

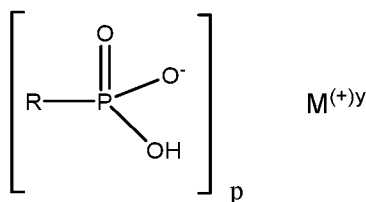
METHOD OF PREPARING PHOSPHORUS-CONTAINING FLAME RETARDANTS AND THEIR USE IN POLYMER COMPOSITIONS

This application claims priority benefit to U.S. Provisional Application No. 62/782,948, filed December 20, 2018, and U.S. Provisional Application No. 62/923,446, filed October 18, 2019, both of which are incorporated herein by reference in their entirety.

A highly effective, thermally stable, phosphorus-containing flame retardant is produced by a process comprising reacting a metal or suitable metal compound with a stoichiometric excess of a phosphonic or pyrophosphonic acid. The chemical composition of the resulting flame retardant, in many embodiments produced as one or predominantly one compound, leads to excellent flame retardancy and exhibits high thermal stability. The presently disclosed flame retardants are useful, for example, in polymer compositions, particularly thermoplastics processed at high temperatures, over a wide range of applications.

BACKGROUND

Phosphonic acid salts, i.e., compounds of the formula directly below, are known flame retardants in many polymer compositions:



wherein R is an optionally substituted alkyl, aryl, alkylaryl or arylalkyl group, p is typically a number of from 1 to 4, M is a metal, and y is typically a number of from 1 to 4, so that $\text{M}^{(+)}y$ is a metal cation where (+)y represents the charge formally assigned to the cation.

As disclosed in US 2007/0029532, decomposition of phosphonic acid salts is known at temperatures encountered during processing of polyesters and polyamides, damaging the polymers in the process, e.g., temperatures above 260 or 270 °C.

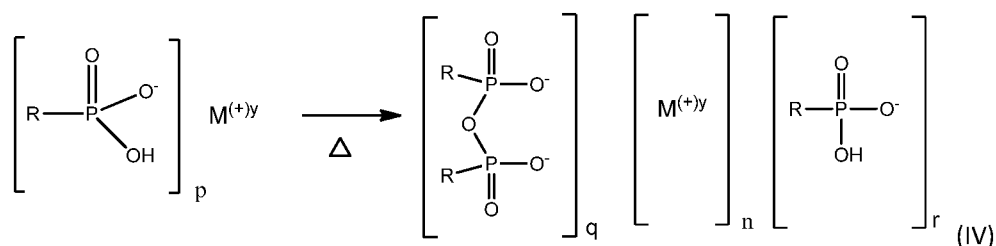
US Pat 5,053,148 discloses that brittle, heat resistant foams can be obtained by heating phosphonic acid salts at elevated temperatures.

In Comparative Examples 1 and 2 of US Pat. 9,745,449, glass filled polyamide compositions comprising 10 to 25 wt% of methylphosphonic acid aluminum salt were processed at elevated temperatures. A decrease in torque was observed during compounding, consistent with polymer degradation, producing a final product material that was friable upon cooling,

dusty after grinding, and which could not be molded. Analysis of the compounded material by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) provided additional evidence of degradation. The loss of desired polymer properties observed is consistent with the degradation of polymers suggested in US 2007/0029532 and the brittle foam formed in US Pat 5,053,148.

Thus, simple phosphonic acid salts are not suitable for use in many polymers that are processed at, or subsequently exposed to, high temperatures, such as 250 °C, 260 °C, 270 °C or higher, as they undergo chemical transformation at such temperatures via processes that harm the polymer. This may happen during compounding, e.g., in an extruder, or while the salt is present in a polymer in a high temperature application.

On the other hand, US Pat. 9,745,449 discloses that heating a phosphonic acid salt at high enough temperatures generally in the absence of other materials thermally transforms the salt into a different, more thermally stable material exhibiting excellent flame retardant activity when incorporated into polymeric substrates. The thermally transformed materials do not degrade at high temperatures, nor do they cause degradation of a polymer, when processed in polymer compositions at elevated temperatures, e.g., 240°C, 250°C, 260°C, 270°C or higher, which is an important advantage over previously known phosphonate salts, which exhibit flame retardant activity but often degrade the polymer during processing. The thermally transformed materials are described as comprising one or more compounds represented by empirical formula (IV):



wherein R is alkyl or aryl, M is a metal, q is a number of from 1 to 7, e.g., 1, 2 or 3, r is a number from 0 to 5, e.g., 0, 1 or 2, y is a number of from 1 to 7, e.g., from 1 to 4, and n is 1 or 2, provided that $2(q+r) = n(y)$.

Challenges, however, are encountered with the process and materials of US Pat. 9,745,449, such as the production of product generally in the form of a solid mass requiring grinding, milling, or other such physical processing before use; formation of product mixtures containing water soluble or thermally unstable compounds; and difficulty in controlling the phosphorus to metal ratio of the resulting product. In addition, the Examples of US Pat.

9,745,449 describe producing a phosphorus-containing flame retardant in several steps wherein an intermediate metal salt of a phosphonic acid is produced and the dried salt is then heated at temperatures over 200 °C.

- 5 The present disclosure addresses the above-identified challenges, while also producing a phosphorus-containing flame retardant without requiring the production or use of the intermediate salt as described in US Pat. 9,745,449.

SUMMARY

- 10 In accordance with the present disclosure, a phosphorus-containing flame retardant is produced by a process comprising reacting at a reaction temperature a mixture comprising a metal or suitable metal compound and a stoichiometric excess relative to the metal or suitable metal compound of an unsubstituted or alkyl or aryl substituted phosphonic acid, wherein:

- 15 the metal is capable of forming a polycation (i.e., a metal represented in its corresponding cationic form by the formula $M^{(+y)}$ where M is a metal, (+)y represents the charge of the metal cation, and y is 2 or higher), or the suitable metal compound is represented by the formula $M_p^{(+y)}X_q$ where M is a metal, (+)y represents the charge of the metal cation, y is 2 or higher, X is an anion, and the values for p and q provide a charge
20 balanced metal compound;

the molar ratio of the unsubstituted or alkyl or aryl substituted phosphonic acid to the metal or suitable metal compound in the mixture is higher than 4:1;

the reaction temperature is 105 °C or higher; and

- the unsubstituted or alkyl or aryl substituted phosphonic acid is in a molten state at
25 the reaction temperature.

Also disclosed is a process of producing a phosphorus-containing flame retardant, comprising reacting at a reaction temperature a mixture comprising a metal or suitable metal compound and a stoichiometric excess of an unsubstituted or alkyl or aryl substituted
30 pyrophosphonic acid, wherein:

- the metal is capable of forming a polycation (i.e., a metal represented in its corresponding cationic form by the formula $M^{(+y)}$ as above), or the suitable metal compound is represented by the formula $M_p^{(+y)}X_q$ where M is a metal, (+)y represents the charge of the metal cation, y is 2 or higher, X is an anion, and the values for p and q provide a charge
35 balanced metal compound;

the molar ratio of the unsubstituted or alkyl or aryl substituted pyrophosphonic acid to the metal or suitable metal compound in the mixture is higher than 2:1; and

the unsubstituted or alkyl or aryl substituted pyrophosphonic acid is in a molten state at the reaction temperature.

In the process of the present disclosure, the unsubstituted or alkyl or aryl substituted phosphonic or pyrophosphonic acid, used at a stoichiometric excess as described herein, acts as a reagent and solvent for the reaction. Often, the reaction product forms as a slurry as the resulting flame retardant product of the present invention precipitates from the reaction mixture. Excess phosphonic or pyrophosphonic acid remaining after the reaction can be removed along with any possible byproducts by filtration and/or washing, e.g., with water. In many embodiments, a substantially pure flame retardant material is produced, e.g., a flame retardant comprising essentially a single compound with flame retardant activity or essentially a mixture of active compounds. Conversion based on the metal or metal compound is typically high, and the product can be readily isolated and optionally further purified if desired.

The present process overcomes difficulties observed in processes such as found in US Pat. 9,745,449, because, e.g., production of water soluble or thermally unstable compounds are reduced or avoided, and the flame retardant product, which typically crystallizes as a powder or small particles, can be produced directly in a readily processable form, i.e., without requiring or necessitating grinding, granulating, or other such physical processing. Further, in many embodiments, the resulting flame retardant material produced according to the present disclosure has a higher phosphorus to metal ratio than seen with simple metal phosphonates, as further explained herein. High phosphorus to metal ratios in the produced flame retardant leads to greater efficiency and can therefore permit lower loading levels when the flame retardant material is compounded into thermoplastics.

Additional embodiments of the present disclosure include, but are not limited to, a process for preparing a phosphorus-containing flame retardant, comprising reacting at a reaction temperature a metal or suitable metal compound with a molar excess of an unsubstituted or alkyl or aryl substituted phosphonic acid, wherein the reaction temperature is about 150 °C or higher, the unsubstituted or alkyl or aryl substituted phosphonic acid is in a molten state at the reaction temperature, and the molar ratio of the unsubstituted or alkyl or aryl substituted phosphonic acid to the metal or suitable metal compound is higher than 4:1. In an embodiment, the reaction temperature ranges from about 150 °C to about 300 °C, such as

from about 150°C to about 280°C, from about 160°C to about 260°C, or from about 160°C to about 220°C. In an embodiment, the molar ratio of the unsubstituted or alkyl or aryl substituted phosphonic acid to the metal or suitable metal compound ranges from about 5:1 to about 30:1. In an embodiment, the suitable metal compound is a metal oxide, halide, alkoxide, hydroxide, carboxylate, or phosphonate. In an embodiment, the suitable metal compound is alumina, aluminum trichloride, aluminum trihydroxide, or aluminum isopropoxide.

Other embodiments include, but are not limited to, a phosphorus-containing flame retardant produced according to a process disclosed herein; a flame retardant polymer composition comprising (i) a polymer and (ii) a phosphorus-containing flame retardant of the present disclosure; a process for improving the flame retardancy of a polymer by incorporating therein a flame retardant of the present disclosure; and a process for incorporating into a polymer a flame retardant composition comprising a flame retardant of the present disclosure.

The preceding summary is not intended to restrict in any way the scope of the claimed invention. In addition, it is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 shows the result of thermogravimetric analysis (TGA) of an exemplary flame retardant material produced according to Example 1 of the present disclosure.

DETAILED DESCRIPTION

Unless otherwise specified, the word “a” or “an” in this application means “one or more than one”.

The term “alkyl” in this application includes “arylalkyl,” unless the context dictates otherwise.

The term “aryl” in this application includes “alkylaryl,” unless the context dictates otherwise.

The term “phosphonic acid” as used herein refers to unsubstituted or alkyl or aryl substituted phosphonic acid, unless the context dictates otherwise.

The term "pyrophosphonic acid" as used herein refers to unsubstituted or alkyl or aryl substituted pyrophosphonic acid, unless the context dictates otherwise.

5 As used herein, "stoichiometric excess" of the unsubstituted or alkyl or aryl substituted phosphonic or pyrophosphonic acid relative to the metal or suitable metal compound refers to an amount of the phosphonic or pyrophosphonic acid which exceeds that stoichiometrically required for the reaction between the metal or suitable metal compound and the phosphonic or pyrophosphonic acid. The stoichiometric excess is typically
10 represented by a molar ratio of the phosphonic or pyrophosphonic acid to the metal or suitable metal compound in the reaction mixture, as described herein.

According to one aspect of the present disclosure, a metal or suitable metal compound and a stoichiometric excess of an unsubstituted or alkyl or aryl substituted phosphonic acid are
15 reacted to form a phosphorus-containing flame retardant. The reaction temperature is 105 °C or higher, the phosphonic acid is in a molten state at the reaction temperature, and the molar ratio of the phosphonic acid to the metal or suitable metal compound in the reaction mixture is higher than 4:1. In the reaction, the metal is oxidized and may be represented in its corresponding cationic form by the formula $M^{(+y)}$ where M is a metal, (+)y represents the
20 charge of the metal cation, and y is 2 or higher. The suitable metal compound may be represented by the formula $M_p^{(+y)} X_q$, where M is a metal, (+)y represents the charge of the metal cation, y is 2 or higher, X is an anion, and the values for p and q provide a charge balanced metal compound.

25 In another aspect, a metal or suitable metal compound, as above, and a stoichiometric excess of an unsubstituted or alkyl or aryl substituted pyrophosphonic acid are reacted to form a phosphorus-containing flame retardant. The pyrophosphonic acid is in a molten state at the reaction temperature, and the molar ratio of the pyrophosphonic acid to the metal or suitable metal compound in the reaction mixture is higher than 2:1.

30

In many embodiments, the molar ratio of the phosphonic acid to the metal or suitable metal compound in the reaction mixture is 5:1 or higher, such as about 6:1 or higher, about 8:1 or higher, or about 10:1 or higher. Larger molar excesses of the phosphonic acid to the metal or suitable metal compound may be used in the reaction mixture, such as about 12:1 or
35 higher, about 15:1 or higher, about 20:1 or higher, about 25:1 or higher, about 30:1 or higher, or any range therebetween. A large molar excess of the phosphonic acid relative to

the metal or suitable metal compound may be used. For example, the molar ratio may be up to about 50:1, up to about 100:1, up to about 300:1, up to about 500:1, or any range therebetween. However, as would be understood, process efficiency may suffer at certain large molar excesses, e.g., product precipitation from the reaction mixture may be hindered.

5 In many embodiments, the molar ratio ranges from about 8:1, from about 10:1, from about 12:1, or from about 16:1 to about 100:1 or to about 50:1, such as from about 10:1, from about 15:1, or from about 20:1 to about 50:1 or to about 40:1.

10 In many embodiments, the molar ratio of the pyrophosphonic acid to the metal or suitable metal compound in the reaction mixture is 3:1 or higher, such as about 4:1 or higher, about 6:1 or higher, or about 8:1 or higher. Often larger molar excesses of the pyrophosphonic acid to the metal or suitable metal compound are used in the reaction mixture, such as about 10:1 or higher, about 12:1 or higher, about 15:1 or higher, about 18:1 or higher, about 20:1 or higher, or any range therebetween. A large molar excess of the pyrophosphonic acid
15 relative to the metal or suitable metal compound may be used. For example, the molar ratio may be up to about 30:1, up to about 50:1, up to about 100:1, up to about 250:1, or any range therebetween. However, as would be understood, process efficiency may suffer at certain large molar excesses, e.g., product precipitation from the reaction mixture may be hindered. In many embodiments, the molar ratio ranges from about 4:1, from about 5:1,
20 from about 6:1, or from about 8:1 to about 50:1 or to about 25:1, such as from about 5:1, from about 8:1, or from about 10:1 to about 25:1 or to about 20:1.

The reaction temperature for producing a phosphorus-containing flame retardant according to the present disclosure should be chosen such that the phosphonic or pyrophosphonic acid
25 is in a molten state at the reaction temperature. For example, phosphonic and pyrophosphonic acids (e.g., alkyl substituted phosphonic or pyrophosphonic acids) are often solid at room temperature (e.g., methyl phosphonic acid melts at about 105 °C and ethyl phosphonic acid melts at about 62 °C), and thus heating the phosphonic or pyrophosphonic acid to result in a liquefied physical state (i.e., molten state) is generally appropriate to form
30 a consistent reaction mixture. As one skilled in the art will appreciate, the desired reaction temperature at which the phosphonic or pyrophosphonic acid is in a molten state may vary depending on the chosen reagents and thermodynamic conditions.

The reaction temperature should also be chosen to facilitate the formation of monoanionic
35 and/or dianionic pyrophosphonic acid ligands in the reaction product. For a phosphonic acid, a reaction temperature of 105 °C or higher is used. Without being bound by a particular theory, the reaction temperature is chosen to produce pyrophosphonic acid ligands

via dehydration reaction(s). In many embodiments, the metal or suitable metal compound and the phosphonic acid are reacted at temperatures higher than 105 °C, such as about 115 °C or higher, about 120 °C or higher, about 130 °C or higher, about 140 °C or higher, about 150 °C or higher, about 160 °C or higher, about 170 °C or higher, about 180 °C or higher, about 200 °C or higher, about 220 °C or higher, about 240 °C or higher, about 260 °C or higher, about 280 °C or higher, or any range therebetween. The reaction temperature may be higher than those described above, such as up to about 350 °C, up to about 400 °C, or higher, but it typically does not meet or exceed the boiling temperature of the phosphonic acid. For example, the reaction temperature may range from about 150 °C to about 300 °C, such as from about 150 °C to about 280 °C, from about 160 °C to about 260 °C, or from about 160 °C to about 240 °C. In many embodiments, the reaction temperature ranges from about 110 °C to about 350 °C, from about 115 °C to about 300 °C, from about 125 °C to about 280 °C, or from about 140 °C to about 260 °C. Through the dehydration reaction(s), water is formed, which can potentially lead to the undesirable reverse (hydrolysis) reaction. Thus, in some embodiments, the reaction system is designed to facilitate removal, such as the continuous removal, of water from the reaction. For example, the reaction temperature may be chosen above the boiling temperature of the water to the extent necessary to boil off at least a portion or desired amount (e.g., a majority, substantially all, or all) of the water from the reaction. Additional means, such as a gas purge, vacuum, and/or other known means, may be used to facilitate removal of water from the reaction system.

As dehydration is unnecessary for pyrophosphonic acid, the reaction temperature for pyrophosphonic acid may be lower than that described above for phosphonic acid. Generally, the limiting criterion with respect to choosing a suitable reaction temperature when employing a pyrophosphonic acid is the requirement that the pyrophosphonic acid is in a molten state at the reaction temperature. Often, the metal or suitable metal compound and the pyrophosphonic acid are reacted at a temperature of 20 °C or higher. In many embodiments, the metal or suitable metal compound and the pyrophosphonic acid are reacted at temperatures higher than 20 °C, such as about 40 °C or higher, about 60 °C or higher, about 80 °C or higher, about 100 °C or higher, about 140 °C or higher, about 180 °C or higher, about 200 °C or higher, or any range therebetween. The reaction temperature may be higher than those described above, such as up to about 300 °C, up to about 400 °C, or higher, but it typically does not meet or exceed the boiling temperature of the pyrophosphonic acid. In many embodiments, the reaction temperature ranges from about 25 °C to about 350 °C, from about 25 °C to about 280 °C, from about 30 °C to about 260 °C, from about 40 °C to about 260 °C, from about 60 °C to about 260 °C, from about 80 °C to about 240 °C, from about 100 °C to about 240 °C, from about 110 °C to about 240 °C, or

from about 120 °C to about 240 °C. Depending, for example, on the metal compound used to react with the pyrophosphonic acid, water may be generated from the reaction. As described above, in some embodiments, the reaction system is designed to facilitate removal, such as the continuous removal, of water from the reaction. For example, the reaction temperature may be chosen above the boiling temperature of the water to the extent necessary to boil off at least a portion or desired amount (e.g., a majority, substantially all, or all) of the water from the reaction. Additional means, such as a gas purge, vacuum, and/or other known means, may be used to facilitate removal of water from the reaction system.

Often, as the reaction progresses, the product forms as a slurry as the resulting flame retardant product precipitates from the product reaction mixture. Thus, the reaction is typically run for a time sufficient to achieve such precipitation. In general, the amount of time required to achieve at least substantial conversion to the flame retardant product, based on the metal or suitable metal compound, will depend on the reaction temperature, with higher temperatures generally resulting in shorter reaction times. In many embodiments, the metal or suitable metal compound and the phosphonic or pyrophosphonic acid are heated at the reaction temperature for from about 0.1 to about 48 hours, such as from about 0.2 to about 36 hours, from about 0.5 to about 30 hours, from about 1 hour to about 24 hours, e.g., from about 1 hour to about 12 hours, from about 1 hour to about 8 hours, or from about 2 hours to about 5 hours, although other durations may be used.

The metal or suitable metal compound and the molar excess of the phosphonic or pyrophosphonic acid can be combined in any manner suitable to form the reaction mixture. For example, the phosphonic or pyrophosphonic acid and the metal or metal compound may be mixed (e.g., stirred) together, such as to form a homogenous reaction mixture. In some embodiments, the metal or suitable metal compound is added to the phosphonic or pyrophosphonic acid which has been preheated to the reaction temperature. In some embodiments, the phosphonic or pyrophosphonic acid is pre-heated and stirred upon melting, such as under a nitrogen atmosphere or reduced pressure/vacuum. In still further embodiments, the metal or metal compound is added as rapidly as possible without causing a large change in the reaction temperature due to the exothermic nature of the reaction. In some embodiments, the phosphonic or pyrophosphonic acid and the metal or suitable metal compound are combined without preheating the phosphonic acid, or without sufficient heating to liquefy the phosphonic or pyrophosphonic acid, and the components are subsequently heated to the reaction temperature. The full amount of metal or suitable metal compound or phosphonic or pyrophosphonic acid can be added to the reaction all at once or

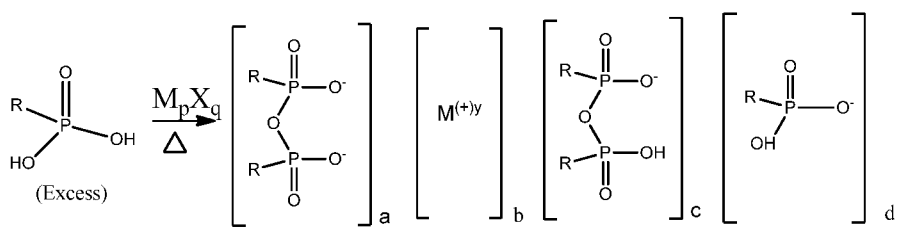
in portions. No additional solvents are needed, as the phosphonic or pyrophosphonic acid, used at a molar excess, acts as reagent and solvent, but additional solvent may be used if desired. In some embodiments, additional solvent is used when employing molar ratios of phosphonic or pyrophosphonic acid to the metal or suitable metal compound that are at or
5 near the lower boundary of the molar ratios disclosed herein.

In some embodiments, after desired conversion, e.g., full or substantially full conversion, to the flame retardant product is achieved, the product reaction mixture is cooled to a temperature above or no less than the melting temperature of the excess phosphonic or
10 pyrophosphonic acid to keep the excess phosphonic or pyrophosphonic acid in a liquefied state. The excess phosphonic or pyrophosphonic acid can be removed by filtration/washing and optionally recovered. The recovered excess phosphonic or pyrophosphonic acid may be recycled, e.g., back into the reactor in which a metal or suitable metal compound reacts with the phosphonic or pyrophosphonic acid. After conversion to the reaction product, a
15 solvent, e.g., water, an alcohol, and/or another suitable (e.g., polar) liquid, may optionally be added to dissolve or otherwise help remove the excess phosphonic or pyrophosphonic acid. The flame retardant product is often isolated by filtration, optionally followed by additional work up (e.g., washing, drying, sieving, etc.). The resulting flame retardant product, which is generally in the form of a powder or small particles, is readily processable, i.e., without
20 requiring or necessitating grinding, milling, or other such physical processing before use. It should be understood that producing the flame retardant material "directly" as a powder or small particles in accordance with the presently disclosed process permits workup of the reaction product, such as isolating the flame retardant product (e.g., separating the flame retardant product from excess phosphonic or pyrophosphonic acid or remaining solvent),
25 which may include, e.g., processing the reaction product by filtering, sieving, washing, drying, and the like. After the reaction, the resulting product reaction mixture, often a slurry, may be cooled to or just above the melting temperature of the excess phosphonic acid and the slurry may be combined with water. The water / slurry mixture may be agitated as necessary to break up any large clumps that might have formed. The solid product may be
30 isolated by filtration, optionally washed with water and dried, to yield the product in the form of a powder or small particles. In some cases, the product may be sieved to refine the particle size.

The process of the present disclosure yields a flame retardant comprising one or more
35 metals and one or more mono- and/or bi-dentate pyrophosphonic acid ligands. In some embodiments, compounds that additionally comprise phosphonate ligands may be

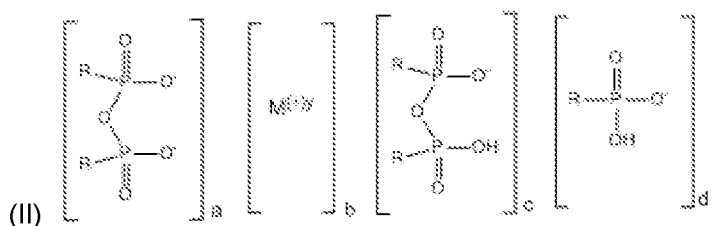
produced, but in all embodiments compounds comprising a pyrophosphonic acid mono-anionic ligand and/or a pyrophosphonic acid di-anionic ligand are obtained.

The process may yield mixtures of flame retardant compounds, but in many embodiments the process yields a flame retardant material as one, or predominately one, compound, with high conversion based on the metal or metal compound, such as at least 70%, 80%, 85%, 90%, 95%, 98% or higher conversion, or any range therebetween, as opposed to the mixtures of compounds that are obtained with the prior art processes involving heat treatment of metal phosphonate salts. In a general embodiment, in which phosphonate ligands may be present in the flame retardant product, the reaction proceeds generally as shown:



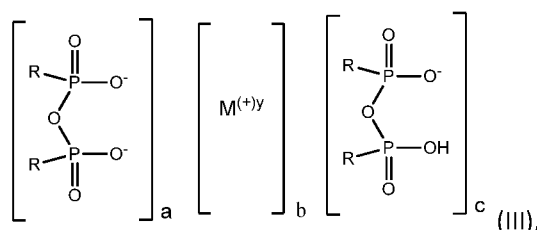
wherein M is a metal cation and (+)y represents the charge of the cation, e.g., M is a di, tri, tetra, penta- cationic metal; X is an anionic ligand or ligands attached to the metal and the stoichiometry of M and X (i.e., p and q) provides a charged balanced compound; R is H, an alkyl, aryl, alkylaryl or arylalkyl; a, b, c and d represent the ratio of the components to which they correspond relative to one another in the reaction product, and y, a, b, c and d are values that provide a charged balanced product, with the proviso that y is 2 or more and only one of a or c can be 0 (often, c is not zero). In some embodiments, the phosphonic acid ligand above with the coefficient d, when present, may be present as a dianion. In many embodiments, d is 0.

In a further aspect, a flame retardant product produced according to the present disclosure, typically in the form of a powder or small particles, comprises a compound or mixture of different compounds of empirical formula (II)



wherein R is H, an alkyl, aryl, alkylaryl or arylalkyl group, a, b, c and d represent the ratio of the components to which they correspond relative to one another in the compound, and a is generally a number of from 0 to 8, e.g., from 0 to 6, from 0 to 4, or from 0 to 2, c is generally a number of from 0 to 10, e.g., from 0 to 8, from 0 to 6, from 0 to 4 or from 0 to 2, d is generally a number of from 0 to 6, e.g., 0 to 4 or 0 to 2, M is a metal, y is a number of from 2 to 5, such as 2, 3 or 4, often 2 or 3, and $M^{(+)y}$ is a metal cation where (+)y represents the charge formally assigned to the cation. The values of a, b, c, d and y may vary, but will satisfy the charge-balance equation $2(a)+c+d=b(y)$, and only one of a or c can be 0. In many embodiments, c is not zero. In instances where a di-anionic phosphonic acid ligand is present in the compound, the charge balance equation becomes $2(a)+c+d+2(d)=b(y)$. The value for b is limited only in that it must satisfy the preceding equations, but in many embodiments b is a number of from 1 to 4, e.g., 1 or 2. In some embodiments, a is 0, 1, or 2 (e.g., 0 or 1), c is 1 or 2, and d is 0, 1, or 2 (e.g., 0 or 1), and the product is charged balanced.

In many embodiments, d is 0, as in:



where R, M, y, a, b, and c are as described above and the product charge balance equation becomes $2(a)+c=b(y)$.

Often, c in the formulas (II) and (III) above is not zero (e.g., c is from 1 to 10, from 1 to 8, from 1 to 6, from 1 to 4, or 1 or 2).

In accordance with the presently disclosed process, it was surprisingly discovered in many embodiments, such as when employing di-cationic or tri-cationic metals, that a flame retardant compound is produced where c in the formulas above is not zero and the product has a more favorable ratio of phosphorus atoms to metal atoms (i.e., P to M) for providing flame retardancy as compared to phosphorus-containing flame retardants described in the art. For example, tri-cationic metals (e.g., aluminum) and di-cationic metals (e.g., zinc) are known to form tri-substituted and di-substituted charge balanced compounds, respectively. As seen in the art, tris-phosphonate aluminum salts—having a phosphorus to aluminum ratio of 3:1—and di-phosphonate zinc salts—having a phosphorus to zinc ratio of 2:1—are known

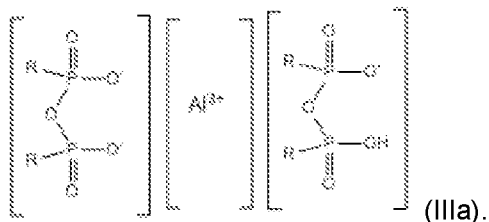
as flame retardants. However, in accordance with the pyrophosphonic acid ligand formation of the present disclosure, and particularly where c in the formulas above is not zero, the ratio of phosphorus to metal in the flame retardant product is higher. For example, as demonstrated in the Examples disclosed herein, when employing the process of the present disclosure the ratio of phosphorus to aluminum, or the ratio of phosphorus to iron, in the resulting flame retardant product was 4:1. Such a higher phosphorus to metal ratio leads to high efficiency and can allow for reduced loadings when compounded into thermoplastic polymers.

In certain specific embodiments, y in formula (III) is 2 (i.e., $M^{(+y)}$ is a di-cationic metal, such as described herein), a is 0, b is 1, and c is 2. In certain embodiments, the di-cationic metal M is Mg, Ca, or Zn. In other embodiments, y in formula (III) is 3 (i.e., $M^{(+y)}$ is a tri-cationic metal, such as described herein), a is 1, b is 1, and c is 1. In certain embodiments, the tri-cationic metal M is chosen from Al, Ga, Sb, Fe, Co, B, and Bi. In certain embodiments, the tri-cationic metal M is Al, Fe, Ga, Sb, or B.

As is common with inorganic coordination compounds, the reaction product in the above described reaction and the compounds of empirical formulas (II) and (III) are idealized such that the reaction product or compounds may include coordination polymers, complex salts, salts where certain atomic valences are shared, etc.

For example, in many embodiments, empirical formula (II) or (III) represents a monomer unit (i.e., coordination entity) of a coordination polymer, the extended coordination polymer structure thereby forming the flame retardant compound of the present disclosure.

In one example, where M is Al and y is 3, a compound of empirical formula (III) is produced according to the following empirical formula (IIIa):



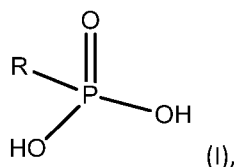
As shown herein, the absence of subscripts a, b and c in empirical formulas indicates that the subscripts are each 1, signifying a 1:1:1 ratio of the components (which, in the case of empirical formula (IIIa), a 1:1:1 ratio of di-anionic pyrophosphonic acid ligand, metal atom, and mono-anionic pyrophosphonic acid ligand). In this example, empirical formula (IIIa) represents a repeating monomer unit (i.e., coordination entity) of a coordination polymer, the

extended coordination polymer structure thereby forming the flame retardant compound of the present disclosure.

Often, a compound of empirical formula (II) or (III), which in many embodiments is an
 5 extended coordination polymer as described herein, makes up all, substantially all, or at least a majority of the flame retardant product, such as at least 75%, 85%, 90%, 95%, 98%, or higher, or any range therebetween, by weight of the flame retardant product.

A compound of empirical formula (II) or (III) (e.g., (IIIa)) may be produced with high
 10 conversion based on the metal or metal compound, such as at least 70%, 80%, 85%, 90%, 95%, 98% or higher conversion, e.g., at least 70 to 95% conversion. In certain of these embodiments, M is aluminum (i.e., the reaction product is produced using aluminum or one or more aluminum compounds, such as those described herein) or iron (i.e., the reaction product is produced using iron or one or more iron compounds, such as those described
 15 herein).

The phosphonic acid used in the present process may be represented by formula (I)



wherein R is H, alkyl, aryl, alkylaryl, or arylalkyl. In many embodiments, R is H, C₁₋₁₂ alkyl,
 20 C₆₋₁₀ aryl, C₇₋₁₈ alkylaryl, or C₇₋₁₈ arylalkyl, wherein said alkyl, aryl, alkylaryl, or arylalkyl are unsubstituted or are substituted by halogen, hydroxyl, amino, C₁₋₄ alkylamino, di-C₁₋₄ alkylamino, C₁₋₄ alkoxy, carboxy or C₂₋₅ alkoxycarbonyl. In some embodiments, said alkyl, aryl, alkylaryl, or arylalkyl are unsubstituted C₁₋₁₂ alkyl, C₆ aryl, C₇₋₁₀ alkylaryl, or C₇₋₁₀ arylalkyl, for example, C₁₋₆ alkyl, phenyl, or C₇₋₉ alkylaryl. In some embodiments, R is
 25 substituted or unsubstituted C₁₋₆ alkyl, C₆ aryl, C₇₋₁₀ alkylaryl, or C₇₋₁₂ arylalkyl, e.g., C₁₋₄ alkyl, C₆ aryl, C₇₋₉ alkylaryl, or C₇₋₁₀ arylalkyl. In many embodiments, R is unsubstituted C₁₋₁₂ alkyl, e.g., C₁₋₆ alkyl. In many embodiments, lower alkyl phosphonic acids are used, e.g., methyl-, ethyl-, propyl-, isopropyl-, butyl-, t-butyl- and the like.

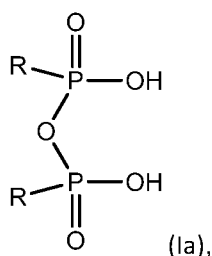
30 R as alkyl may be a straight or branched chain alkyl group having the specified number of carbons and includes e.g., unbranched alkyls such as methyl, ethyl, propyl, butyl, pentyl, hexyl heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and branched alkyl such as isopropyl, isobutyl, sec-butyl, t-butyl, ethyl hexyl, t-octyl and the like. For example, R as alkyl may be

chosen from methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-buty, and t-butyl. In many embodiments, R is methyl, ethyl, propyl or isopropyl, for example methyl or ethyl.

Often, when R is aryl it is phenyl. Examples of R as alkylaryl include phenyl substituted by one or more alkyl groups, for example groups selected from methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-buty, t-butyl, and the like. Examples of R as arylalkyl, include for example, benzyl, phenethyl, styryl, cumyl, phenpropyl and the like.

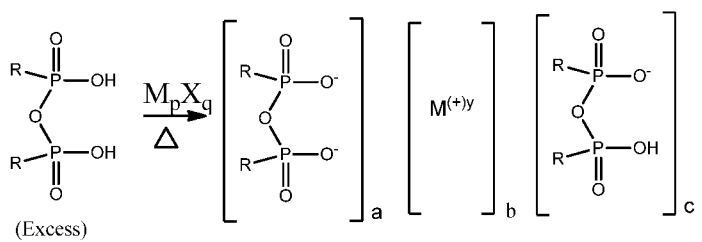
In many embodiments, R is chosen from methyl, ethyl, propyl, isopropyl, butyl, phenyl and benzyl.

The pyrophosphonic acid used in the present process may be represented by the formula (Ia):



wherein R is the same as disclosed above for formula (I).

The general reaction scheme with a pyrophosphonic acid and a suitable metal compound can be represented as:



where R, M, X, p, q, y, a, b and c are as described herein.

The process of the present disclosure may employ more than one phosphonic acid, more than one pyrophosphonic acid, or a combination of phosphonic and pyrophosphonic acids, so long as the mixture of phosphonic acids and/or pyrophosphonic acids are in a molten state at the reaction temperature. In some embodiments, the phosphonic acid or pyrophosphonic acid is generated in situ. For example, phosphonic or pyrophosphonic acid

may be prepared, such as by hydrolysis of higher oligomer phosphonic acid and/or cyclic phosphonic acid anhydride starting materials.

As used herein, "suitable metal compound" and the like refer to a compound of the formula $M_p^{(+y)} X_q$, where M is a metal capable of forming a polycation, e.g., a metal that forms a cation of 2+, 3+, 4+, or 5+, typically 2+, 3+ or 4+, and X is any anion that provides a charged balanced compound with metal M. Suitable examples for X include, but are not limited to, anions that, together with the metal M, form oxides, halides, alkoxides, hydroxides, carbonates, carboxylates, and phosphonates. The values for p and q provide a charge balanced metal compound, for example, alumina, Al_2O_3 . In some embodiments, an unsubstituted metal, M, is used as described herein. Examples of suitable metals (M) include, but are not limited to, Mg, Ca, Ba, Zn, Zr, Ge, B, Al, Si, Ti, Cu, Fe, Co, Ga, Bi, Mn, Sn or Sb. In some embodiments, M is chosen from Mg, Ca, Ba, Zn, Zr, Ga, B, Al, Si, Ti, Cu, Fe, Sn or Sb. In some embodiments, M is chosen from Mg, Ca, Ba, Zn, Zr, B, Al, Si, Ti, Fe, Sn or Sb, e.g., M may be Mg, Zn, Ca, Fe or Al.

Suitable metal compounds include, but are not limited to, compounds having a metal-oxygen bond, metal-nitrogen bond, metal-halogen bond, metal-hydrogen bond, metal-phosphorus bond, metal sulfur bond, metal boron bond, etc., for example, oxides, halides, alkoxides, hydroxides, carboxylates, carbonates, phosphonates, phosphinates, phosphonites, phosphates, phosphites, nitrates, nitrites, borates, hydrides, sulfonates, sulfates, sulfides, etc., of Mg, Ca, Ba, Zn, Zr, Ge, B, Al, Si, Ti, Cu, Fe, Co, Ga, Bi, Mn, Sn or Sb, for example, oxides, hydroxides, halides, or alkoxides of Mg, Ca, Ba, Zn, Zr, Ga, B, Al, Si, Ti, Cu, Fe, Sn or Sb; such as, oxides, hydroxides, halides, or alkoxides of Mg, Ca, Ba, Zn, Zr, B, Al, Si, Ti, Fe, Sn or Sb, e.g., oxides, hydroxides, halides, or alkoxides of Mg, Zn, Ca, Fe or Al.

In some embodiments, the metal, M, of the metal or suitable metal compound is aluminum or iron. In some embodiments, the suitable metal compound is chosen from halides, oxides, hydroxides, alkoxides, carbonates, carboxylates and phosphonates of aluminum. In some embodiments, the suitable metal compound is chosen from halides, oxides, hydroxides, and alkoxides of aluminum. In some embodiments, the suitable metal compound is chosen from alumina, aluminum trichloride, aluminum trihydroxide, aluminum isopropoxide, aluminum carbonate, and aluminum acetate. In other embodiments, the suitable metal compound is chosen from halides, oxides, alkoxides, carbonates, and acetates of iron. In some embodiments, the suitable metal compound is chosen from iron(III) oxide, iron(III) chloride, iron(III) isopropoxide, and iron(III) acetate.

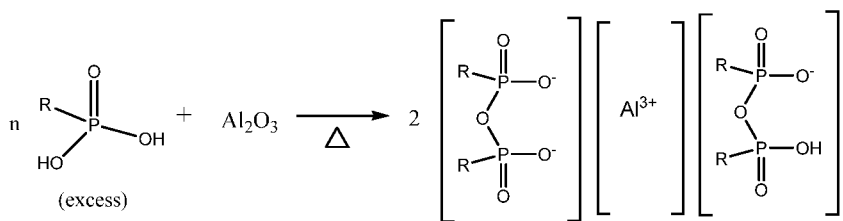
In certain embodiments, R is methyl, ethyl, propyl, isopropyl or butyl and M is Al, Fe, Zn or Ca. In further embodiments, X is an oxygen, hydroxy, alkoxy or halogen.

The reaction as described herein may, but need not, be run under reduced pressure or vacuum.

The product reaction mixture formed from the reaction described herein, often presenting as a slurry, may be combined with a liquid (e.g., water) and agitated as desired to break up any clumps that may have formed. The solid product may be isolated by filtration, optionally washed and dried, to yield the product in the form of a powder or small particles. In some cases, the product may be sieved to refine the particle size.

The reaction as described herein may optionally be facilitated with a seeding material. For example, use of a seeding material may reduce the time to achieve conversion to the flame retardant product and may lead to increased consistency in the product's physical characteristics. Often, the seeding material is added to the reaction mixture upon or after heating to the reaction temperature. In some embodiments, the seeding material comprises a flame retardant material produced according to the process of the present disclosure, such as a flame retardant compound of empirical formula (II), (III), or (IIIa) as described herein. The seeding material may be selected or refined to have a desired particle size.

In some embodiments, the suitable metal compound is alumina, and the flame retardant material is produced as follows:

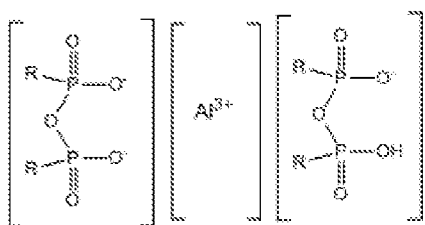


25

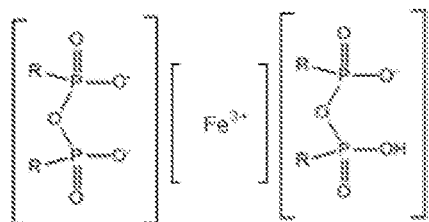
In one example, a phosphonic acid, such as a C₁-C₁₂ alkyl phosphonic acid (e.g., methyl, ethyl, propyl, iso-propyl, butyl or t-butyl phosphonic acid) is heated to or above its melting point, 105 °C, such as to 115 °C, 125 °C, 140 °C, 150 °C, 160 °C, 180 °C, 200 °C, 220 °C, or 240 °C or higher, with stirring (e.g., under nitrogen) upon melting. An oxide, hydroxide, halide, alkoxide, carbonate or carboxylate of Al, such as alumina, aluminum trichloride, aluminum trihydroxide, aluminum isopropoxide, aluminum carbonate or aluminum acetate, is added with stirring at a stoichiometric excess of the phosphonic acid, such as at a molar

30

ratio of phosphonic acid to the metal compound as described herein, e.g., 5:1 or higher, 10:1 or higher, or 15:1 or higher. Typically, a slurry forms as the reaction proceeds, and the solid flame retardant product may be isolated, such as by filtration, washing, etc. to yield the product in the form of a powder or small particles. Additional workup on the product reaction mixture may be performed prior to isolating the solid product, such as cooling the product reaction mixture above or no less than the melting point of the excess phosphonic acid and combining with a liquid, e.g., water, and optionally agitated as described above. The solid flame retardant product may be isolated by filtration, optionally washed with additional solvent and dried, to yield the product in the form of a powder or small particles. The flame retardant product contains phosphorus and aluminum in a 4:1 ratio according to the following empirical formula:

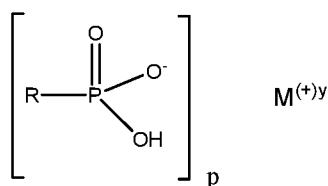


In a further example, the example described directly above is performed with iron or a suitable iron compound, such as halides, oxides, alkoxides, carbonates, or acetates of iron, e.g., iron(III) oxide, iron(III) chloride, iron(III) isopropoxide, or iron(III) acetate. The flame retardant product contains phosphorus and iron in a 4:1 ratio according to the following empirical formula:



Often, the compound of the empirical formulas above (which in many embodiments is an extended coordination polymer as described herein) makes up all, substantially all, or at least a majority of the flame retardant product, such as at least 75%, 85%, 90%, 95%, 98%, or higher, or any range therebetween, by weight of the flame retardant product.

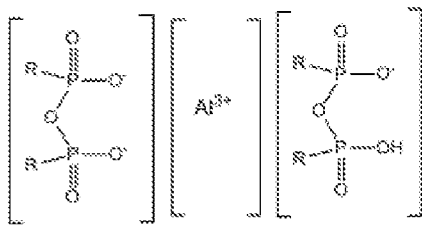
In some embodiments, the suitable metal compound is a metal phosphonate salt. The metal in the metal phosphonate salt may be a metal, M, as described herein. The suitable metal compound may be a metal phosphonate salt of the following formula:



wherein R and M are as described above, p is a number of from 2 to 5, e.g., 2, 3 or 4, and y is a number of from 2 to 5, e.g., 2, 3 or 4, so that $\text{M}^{(+y)}$ is a metal cation where (+)y represents the charge formally assigned to the cation. Typically the metal phosphonate salt is charge balanced (i.e., $p=y$). The metal phosphonate salt may be prepared according to methods known in the art.

In some embodiments, the metal phosphonate salt is prepared from the reaction of an initial metal compound and a phosphonic acid with a solvent (e.g., water) for the phosphonic acid. The initial metal compound may be a compound according to the suitable metal compound described herein. In some embodiments, the initial metal compound and the phosphonic acid are reacted at a temperature at or around room temperature or at a temperature ranging from about 0 to about 20 °C. The resulting metal phosphonate salt may then be used as the suitable metal compound according to the inventive process herein.

For example, a phosphonic acid, such as an alkyl phosphonic acid, e.g., methyl, ethyl, propyl, iso-propyl, butyl or t-butyl phosphonic acid, and a solvent (e.g., water) may be stirred to form a homogeneous solution. Any convenient ratio of water to phosphonic acid may be used, e.g., 10:1 to 1:10 by weight, more typically 5:1 to 1:5, and good results have been achieved using 2:1 to 1:2 mixtures. The solution may be cooled to, e.g., in the range from about 0 to about 20 °C, and an initial metal compound, such as a metal oxide, halide, alkoxide, or hydroxide, is added to react with the phosphonic acid. A metal phosphonate salt is formed, which is then used as the suitable metal compound in accordance with the presently disclosed process. For instance, in a separate reactor, a molar excess of phosphonic acid as described herein (such as at a 5:1 molar ratio of phosphonic acid relative to the metal phosphonate salt) is preheated to a molten state and is reacted with the metal phosphonate salt to form the flame retardant product. In embodiments involving an aluminum phosphonate salt as the suitable metal compound, the flame retardant product contains phosphorus and aluminum in a 4:1 ratio of phosphorus to aluminum according to the following empirical formula:



Often, the compound of the empirical formula (which in many embodiments is an extended coordination polymer as described herein) makes up all, substantially all, or at least a majority of the flame retardant product, such as at least 75%, 85%, 90%, 95%, 98%, or higher, or any range therebetween, by weight of the flame
 5 retardant product.

The flame retardant of the invention may be used with a variety of other flame retardants and/or synergists or flame retardant adjuvants as known in the art. For example, the flame retardant of the invention may be formulated with one or more materials selected from:

10 carbon black, graphite, carbon nanotubes, siloxanes, polysiloxanes; polyphenylene ether (PPE), phosphine oxides and polyphosphine oxides, e.g., benzylic phosphine oxides, poly benzylic phosphine oxides and the like;
 melamine, melamine derivatives and melamine condensation products, melamine salts such as, but not limited to, melamine cyanurate, melamine borate, melamine phosphates,
 15 melamine metal phosphates, melam, melem, melon, and the like;
 inorganic compounds including clays, metal salts such as hydroxides, oxides, oxide hydrates, borates, carbonates, sulfates, phosphates, phosphites, hypophosphites, silicates, mixed metal salts, etc., e.g., talc and other magnesium silicates, calcium silicate, aluminosilicate, aluminosilicate as hollow tubes (DRAGONITE), calcium carbonate,
 20 magnesium carbonate, barium sulfate, calcium sulfate, HALLOYSITE or boron phosphate, calcium molybdate, exfoliated vermiculite, zinc stannate, zinc hydroxystannate, zinc sulfide and zinc borate, zinc molybdate (or complexes thereof, e.g., Kemgard 911B), zinc molybdate/magnesium hydroxide complex (e.g., Kemgard MZM), zinc molybdate/magnesium silicate complex (Kemgard 911C), calcium molybdate/zinc complex
 25 (e.g., Kemgard 911A), zinc phosphate (or complexes thereof, e.g., Kemgard 981), magnesium oxide or hydroxide, aluminum oxide, aluminum oxide hydroxide (Boehmite), aluminum trihydrate, silica, tin oxide, antimony oxide (III and V) and oxide hydrate, titanium oxide, and zinc oxide or oxide hydrate, zirconium oxide and/or zirconium hydroxide and the like.

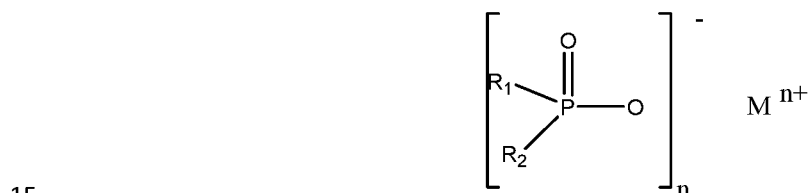
30

Unless otherwise specified, in the context of the present application, the term "phosphate" when used as a component in a "phosphate salt", such as in metal phosphate, melamine

phosphate, melamine metal phosphate, etc., refers to a phosphate, hydrogen phosphate, dihydrogen phosphate, pyrophosphate, polyphosphate, or a phosphoric acid condensation products anion or polyanion.

- 5 Likewise, unless otherwise specified, in the context of the present application, the term "phosphite" when used as a component in a "phosphite salt", such as in metal phosphite, etc., refers to a phosphite or hydrogen phosphite.

10 The flame retardant of the invention may also be formulated with other flame retardants such as halogenated flame retardants, alkyl or aryl phosphine oxide flame retardants, alkyl or aryl phosphate flame retardants, alkyl or aryl phosphonates, alkyl or aryl phosphinates, and salts of alkyl or aryl phosphinic acid. In some embodiments, the flame retardant comprises a mixture of the flame retardant according to the instant disclosure and a phosphinic salt of the following formula (e.g., an aluminum tris(dialkylphosphinate),



R_1 and R_2 each independently may be a group according to R as described herein, M is a metal as described herein (e.g., Al or Ca), and n is a number of from 2 to 7, e.g., from 2 to 4, often 2 or 3.

- 20 In many embodiments, a flame retardant polymer composition according to the present disclosure comprises (i) a polymer, (ii) a flame retardant material of the present disclosure, and (iii) one or more additional flame retardants and/or one or more synergists or flame retardant adjuvants.
- 25 For example, in some embodiments the flame retardant polymer composition comprises one or more additional flame retardants, e.g., halogenated flame retardants, phosphine oxide flame retardants, alkyl or aryl phosphonates, or salts of alkyl or aryl phosphinates, e.g., an aluminum tris(dialkylphosphinate) such as aluminum tris(diethylphosphinate).
- 30 In some embodiments the flame retardant polymer composition comprises one or more synergists or flame retardant adjuvants, e.g., melamine, melamine derivatives and melamine condensation products (e.g., melam, melem, melon), melamine salts, phosphine oxides and polyphosphine oxides, metal salts such as hydroxides, oxides, oxide hydrates, borates,

phosphates, phosphonates, phosphites, silicates and the like, e.g. aluminum hydrogen phosphite, melem or a melamine metal phosphate, e.g., a melamine metal phosphate wherein the metal comprises aluminum, magnesium or zinc. In particular embodiments the one or more additional flame retardant, synergist or flame retardant adjuvant comprises an aluminum tris(dialkylphosphinate), aluminum hydrogen phosphite, methylene-diphenylphosphine oxide-substituted polyaryl ether, xylylenebis(diphenylphosphine oxide), 4,4'-bis(diphenylphosphinylmethyl)-1,1'-biphenyl, ethylene bis-1,2-bis-(9,10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide)ethane, melem, melam, melon, or dimelamine zinc pyrophosphate.

Certain embodiments provide a halogen free polymer composition. In such embodiments, halogen containing flame retardants or synergists would be excluded as much as possible.

The flame retardant material of the present disclosure may be combined with an additional flame retardant, synergist or adjuvant in a range of 100:1 to 1:100 by weight of the inventive flame retardant to the total weight of additional flame retardant, synergist and/or adjuvant. In some embodiments, the flame retardant material of the present disclosure is present in a range of 10:1 to 1:10 by weight of the inventive flame retardant to the total weight of additional flame retardant, synergist and/or adjuvant, for example, weight ratios ranging from 7:1 to 1:7, 6:1 to 1:6, 4:1 to 1:4, 3:1 to 1:3 and 2:1 to 1:2. The inventive flame retardant is often the majority component in such a combination, e.g., a 10:1 to 1.2:1 ratio or a 7:1 to 2:1 ratio by weight of the inventive flame retardant material to the total weight of additional flame retardant, synergist and/or adjuvant, but the inventive material can also be the minor component of the mixture, e.g., a 1:10 to 1:1.2 ratio or a 1:7 to 1:2 ratio.

The thermally stable flame retardant of the invention can be compounded into thermoplastic polymers at high temperatures, such as high temperature polyamides and polyterephthalate esters, without decomposing or negatively impacting the physical properties of the polymer, and the flame retardant activity is excellent. The flame retardant of the invention may be used in other polymers, with other synergists and with conventional polymer additives.

The polymer of the flame retardant composition of the present invention may be any polymer known in the art, such as polyolefin homopolymers and copolymers, rubbers, polyesters including polyalkylene terephthalates, epoxy resins, polyurethanes, polysulfones, polyimides, polyphenylene ethers, styrenic polymers and copolymers, polycarbonates, acrylic polymers, polyamides, polyacetals, and biodegradable polymers. Mixtures of different polymers, such as polyphenylene ether/styrenic resin blends, polyvinyl chloride/acrylonitrile butadiene

styrene (ABS) or other impact modified polymers, such as methacrylonitrile and α -methylstyrene containing ABS, and polyester/ABS or polycarbonate/ABS and polyester or polystyrene plus some other impact modifier may also be used. Such polymers are available commercially or made by means well known in the art.

5

The flame retardant of the invention is particularly useful in thermoplastic polymers that are processed and/or used at high temperatures, for example, styrenic polymers including high impact polystyrene (HIPS), polyolefins, polyesters, polycarbonates, polyamides, polyurethanes, polyphenylene ethers and the like.

10

For example, the polymer may be a polyester-series resin, a styrenic resin, a polyamide-series resin, a polycarbonate-series resin, a polyphenylene oxide-series resin, a vinyl-series resin, an olefinic resin, an acrylic resin, epoxy resin, or a polyurethane. The polymer can be a thermoplastic or a thermoset resin and may be reinforced, e.g., glass reinforced. In some
15 embodiments, the polymer is a thermoplastic polyurethane. In some embodiments, the polymer is a thermosetting epoxy resin. More than one polymer resin may be present. In particular embodiments the polymer is an engineering polymer, e.g., a thermoplastic or reinforced thermoplastic polymer, e.g., glass reinforced thermoplastic polymer, such as an optionally glass filled polyester, epoxy resin or polyamide, for example, a glass-filled
20 polyester such as a glass filled polyalkylene terephthalate, or a glass filled polyamide.

Polyester-series resins include homopolyesters and copolyesters obtained by, for example, polycondensation of a dicarboxylic acid component and a diol component, and polycondensation of a hydroxycarboxylic acid or a lactone component, for example, aromatic
25 saturated polyester-series resin, such as polybutylene terephthalate or polyethylene terephthalate.

Polyamide (PA)-series resins include polyamides derived from a diamine and a dicarboxylic acid; polyamides obtained from an aminocarboxylic acid, if necessary in combination with a
30 diamine and/or a dicarboxylic acid; and polyamides derived from a lactam, if necessary in combination with a diamine and/or a dicarboxylic acid. The polyamide also includes a copolyamide derived from at least two different kinds of polyamide constituent components. Examples of polyamide-series resins include aliphatic polyamides such as PA 46, PA 6, PA 66, PA 610, PA 612, PA 11 and PA 12, polyamides obtained from an aromatic dicarboxylic
35 acid, e.g., terephthalic acid and/or isophthalic acid, and an aliphatic diamine, e.g., hexamethylenediamine or nonamethylenediamine, and polyamides obtained from both aromatic and aliphatic dicarboxylic acids, e.g., both terephthalic acid and adipic acid, and an

aliphatic diamine, e.g., hexamethylenediamine, and others. These polyamides may be used singly or in combination. In some embodiments, the polymer comprises PA 6. In some embodiments, the polymer comprises PA 66. In some embodiments, the polymer comprises a polyphthalamide.

5

Polyamides with melting points of at least 280°C are used extensively for producing molding compositions which make possible the production of molded articles, e.g. for the electrical and electronics industry, with excellent dimensional stability at high temperatures and with very good flame-retardant properties. Molding compositions of this type are demanded for example in the electronics industry for producing components which are mounted on printed circuit boards according to the so-called surface mounting technology, SMT. In this application, these components must withstand temperatures of up to 270°C for short periods of time without dimensional change.

10

Such high temperature polyamides include certain polyamides produced from alkyl diamines and diacids as polyamide 4,6, however many high temperature polyamides are aromatic and semi-aromatic polyamides, i.e., homopolymers, copolymers, terpolymers, or higher polymers that are derived from monomers containing aromatic groups. A single aromatic or semi-aromatic polyamide may be employed or blends of aromatic and/or semi-aromatic polyamides are used. It is also possible that the preceding polyamide and polyamide blends are blended with other polymers, including aliphatic polyamides.

20

Examples of these high temperature aromatic or semi-aromatic polyamides include polyamide 4T, poly(m-xylylene adipamide) (polyamide MXD,6), poly(dodecamethylene terephthalamide) (polyamide 12,T), poly(decamethylene terephthalamide) (polyamide 10,T), poly(nonamethylene terephthalamide) (polyamide 9,T), hexamethylene adipamide/hexamethylene terephthalamide copolyamide (polyamide 6,T/6,6), hexamethylene terephthalamide/2-methylpentamethylene terephthalamide copolyamide (polyamide 6,T/D,T); hexamethylene adipamide/hexamethylene terephthalamide/hexamethylene isophthalamide copolyamide (polyamide 6,6/6,T/6,I); poly(caprolactam-hexamethylene terephthalamide) (polyamide 6/6,T); hexamethylene terephthalamide/hexamethylene isophthalamide (6,T/6,I) copolymer; and the like.

25

30

Certain embodiments of the invention are thus to compositions comprising a polyamide that melts at high temperatures, e.g., 280° C or higher, 300°C, or higher, in some embodiments 320°C or higher, e.g. from 280 to 340°C, such as polyamide 4,6 and the aromatic and semi-aromatic polyamide described above, articles comprising high temperature polyamides and

35

the flame retardant material of the invention, methods for preparing the compositions and methods for shaping the articles.

As described herein, in many embodiments of the present disclosure, the flame retardant polymer composition comprises (i) a polymer, (ii) the flame retardant of the present disclosure, and (iii) one or more additional flame retardants and/or one or more synergists or flame retardant adjuvants. Thus, while the flame retardant (ii) alone exhibits excellent activity in polymer systems, it may be used in combination with (iii) one or more compounds chosen from other flame retardants, synergists and adjuvants. Exemplary compounds (iii) include halogenated flame retardants, alkyl or aryl phosphine oxides, alkyl or aryl polyphosphine oxides, alkyl or aryl phosphates, alkyl or aryl phosphonates, alkyl or aryl phosphinates, salts of alkyl or aryl phosphinic acid, carbon black, graphite, carbon nanotubes, siloxanes, polysiloxanes, polyphenylene ether, melamine, melamine derivatives, melamine condensation products, melamine salts, metal hydroxides, metal oxides, metal oxide hydrates, metal borates, metal carbonates, metal sulfates, metal phosphates, metal phosphonates, metal phosphites, metal hypophosphites, metal silicates, and mixed metal salts. For example, the one or more compounds (iii) may be chosen from aluminum tris(dialkylphosphinate), aluminum hydrogen phosphite, benzylic phosphine oxides, poly benzylic phosphine oxides, melam, melem, melon, melamine phosphates, melamine metal phosphates, melamine cyanurate, melamine borate, talc, clays, calcium silicate, aluminosilicate, aluminosilicate as hollow tubes, calcium carbonate, magnesium carbonate, barium sulfate, calcium sulfate, boron phosphate, calcium molybdate, exfoliated vermiculite, zinc stannate, zinc hydroxystannate, zinc sulfide, zinc borate, zinc molybdate, zinc phosphate, magnesium oxide, magnesium hydroxide, aluminum oxide, aluminum oxide hydroxide, aluminum trihydrate, silica, tin oxide, antimony oxide (III and V), antimony (III and V) oxide hydrate, titanium oxide, zinc oxide, zinc oxide hydrate, zirconium oxide, and zirconium hydroxide. For example, the one or more compounds (iii) may be chosen from aluminum tris(dimethylphosphinate), aluminum tris(diethylphosphinate), aluminum tris(dipropylphosphinate), aluminum tris(dibutylphosphinate), methylene-diphenylphosphine oxide-substituted polyaryl ether, xylylenebis(diphenylphosphine oxide), 1,2-bis-(9,10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide)ethane, 4,4'-bis(diphenylphosphinylmethyl)-1,1'-biphenyl, melam, melem, melon, and dimelamine zinc pyrophosphate.

In some embodiments, the flame retardant synergist comprises a material chosen from melam, melem, melon, melamine cyanurate, melamine polyphosphate, and melamine-poly(metal phosphate) (e.g., melamine-poly(zinc phosphate) (Safire 400)). In some

embodiments, the synergist comprises a triazine-based compound, such as a reaction product of trichlorotriazine, piperazine and morpholine, e.g., poly-[2,4-(piperazine-1,4-yl)-6-(morpholine-4-yl)-1,3,5-triazine]/piperazin (MCA[®] PPM Triazine HF). In some embodiments, the synergist comprises a metal hypophosphite, such as aluminum hypophosphite (e.g.,
5 Italmatch Phoslite[®] IP-A). In some embodiments, the synergist comprises an organic phosphinate, such as aluminum dialkylphosphinate, e.g., aluminum diethylphosphinate (Exolit OP).

In some embodiments, the flame retardant polymer composition comprises one or more
10 compounds chosen from hydrotalcite clays, metal borates, metal oxides, and metal hydroxides, such as metal borates, metal oxides, or metal hydroxides wherein the metal is zinc or calcium.

The concentration of the inventive flame retardant in the polymer composition is of course
15 dependent on the exact chemical composition of the flame retardant, the polymer and other components found in the final polymer composition. For example, when used as the sole flame retarding component of a polymer formulation the inventive flame retardant may be present in a concentration of from 1 to 50%, e.g., 1 to 30%, by weight of the total weight of the final composition. Typically, when used as the sole flame retardant there will be at least
20 2% of the inventive material present, for example 3% or more, 5% or more, 10% or more, 15% or more, 20% or more or 25% or more. In many embodiments, the inventive flame retardant is present in amounts up to 45%, while in other embodiments, the amount of inventive flame retardant is 40% of the polymer composition or less, e.g., 35% or less. When used in combination with other flame retardants or flame retardant synergists, less of
25 the inventive material may be needed.

Any known compounding techniques may be used to prepare the flame retardant polymer composition of the present disclosure, for example, the flame retardant may be introduced into molten polymer by blending, extrusion, fiber or film formation etc. In some cases the
30 flame retardant is introduced into the polymer at the time of polymer formation or curing, for example, the flame retardant of the invention may be added to a polyurethane prepolymer prior to crosslinking or it may be added to a polyamine or alkyl-polycarboxyl compound prior to polyamide formation or to an epoxy mixture prior to cure.

35 The flame retardant polymer composition of the invention will often contain one or more of the common stabilizers or other additives frequently encountered in the art, such as phenolic antioxidants, hindered amine light stabilizers (HALS), the ultraviolet light absorbers,

phosphites, phosphonites, alkaline metal salts of fatty acids, hydrotalcites, metal oxides, borates, epoxidized soybean oils, hydroxylamines, tertiary amine oxides, lactones, thermal reaction products of tertiary amine oxides, thiosynergists, basic co-stabilizers, for example, melamine, melem, etc., polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, hydrotalcites, alkali metal salts and alkaline earth metal salts of higher fatty acids, for example, Ca stearate, calcium stearoyl lactate, calcium lactate, Zn stearate, Zn octoate, Mg stearate, Na ricinoleate and K palmitate, antimony pyrocatecholate or zinc pyrocatecholate, nucleating agents, clarifying agents, etc.

Other additives may also be present, for example, plasticizers, lubricants, emulsifiers, pigments, dyes, optical brighteners, other flame proofing agents, anti-static agents, blowing agents, anti-drip agents, e.g., PTFE, and the like.

Optionally the polymer may include fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibers, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black and graphite. Such fillers and reinforcing agents may often be present at relatively high concentrations, including formulations where the filler or reinforcement is present in concentrations of over 50 wt% based on the weight of the final composition. More typically, fillers and reinforcing agents are present from about 5 to about 50 wt%, e.g., about 10 to about 40 wt% or about 15 to about 30 wt% based on the weight of the total polymer composition.

In some embodiments, the flame retardant polymer composition of the present disclosure is formulated with any one or more materials selected from carbon black, graphite, carbon nanotubes, siloxanes, polysiloxanes, talc, calcium carbonate, magnesium carbonate, barium sulfate, calcium sulfate, calcium silicate, magnesium silicate, aluminosilicate hollow tubes (Dragonite), Halloysite, boron phosphate, calcium molybdate, exfoliated vermiculite, zinc stannate, zinc hydroxystannate, zinc sulfide, zinc borate, zinc molybdate (or complexes thereof, e.g., Kemgard 911B), zinc molybdate/magnesium hydroxide complex (e.g., Kemgard MZM), zinc molybdate/magnesium silicate complex (Kemgard 911C), calcium molybdate/zinc complex (e.g., Kemgard 911A), zinc phosphate (or complexes thereof, e.g., Kemgard 981) and the like;

hydroxides, oxides, and oxide hydrates of group 2, 4, 12, 13, 14, 15 (semi)metals, e.g., magnesium oxide or hydroxide, aluminum oxide, aluminum oxide hydroxide (Boehmite), aluminum trihydrate, silica, silicates, tin oxide, antimony oxide (III and V) and oxide hydrate, titanium oxide, and zinc oxide or oxide hydrate, zirconium oxide and/or zirconium hydroxide

and the like; melamine and urea based resins such as melamine cyanurate, melamine borate, melamine polyphosphate, melamine pyrophosphate, polyphenylene ether (PPE) and the like; and clays, including e.g., hydrotalcite, boehmite, kaolin, mica, montmorillonite, wollastonite, nanoclays or organically modified nanoclays and the like.

5

In some embodiments, the flame retardant polymer composition of the present disclosure is formulated with any one or more materials selected from zinc borate, zinc stannate, polysiloxanes, kaolin, silica, magnesium hydroxide, zinc molybdate complex (e.g., Kemgard 911B), zinc molybdate/magnesium hydroxide complex (e.g., Kemgard MZM), zinc
 10 molybdate/magnesium silicate complex (Kemgard 911C), calcium molybdate/zinc complex (e.g., Kemgard 911A), zinc phosphate complex (e.g., Kemgard 981), and melamine-poly(metal phosphate) (e.g., melamine-poly(zinc phosphate) (Safire 400)).

15

In some embodiments, in addition to a polymer (such as described herein) and the flame retardant of the present disclosure, the flame retardant polymer composition comprises melam and any one or more materials selected from zinc borate, zinc stannate, zinc molybdate complex, zinc molybdate/magnesium hydroxide complex, zinc molybdate/magnesium silicate complex, calcium molybdate/zinc complex, zinc phosphate complex, and zinc oxide, optionally with additional additives, such as described herein.

20

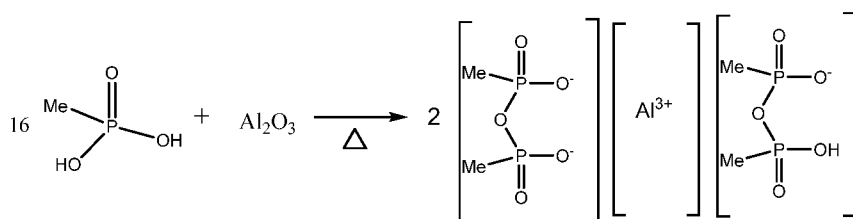
In some embodiments, in addition to a polymer (such as described herein) and the flame retardant of the present disclosure, the flame retardant polymer composition comprises melon and any one or more materials selected from zinc borate, zinc stannate, zinc molybdate complex, zinc molybdate/magnesium hydroxide complex, zinc
 25 molybdate/magnesium silicate complex, calcium molybdate/zinc complex, zinc phosphate complex, and zinc oxide, optionally with additional additives, such as described herein.

Further non-limiting disclosure is provided in the Examples that follow.

30

EXAMPLES

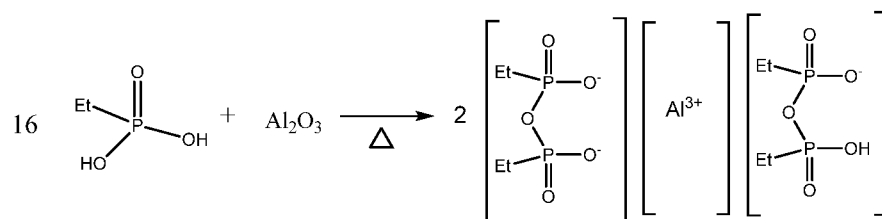
Example 1



A three-neck 250 mL flask was charged with 114.6 g methylphosphonic acid, which was then heated. At 105 °C the methylphosphonic acid melts, and vigorous stirring was begun under a N₂ blanket. The methylphosphonic acid was heated to 240 °C and 7.78 g of alumina was added as quickly as possible without causing a large exotherm. The slurry was cooled until it was just above the melting point of the excess methyl phosphonic acid, ~110 °C, and then added to 250 mL of H₂O while ensuring that the rate of addition did not cause excessive steam formation. The resulting mixture was agitated to break up any large clumps that might have formed, the product was isolated by filtration, washed with an additional 750 mL of H₂O, and dried to yield 45.08 g of the product as fine colorless crystals at 87% yield.

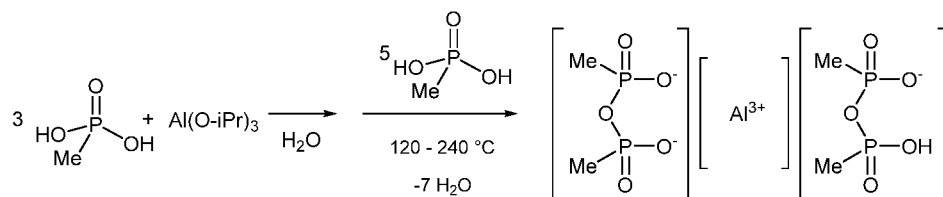
The product empirical formula above represents repeating monomer units (i.e., coordination entities) of a coordination polymer forming the pure crystalline product. Thermogravimetric analysis (TGA) of the product is shown in FIG. 1.

Example 2



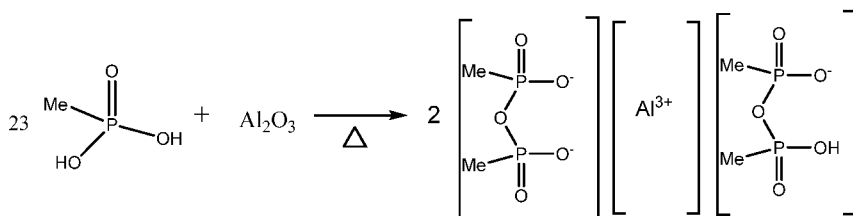
A three-neck 250 mL flask was charged with 149.8 g ethylphosphonic acid, which was heated to melting, 62 °C. Vigorous stirring was begun under a N₂ blanket, the ethylphosphonic acid was heated to 240 °C and 6.9 g of alumina was added as quickly as possible without causing a large exotherm. The slurry was cooled to ~80 °C, and then added to 250 mL of H₂O while ensuring that the rate of addition did not cause excessive steam formation. The resulting mixture was agitated to break up any large clumps that might have formed, the product was isolated by filtration, washed with an additional 750 mL of H₂O, and dried to yield 49.07 g of the product as fine colorless crystals at 84% yield. The product empirical formula above represents repeating monomer units (i.e., coordination entities) of a coordination polymer forming the pure crystalline product.

Example 3



A resin kettle was charged with 83 g of methylphosphonic acid, which was heated to 120 °C. An intermediate material prepared from 50 g. methyl phosphonic acid and 35.4 g. aluminum tris(isopropoxide) in the presence of water was added to the resin kettle as a syrup. The resulting solution contained a 5:1 molar ratio of methylphosphonic acid : aluminum methylphosphonic acid intermediate, which was heated to 240 °C with mechanical stirring. Stirred continued at 240 °C for about 30 min after a solid had formed. 500 mL of H₂O was added and the mixture was stirred for 16 h while a uniform slurry was made. As above, the product was isolated by filtration, washed with an additional 750 mL of H₂O, and dried to yield 64.3 g of the product as fine colorless crystals at 93% yield. The product empirical formula above represents repeating monomer units (i.e., coordination entities) of a coordination polymer forming the pure crystalline product.

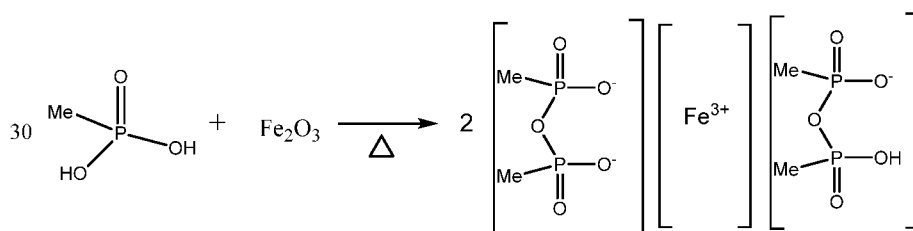
Example 4



A three-neck 1 L flask was charged with 1305 g methylphosphonic acid, which was then heated. At 105 °C the methylphosphonic acid melted, and vigorous stirring was begun under vacuum. The methylphosphonic acid was heated to 180 °C and 61 g of alumina was added as quickly as possible without causing a large exotherm or excessive foaming. The slurry was cooled until it was just above the melting point of the excess methyl phosphonic acid, ~110 °C, and then added to 1 L of H₂O while ensuring that the rate of addition did not cause excessive steam formation. The resulting mixture was agitated to break up any large clumps that might have formed, and the product was isolated by filtration, washed with an additional 1.5 L of H₂O, and dried to yield 408 g of the product as fine colorless crystals at 84% yield. The product empirical formula above represents repeating monomer units (i.e., coordination entities) of a coordination polymer forming the pure crystalline product.

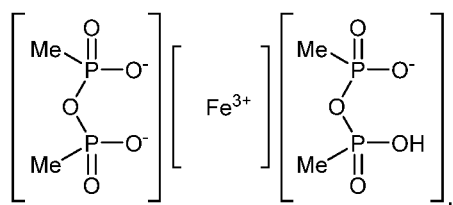
The products from each of Examples 1-4 had a 4:1 P to Al ratio (ICP Elemental Analysis).

Example 5



A 1 L reaction vessel was charged with 1412.6 g methylphosphonic acid, which was then heated to 165 °C under nitrogen purge (4L/min) at 250 RPM stirring. 78.2 g of iron oxide was added in portions without causing a large exotherm. The reaction mixture was heated at 165 °C for about 24 hours. The product reaction mixture containing an off-white slurry product was then cooled to about 130 °C and poured into 1.5 L of water in a beaker cooled in an ice water bath. The product was isolated by filtration, washed with an additional 500 mLx3 of water, and dried to yield fine off-white color crystals at 83% yield. The product had a 4:1 phosphorus to iron ratio (ICP Elemental Analysis) according to the following empirical

formula:



The product empirical formula above represents repeating monomer units (i.e., coordination entities) of a coordination polymer forming the pure crystalline product.

Example 6

Polymer compositions were prepared and evaluated for flame retardant activity under UL-94 testing. UL-94 V-0 ratings at 0.8 mm thickness were measured for glass filled polymer compositions of polyamide 6,6; polyamide 6, polybutylene terephthalate (PBT), and a high temperature polyamide containing the flame retardant produced according to Examples 1, 3, and 4 above (shown as follows):

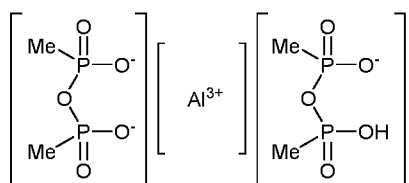


Table 1. Compositions with UL-94 V-0 rating at 0.8 mm

Substrate	Glass fiber	Inventive FR	Melam	Melamine cyanurate
PA 6,6	30%	12.5%	10%	-
PA6	25%	15%	-	10%
PBT	25%	15%	15%	-
High temp nylon	25%	18%	-	-

Additional polymer compositions containing the flame retardant produced according to Examples 1, 3 and 4 above combined with various synergists in glass filled PA 66, PBT and polyphthalamide were prepared and evaluated under UL-94 testing at 0.8 mm thickness. The results are provided in Table 2 (PA 66), Table 3 (PBT) and Table 4 (polyphthalamide). Samples 15, 20 and 22, which did not contain the inventive flame retardant, failed the UL-94 test.

Table 2. PA66

Sample	5	6	7	8	9	10	11	12	13	14	15
Formulation											
PA 66 wt%	47.5	46.5	46.5	46.3	45	50	40.3	45.3	45.3	46.3	70
Glass wt%	30	30	30	30	30	30	30	30	30	30	30
Inventive FR wt%	12.5	10	10	12.2	14	12	13.7	13.7	13.7	13.7	-
Melam wt%	10	10	10	10	10	-	-	-	-	-	-
Melem wt%	-	-	-	-	-	-	16	-	-	-	-
Melon wt%	-	-	-	-	-	-	-	10	10	-	-
Melamine polyphosphate wt%	-	-	-	-	-	8	-	-	-	-	-
Exolit OP 1230 wt%	-	3.5	-	-	-	-	-	-	-	-	-
Exolit OP 1400 wt%	-	-	3.5	-	-	-	-	-	-	-	-
PPM Triazine HF wt%	-	-	-	-	-	-	-	-	-	10	-
Zinc borate wt%	-	-	-	1.5	-	-	-	1	-	-	-
Zinc stannate wt%	-	-	-	-	1	-	-	-	1	-	-
UL 94 @ 1/32" (0.8 mm)	V-0	V-0	V-0	V-0	V-0	V-0	V-1	V-0	V-0	V-1	Fail

10

Table 3. PBT

Sample Formulation	16	17	18	19	20
PBT wt%	50	50	50	45	75
Glass wt%	25	25	25	25	25
Inventive FR wt%	15	16	15	15	-
Melam wt%	10	9	9	15	-
Polysiloxane wt%	-	-	1	-	-
UL 94 @ 1/32"	V-0	V-0	V-0	V-0	Fail

Table 4. Polyphthalamide (High temperature polyamide)

Sample Formulation	21	22
Polyphthalamide wt%	57	70
Glass wt%	25	30
Inventive FR wt%	18	-
UL 94 @ 1/32"	V-0	Fail

Example 7

5

Polymer compositions containing the flame retardant produced according to Example 5 above in PA 66 were prepared and evaluated for flame retardant activity under UL-94 testing at 0.8 mm thickness. The results are provided in Table 5. Sample 24, which did not contain the inventive flame retardant, failed the UL-94 test.

10

Table 5. PA 66

Sample Formulation	23	24
PA 66 wt%	45	70
Glass wt%	30	30
Inventive FR wt%	15	-
Melam wt%	10	-
UL 94 @ 1/32" (0.8 mm)	V-0	Fail

Although particular embodiments of the present invention have been illustrated and described, it will be apparent to those skilled in the art from consideration of the specification

and practice of the present disclosure that various modifications and variations can be made without departing from the scope of the invention, as claimed. Thus, it is intended that the specification and examples be considered as exemplary only, with a true scope of the present invention being indicated by the following claims and their equivalents.

CLAIMS

1. A process for producing a phosphorus-containing flame retardant, comprising reacting at a reaction temperature a mixture comprising a metal or suitable metal compound and a stoichiometric excess relative to the metal or suitable metal compound of an unsubstituted or alkyl or aryl substituted phosphonic acid, wherein:

- the metal is capable of forming a polycation, preferably a 2+, 3+ or 4+ polycation, or the suitable metal compound is

represented by the formula $M_p^{(+y)} X_q$ where M is a metal, (+)y represents the charge of the metal cation, y is 2 or higher, X is an anion, and the values for p and q provide a charge balanced metal compound;

- the molar ratio of the unsubstituted or alkyl or aryl substituted phosphonic acid to the metal or suitable metal compound in the mixture is higher than 4:1;

- the reaction temperature is 105 °C or higher, preferably 150 °C or higher, most preferably in the range from 140 °C to 260 °C; and

- the unsubstituted or alkyl or aryl substituted phosphonic acid is in a molten state at the reaction temperature.

2. A process for producing a phosphorus-containing flame retardant, comprising reacting at a reaction temperature a mixture comprising a metal or suitable metal compound and a stoichiometric excess relative to the metal or suitable metal compound of an unsubstituted or alkyl or aryl substituted pyrophosphonic acid, wherein:

- the metal is capable of forming a polycation, preferably a 2+, 3+ or 4+ polycation, or the suitable metal compound is

represented by the formula $M_p^{(+y)} X_q$ where M is a metal, (+)y represents the charge of the metal cation, y is 2 or higher, X is an anion, and the values for p and q provide a charge balanced metal compound;

- the molar ratio of the unsubstituted or alkyl or aryl substituted pyrophosphonic acid to the metal or suitable metal compound in the mixture is higher than 2:1; and

- the unsubstituted or alkyl or aryl substituted pyrophosphonic acid is in a molten state at the reaction temperature.

3. The process according to claim 2, wherein the reaction temperature is 40 °C or higher, preferably from 60 °C to 260 °C.

4. The process according to claim 1, wherein the molar ratio is 8:1 or higher, preferably from 10:1 to 50:1.

5. The process according to any one of claims 2 and 3, wherein the molar ratio is 4:1 or higher, preferably from 5:1 to 25:1.

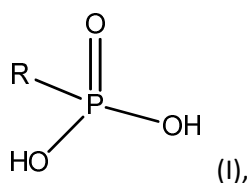
6. The process according to claim 1 or 2, wherein the mixture comprises a suitable metal compound which is represented by the formula $M_p^{(+y)} X_q$ where M is a metal, (+)y represents the charge of the metal cation, y is 2, 3 or 4, X is an anion, and the values for p and q provide a charge balanced metal compound, preferably wherein the suitable metal compound is chosen from a metal oxide, halide, alkoxide, hydroxide, carbonate, carboxylate, or phosphonate.

7. The process according to claim 6, wherein y is 3.

8. The process according to claim 7, wherein M is chosen from Al, Ga, Sb, Fe, Co, B, and Bi, preferably Al or Fe.

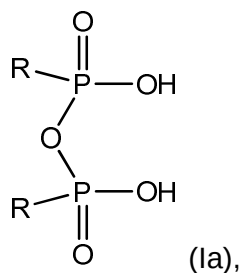
9. The process according to claim 8, wherein the suitable metal compound is chosen from alumina, aluminum trichloride, aluminum trihydroxide, aluminum isopropoxide, aluminum carbonate, aluminum acetate, iron(III) oxide, iron(III) chloride, iron(III) isopropoxide, and iron(III) acetate.

10. The process according to claim 1, wherein the unsubstituted or alkyl or aryl substituted phosphonic acid is represented by formula (I)



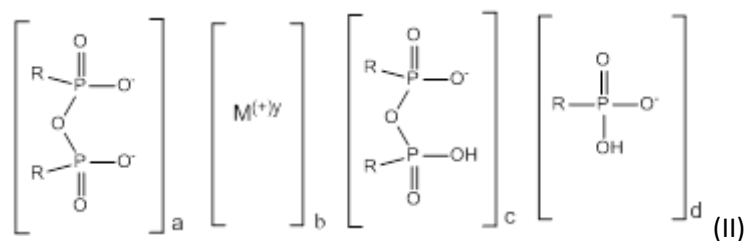
wherein R is H, C₁₋₁₂ alkyl, C₆₋₁₀ aryl, C₇₋₁₈ alkylaryl, or C₇₋₁₈ arylalkyl, wherein the alkyl, aryl, alkylaryl, or arylalkyl are unsubstituted or are substituted by halogen, hydroxyl, amino, C₁₋₄ alkylamino, di-C₁₋₄ alkylamino, C₁₋₄ alkoxy, carboxy or C₂₋₅ alkoxycarbonyl, preferably unsubstituted C₁₋₁₂ alkyl, C₆ aryl, C₇₋₁₀ alkylaryl, or C₇₋₁₀ arylalkyl, more preferably unsubstituted C₁₋₆ alkyl and most preferably methyl, ethyl, propyl, isopropyl, butyl or t-butyl.

11. The process according to claim 2, wherein the unsubstituted or alkyl or aryl substituted pyrophosphonic acid is represented by formula (Ia)



wherein R is H, C₁₋₁₂ alkyl, C₆₋₁₀ aryl, C₇₋₁₈ alkylaryl, or C₇₋₁₈ arylalkyl, wherein the alkyl, aryl, alkylaryl, or arylalkyl are unsubstituted or are substituted by halogen, hydroxyl, amino, C₁₋₄ alkylamino, di-C₁₋₄ alkylamino, C₁₋₄ alkoxy, carboxy or C₂₋₅ alkoxy carbonyl, preferably unsubstituted C₁₋₁₂ alkyl, C₆ aryl, C₇₋₁₀ alkylaryl, or C₇₋₁₀ arylalkyl, more preferably unsubstituted C₁₋₆ alkyl and most preferably methyl, ethyl, propyl, isopropyl, butyl or t-butyl.

12. A crystalline phosphorus-containing flame retardant produced according to the process of any one of claims 1 through 11 directly in the form of a powder or small particles, wherein said flame retardant is a compound or mixture of compounds of empirical formula (II)

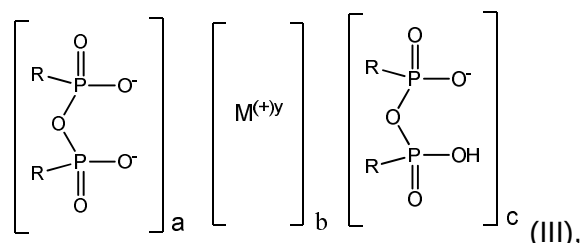


wherein R is H, an alkyl, aryl, alkylaryl, or arylalkyl group;

M is a metal and y is a number from 2 to 5, such that M^(+y) is a metal cation where (+)y represents the charge formally assigned to the cation;

a, b, c, and d represent the ratio of the components to which they correspond relative to one another in the compound and satisfy the charge-balance equation 2(a)+c+d=b(y); and c is not zero.

13. A flame retardant material comprising a compound of empirical formula (III)



wherein R is H, an alkyl, aryl, alkylaryl, or arylalkyl group;

M is a metal and y is 2 or 3, such that M^(+y) is a metal cation where (+)y represents the charge formally assigned to the cation;

a, b, and c represent the ratio of the components to which they correspond relative to one another in the compound and satisfy the charge-balance equation $2(a)+c=b(y)$; and c is not zero; and

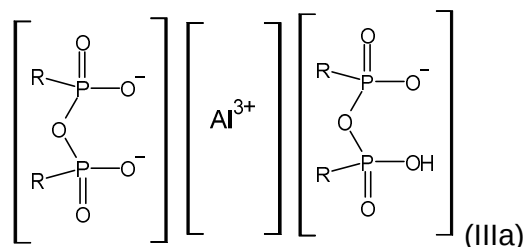
wherein the compound of empirical formula (III) makes up at least a majority by weight of the flame retardant material.

14. The flame retardant material according to claim 13, wherein y is 3, a is 1, b is 1, and c is 1.

15. The flame retardant material according to claim 14, wherein M is chosen from Al, Ga, Sb, Fe, Co, B, and Bi, preferably Al, Fe, Ga, Sb, or B.

16. The flame retardant material according to any one of claims 13-15, wherein R is H, C₁₋₁₂ alkyl, C₆₋₁₀ aryl, C₇₋₁₈ alkylaryl, or C₇₋₁₈ arylalkyl, wherein the alkyl, aryl, alkylaryl, or arylalkyl are unsubstituted or are substituted by halogen, hydroxyl, amino, C₁₋₄ alkylamino, di-C₁₋₄ alkylamino, C₁₋₄ alkoxy, carboxy or C₂₋₅ alkoxycarbonyl, preferably unsubstituted C₁₋₁₂ alkyl, C₆ aryl, C₇₋₁₀ alkylaryl, or C₇₋₁₀ arylalkyl, more preferably unsubstituted C₁₋₆ alkyl, most preferably methyl, ethyl, propyl, isopropyl, butyl or t-butyl.

17. The flame retardant material according to claim 13, wherein the compound of empirical formula (III) is a compound of empirical formula (IIIa)



wherein R is H or alkyl, preferably unsubstituted C₁₋₆ alkyl, most preferably methyl or ethyl.

18. The flame retardant material according to any one of claims 13-17, wherein the compound of empirical formula (III) or (IIIa) makes up at least 75% by weight, preferably at least 90% by weight, of the flame retardant material.

19. A flame retardant polymer composition comprising (i) a polymer and (ii) the flame retardant material according to any one of claims 13-18.

20. The flame retardant polymer composition according to claim 19, wherein the polymer comprises one or more of a polyolefin homopolymer or copolymer, rubber, polyester, epoxy resin, polyurethane, polysulfone, polyimide, polyphenylene ether, styrenic polymer or copolymer, polycarbonate, acrylic polymer, polyamide, or polyacetal, preferably polyalkylene terephthalate or glass filled polyalkylene terephthalate, high impact polystyrene (HIPS), epoxy resin or glass reinforced epoxy resin, or polyamide or glass filled polyamide, preferably a polyamide selected from polyamide 46, polyamide 6, polyamide 66, polyamide 4T, polyamide 9T, polyamide MXD,6, polyamide 12,T, polyamide 10,T, polyamide 6,T/6,6, polyamide 6,T/D,T, polyamide 6,6/6,T/6,I, polyamide 6/6,T, or polyamide 6,T/6,I, or a polyphthalamide.

21. The flame retardant polymer composition according to claim 19, wherein the polymer comprises a polyphenylene ether/styrenic resin blend, acrylonitrile butadiene styrene (ABS), polyvinyl chloride/ABS blend, methacrylonitrile/ABS blend, α -methylstyrene containing ABS, polyester/ABS, polycarbonate/ABS, impact modified polyester, or impact modified polystyrene.

22. The flame retardant polymer composition according to any one of claims 19 through 21, further comprising (iii) one or more compounds chosen from additional flame retardants, synergists, and flame retardant adjuvants.

23. The flame retardant polymer composition according to claim 22, wherein the one or more compounds are chosen from halogenated flame retardants, alkyl or aryl phosphine oxides, alkyl or aryl polyphosphine oxides, alkyl or aryl phosphates, alkyl or aryl phosphonates, alkyl or aryl phosphinates, salts of alkyl or aryl phosphinic acid, carbon black, graphite, carbon nanotubes, siloxanes, polysiloxanes, polyphenylene ether, melamine, melamine derivatives, melamine condensation products, melamine salts, metal hydroxides, metal oxides, metal oxide hydrates, metal borates, metal carbonates, metal sulfates, metal phosphates, metal phosphonates, metal phosphites, metal hypophosphites, metal silicates, and mixed metal salts, preferably wherein the one or more compounds are chosen from aluminum tris(dialkylphosphinate), aluminum hydrogen phosphite, benzylic phosphine oxides, poly benzylic phosphine oxides, melam, melem, melon, melamine phosphates, melamine metal phosphates, melamine cyanurate, melamine borate, talc, clays, calcium silicate, aluminosilicate, aluminosilicate as hollow tubes, calcium carbonate, magnesium carbonate, barium sulfate, calcium sulfate, boron phosphate, calcium molybdate, exfoliated vermiculite, zinc stannate, zinc hydroxystannate, zinc sulfide, zinc borate, zinc molybdate, zinc phosphate, magnesium oxide, magnesium hydroxide, aluminum oxide, aluminum oxide

hydroxide, aluminum trihydrate, silica, tin oxide, antimony oxide (III and V), antimony (III and V) oxide hydrate, titanium oxide, zinc oxide, zinc oxide hydrate, zirconium oxide, and zirconium hydroxide, or preferably wherein the one or more compounds are chosen from aluminum tris(dimethylphosphinate), aluminum tris(diethylphosphinate), aluminum tris(dipropylphosphinate), aluminum tris(dibutylphosphinate), methylene-diphenylphosphine oxide-substituted polyaryl ether, xylylenebis(diphenylphosphine oxide), 1,2-bis-(9,10-dihydro-9-oxy-10-phosphaphenanthrene-10-oxide)ethane, 4,4'-bis(diphenylphosphinylmethyl)-1,1'-biphenyl, melam, melem, melon, and dimelamine zinc pyrophosphate.

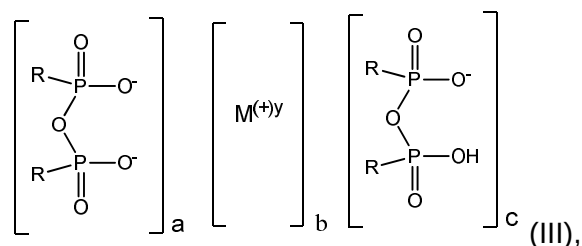
24. The flame retardant polymer composition according to claim 22, wherein the one or more compounds are chosen from melam, melem, melon, melamine cyanurate, melamine polyphosphate, melamine poly(metal phosphate), poly-[2,4-(piperazine-1,4-yl)-6-(morpholine-4-yl)-1,3,5-triazine]/piperazin, aluminum hypophosphite, and aluminum dialkylphosphinate, or wherein the one or more compounds are chosen from zinc borate, zinc stannate, polysiloxanes, kaolin, silica, magnesium hydroxide, zinc molybdate complex, zinc molybdate/magnesium hydroxide complex, zinc molybdate/magnesium silicate complex, calcium molybdate/zinc complex, zinc phosphate complex, and melamine-poly(zinc phosphate).

25. The flame retardant polymer composition according to claim 22, wherein the one or more compounds comprise melam and any one or more materials selected from zinc borate, zinc stannate, zinc molybdate complex, zinc molybdate/magnesium hydroxide complex, zinc molybdate/magnesium silicate complex, calcium molybdate/zinc complex, zinc phosphate complex, and zinc oxide.

26. The flame retardant polymer composition according to claim 22, wherein the one or more compounds comprise melon and any one or more materials selected from zinc borate, zinc stannate, zinc molybdate complex, zinc molybdate/magnesium hydroxide complex, zinc molybdate/magnesium silicate complex, calcium molybdate/zinc complex, zinc phosphate complex, and zinc oxide.

27. A process for increasing the flame resistance of a polymer, comprising incorporating the flame retardant material according to any one of claims 13 through 18 into a polymer resin, optionally with one or more additional flame retardant, synergist or flame retardant adjuvant.

28. A crystalline compound of empirical formula (III)



wherein R is H, an alkyl, aryl, alkylaryl, or arylalkyl group;

M is a metal and y is 2 or 3, such that $\text{M}^{(+y)}$ is a metal cation where (+)y represents the charge formally assigned to the cation;

a, b, and c represent the ratio of the components to which they correspond relative to one another in the compound and satisfy the charge-balance equation $2(a)+c=b(y)$; and c is not zero.

29. The crystalline compound of claim 28, wherein y is 3.

30. The crystalline compound of claim 28, wherein M is aluminum or iron.

31. The crystalline compound of any one of claims 28-30, wherein R is unsubstituted C_{1-6} alkyl.

32. The crystalline compound of claim 31, wherein R is methyl or ethyl.