate with aromatic polycarboxylic acids, or benzoguanamine, acetoguanamine, tris(hydroxyethyl) isocyanurate, allantoin, glycoluril, cyanurates, cyanurate-epoxide compounds, urea cyanurate, dicyanamide, guanidine, guanidine phosphate and/or sulfate.

~~127~~. The mixture as claimed in one or more of claims 1 to ~~116~~, which comprises 99 to 1% by weight of the mixture of diphosphinic acid of the formula (I) and

alkylphosphinic acid of the formula (II) as claimed in at least one of claims 1 to ~~11~~ 6 and 1 to 99% by weight of synergist.

~~13~~8. A process for preparing the mixtures as claimed in at least one of claims 1 to ~~10~~5, wherein a phosphinic acid source is reacted with an alkyne in a solvent, in the presence of an initiator.

~~14~~9. The process as claimed in claim ~~13~~8, wherein the phosphinic acid source is ethylphosphinic acid and the alkyne is acetylene or~~, methylacetylene,~~ 1-butyne~~, 1-hexyne, 2-hexyne, 1-octyne, 4-octyne, 1-butyn-4-ol, 2-butyn-1-ol, 3-butyn-1-ol, 5-hexyn-1-ol, 1-octyn-3-ol, 1-pentyne, phenylacetylene, trimethylsilylacetylene and/or diphenylacetylene~~.

~~15~~10. The process as claimed in claim ~~13~~8 or ~~14~~9, wherein the initiator is a free-radical initiator having a nitrogen-nitrogen or an oxygen-oxygen bond.

~~16~~11. The process as claimed in claim ~~15~~10, wherein the free-radical initiator is 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride, azobis(isobutyronitrile), 4,4'-azobis(4-cyanopentanoic acid) and/or 2,2'-azobis(2-methylbutyronitrile) or hydrogen peroxide, ammonium peroxodisulfate, potassium peroxodisulfate, dibenzoyl peroxide, di-tert-butyl peroxide, peracetic acid, diisobutyryl peroxide, cumene peroxyneodecanoate, tert-butyl peroxyneodecanoate, tert-butyl peroxypivalate, tert-amyl peroxypivalate, dipropyl peroxydicarbonate, dibutyl peroxydicarbonate, dimyristyl peroxydicarbonate, dilauroyl peroxide, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexylcarbonate, tert-butyl peroxyisobutyrate, 1,1-di(tert-butylperoxy)cyclohexane, tert-butyl peroxybenzoate, tert-butyl peroxyacetate, tert-butyl peroxydiethylacetate, tert-butyl peroxyisopropylcarbonate, 2,2-di(tert-butylperoxy)butane, tert-amyl hydroperoxide and/or 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane.

17~~12~~. The process as claimed in one or more of claims ~~13~~ 8 to ~~16~~11, wherein the solvent comprises straight-chain or branched alkanes, alkyl-substituted aromatic solvents, water-immiscible or only partly water-miscible alcohols or ethers, water and/or acetic acid.

18~~13~~. The process as claimed in claim ~~17~~12, wherein the alcohol is methanol, propanol, i-butanol and/or n-butanol or comprises mixtures of these alcohols with water.

19~~14~~. The process as claimed in one or more of claims ~~13~~ 8 to ~~18~~13, wherein the reaction temperature is 50 to 150°C.

20~~15~~. The use of mixtures as claimed in at least one of claims 1 to ~~10~~ 5 as an intermediate for further syntheses, as a binder, as a crosslinker and/or accelerator in the curing of epoxy resins, polyurethanes and unsaturated polyester resins, as polymer stabilizers, as crop protection compositions, as sequestrants, as a mineral oil additive, as an anticorrosive, in washing and cleaning composition applications and in electronics applications.

24~~16~~. The use of mixtures as claimed in at least one of claims 1 to ~~12~~ 7 as a flame retardant, especially as a flame retardant for clearcoats and intumescent coatings, as a flame retardant for wood and other cellulosic products, as a reactive and/or nonreactive flame retardant for polymers, for production of flame-retardant polymer molding compositions, for production of flame-retardant polymer moldings and/or for rendering polyester and pure and blended cellulose fabrics flame-retardant by impregnation, and as a synergist.

22~~17~~. A flame-retardant thermoplastic or thermoset polymer molding composition or polymer molding, film, filament or fiber comprising 0.5 to 45% by weight of mixtures as claimed in at least one of claims 1 to ~~12~~7, 55 to 99.5% by weight of thermoplastic or thermoset polymer or mixtures thereof, 0 to 55% by weight of

additives and 0 to 55% by weight of filler or reinforcing materials, where the sum of the components is 100% by weight.

2318. A flame-retardant thermoplastic or thermoset polymer molding composition or polymer molding, film, filament or fiber comprising 1 to 30% by weight of mixtures as claimed in at least one of claims 1 to 127, 10 to 95% by weight of thermoplastic or thermoset polymer or mixtures thereof, 2 to 30% by weight of additives and 2 to 30% by weight of filler or reinforcing materials, where the sum of the components is 100% by weight.