



(51) International Patent Classification:
C08K 5/51 (2006.01)

(21) International Application Number:
PCT/CN2014/084589

(22) International Filing Date:
18 August 2014 (18.08.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PCT/CN2013/082132
23 August 2013 (23.08.2013) CN

(71) Applicant: RHODIA OPERATIONS [FR/FR]; 40 rue de la Haie-Coq, F-93306 Aubervilliers (FR).

(72) Inventors; and

(71) Applicants (for US only): LI, Junli [CN/CN]; Room 501, No. 14, 355 Qingchun Rd., Minghang district, Shanghai 201100 (CN). WOODWARD, Gary [GB/GB]; 6 Kelstern Close, Northwich, Cheshire CW95QR (GB).

(74) Agent: CHINA PATENT AGENT (H.K.) LTD.; 22/F., Great Eagle Center, 23 Harbour Road, Wanchai, Hong Kong (CN).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: FLAME RETARDANT PREPARED FROM AMIDE DERIVATIVES AND PROCESS FOR MAKING THE SAME

(57) Abstract: A method for manufacturing a melamine derivative mixture, comprising: firstly, reacting at least a nitrogen containing compound and a metallic phosphite or hydrogen phosphite salt in an aqueous solution ; and secondly, heating the resultant reaction mixture in solid form, at a temperature comprised between 150-500°C in the presence of an oxidant, to obtain a melamine derivative mixture. The thus obtained melamine derivative mixture is found to be useful as a flame retardant in epoxy polymers and help retain their physical properties.



Description

Flame Retardant Prepared from Amide Derivatives and Process for Making the Same

Cross-reference to related application

[0001] The present application claims priority to PCT international application no. PCT/CN2013/082132 filed on August 23, 2013, the whole content of this application being incorporated herein by reference.

Technical Field

[0002] The present invention pertains to a process for manufacturing a melamine derivative mixture by a reaction between at least an amide derivative and a metallic phosphite salt, and the use of said reaction to produce a flame retardant.

Background Art

[0003] Flame retardants are additives used in plastics and other industrial products for inhibiting or resisting the spread of fire. In the recent years, the industrial applications of halogen free flame retardants have attracted much research attention, due to their environmental advantage brought by the finite halogen level. One commonly used halogen free flame retardant (HFFR) is phosphonate HFFR, such as melamine pyrophosphate (MPP), which is widely used in thermoplastics and has a general molecular formula of $C_3H_6N_6 \cdot (H_3PO_4)_n$. In case of fire, the combination of nitrogen and phosphorus elements in MPP could help form a crosslinked char in the applied product, thus boosting its flame retardant performance.

[0004] Nevertheless, MPP, like other known phosphonate flame retardant additive, has its own constraints and disadvantages when used for thermoplastics. For instance, off-gassing and liquid bleed out have been found in the thermoplastic systems incorporating MPP, and these problems are believed to be caused by phosphonate slat/synergist interactions in the systems.

[0005] Moreover, many of the known phosphonate HFFR additives are found to have a tendency to migrate and/or volatilize from the thermoplastics over time, or decompose at various thermoplastic processing temperatures (particularly, the extrusion processing temperatures), causing the system

to suffer from a gradual loss of flame retardant properties. Further, these existing phosphonate HFFR additives are also known for their hygroscopic properties, which will eventually lead to unwanted water/moisture absorption.

[0006] The present invention thus seeks to provide an economic approach to produce a new phosphonate HFFR additive that overcomes the aforesaid disadvantages of conventional phosphonate HFFR additives, which offers satisfactory and stable flame retardant properties while retaining good mechanical properties of the polymer it adds to.

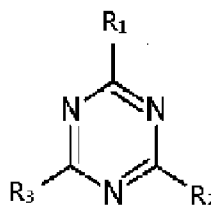
Summary of Invention

[0007] The invention is directed to a melamine derivative mixture having flame retardant properties, and a process for manufacturing the same.

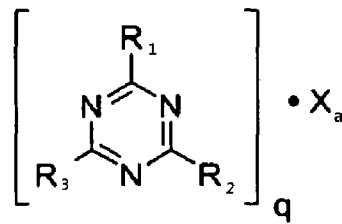
[0008] In one aspect of the present invention, there is provided a process for manufacturing a melamine derivative mixture, comprising at least the following steps:

- (i) providing an aqueous solution of a metallic phosphite or hydrogen phosphite salt [Solution (S)] with a pH of between 1 and 7;
- (ii) mixing the Solution (S) with at least one nitrogen-containing compound [Compound (N)] at a temperature between 5°C and 100°C, to obtain a reaction mixture;
- (iii) separating the reaction mixture obtained in step (ii) by a solid-liquid separation method to obtain a solid phase; and,
- (iv) heating the solid phase obtained in step (iii), at a temperature between 150°C and 500°C in the presence of an oxidant, to obtain the melamine derivative mixture,

wherein the Compound (N) is a compound of formula (I) or formula (II)



(I)



(II)

wherein: R₁, R₂, and R₃ are independently hydrogen, hydroxyl, amino, or mono- or diC₁-C₈ alkyl amino; or C₁-C₈ alkyl, C₅-C₁₆cycloalkyl, -alkylcycloalkyl, each being optionally substituted by a hydroxyl or a C₁-C₄hydroxyalkyl, C₂-C₈alkenyl, C₁-C₈alkoxyl, -acyl, -acyloxy, C₆-C₁₂ aryl, -OR₁ and -N(R₁)R₂; or are N-alicyclic or N-aromatic, where N-alicyclic denotes cyclic nitrogen containing compounds such as pyrrolidine, piperidine, imidazolidine, piperazine and N-aromatic denotes nitrogen containing heteroaromatic ring compounds such as pyrrole, pyridine, imidazole and pyrazine; X is phosphoric acid or pyrophosphoric acid, q is 1, 2, 3, or 4, and a is 1, 2, 3, or 4; provided that at least one of R₁, R₂, and R₃ has an amino end-group;

and wherein the metallic phosphite or hydrogen phosphite salt refers to a salt containing a metallic cation and one anion of HPO₃²⁻ or H₂PO₃⁻.

[0009] The Applicant has surprisingly found out that, by the aforementioned process, a melamine derivative mixture can be produced, which offers excel flame retardant properties and helps retaining good mechanical properties of the polymer it adds to. Particularly, in the flame retardant performance test, the melamine derivative mixture produced by the above process shows a better stability and polymer compatibility compared to the commercial MPP retardant, and can be effective as both vapour-phase and condensed-phase flame retardants. Moreover, comparing to the commercial MPP, the melamine mixture obtained from the process of the invention is also found to be less acidic in the aqueous solution, which gives a better compatibility in resin matrix.

[0010] Thus, in another aspect of the invention, it is directed to a melamine derivative mixture produced by the abovementioned process, or a

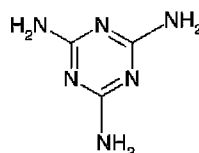
melamine derivative mixture that is characterized by:

- (i) containing metal element in a range between 1 to 20 wt%, phosphorus element in a range between 5 and 25 wt%, and nitrogen element in a range between 15 and 40 wt%, based on the total weight of the melamine derivative mixture; and
- (ii) having a mixture of phosphorus species containing P(III) in a molar percentage between 5% and 100%.

[0011] In yet another aspect of the present invention, it is directed to use of a reaction between at least one Compound (N) and a metallic phosphite or hydrogen phosphite salt in an aqueous solution to produce a flame retardant, wherein the Compound (N) and the metallic phosphite or hydrogen phosphite salt are as defined above.

[0012] Suitable Compound (N) for the present invention may be selected from a group consisting of: melamine, melamine cyanurate, melamine phosphate compounds, dimelamine phosphate compounds, melamine pyrophosphate compounds, melem, melam, melon, ammeline, ammelide and the like. In a preferred embodiment, the Compound (N) is melamine.

[0013] For the purpose of the present invention, the compound of “melamine” refers to a compound of the formula (III):



(III).

[0014] In accordance with the present invention, a metallic phosphite or hydrogen phosphite salt refers to a salt containing a metallic cation and one anion of HPO_3^{2-} or H_2PO_3^- , wherein the metallic cation may be derived from a metal selected from the group consisting of alkali metals, alkaline earth metals, and transition metals. Examples of the metallic phosphite or hydrogen phosphite salt include Li_2HPO_3 , LiH_2PO_3 , Na_2HPO_3 , NaH_2PO_3 , K_2HPO_3 , KH_2PO_3 , CaHPO_3 , $\text{Ca}(\text{H}_2\text{PO}_3)_2$, ZnHPO_3 , $\text{Zn}(\text{H}_2\text{PO}_3)_2$, MgHPO_3 , $\text{Mg}(\text{H}_2\text{PO}_3)_2$, $\text{Al}_2(\text{HPO}_3)_3$, and $\text{Al}(\text{H}_2\text{PO}_3)_3$, of which CaHPO_3 is preferred.

- [0015] In one embodiment of the present invention, the Solution (S) is an aqueous solution comprising the metallic phosphite or hydrogen phosphite salt.
- [0016] Normally, in the step (i) of the above-described process invention, the Solution (S) is acidic and has a pH value preferably between 1.0 to 6.0, more preferably between 1.5 to 4.5. As used throughout the application, the term "acidic" refers to a pH value of less than about 7, and the pH value refer to the pH of aqueous phases. The pH value of the Solution (S) can be adjusted by judiciously adding to it an acid or a base. If the Solution (S) has a pH value higher than the desired pH value, then the pH value is adjusted by the addition of an appropriate acid (e.g. HCl, HNO₃, H₃PO₃, H₃PO₂ or H₃PO₄). Conversely, if the Solution (S) has a pH value lower than the desired pH value, then the pH value is adjusted by the addition of an appropriate base (e.g. NaOH, KOH, Ca(OH)₂, or NH₃).
- [0017] In the step (ii), the reaction of the Compound (N) with Solution (S) is typically carried out at a temperature between 5°C and 100°C, preferably between 15°C and 50°C, and more preferably at a room temperature between 15°C and 25°C.
- [0018] The reaction time of step (ii) of the process invention can vary from 15 minutes to 3 hours, preferably from 30 minutes to 1 hour, and is chosen to be a sufficient period for producing the desired reaction mixture in adequate yield. Specially, the reaction time of step (ii) of the process invention is influenced to a significant degree by the reaction temperature, the concentration and choice of reactants, the presence of a catalyst, and other factors in step (ii) which are selected by one skilled in the art.
- [0019] Preferably, for the reaction in said step (ii), the molar ratio of Compound (N) to the sum of phosphite and hydrogen phosphite salt in the Solution (S) is within the range of 1:5 to 5:1, preferably 1:2 to 2:1, and more preferably 1.1:1 to 1:1.1.
- [0020] In the step (iii) of the process invention, the reaction mixture obtained in step (ii) is separated by a suitable solid-liquid separation method to obtain a solid phase, wherein the solid-liquid separation method may be filtration, spray drying or the like.

- [0021] In the following step (iv), the solid phase separated from step (iii) is heated at a temperature between 150°C and 500°C and in the presence of an oxidant. Notably, the step (iv) generally results in a dry loss between 10 and 40% wt, on the basis of the weight of the solid phase separated from step (iii).
- [0022] The heating temperature set in step (iv) is generally between 150°C and 500°C, preferably between 200°C and 400°C, and more preferably between 300°C and 380°C.
- [0023] The oxidant used in step (iv) may be selected from air, oxygen, gaseous oxidant precursors such as oxides of nitrogen (N_xO_y) and ozone, or other gaseous oxidants commonly used in the art.
- [0024] The heating time in step (iv) is typically selected to be 1 to 8 hours, preferably between 2 to 4 hours, depending on the heating temperature, the presence of a catalyst, and other conditions employed. Typically, the heating time in said step (iv) is selected by one skilled in the art to obtain a dry loss between 10 and 40% wt, based on the weight of the solid phase separated from step (iii).
- [0025] The present invention also relates to a product susceptible to be obtained by the inventive process as afore-described.
- [0026] Elemental analysis of the final product obtained after said step (iv) reveals that the thus resulted melamine derivative mixture is characterized by:
- (i) containing metal element in a range between 1 to 20 wt%, phosphorus element in a range between 5 and 25 wt%, and nitrogen element in a range between 15 and 40 wt%, based on the total weight of the melamine derivative mixture; and
 - (ii) having a mixture of phosphorus species containing P(III) species in a molar percentage between 5 and 100%.
- [0027] It has been found that the melamine derivative mixture according to the present invention provides enhanced stability. The stability of the mixture can be evaluated by measuring the decomposition onset of the mixture by thermo gravimetric analysis (TGA). The procedure of such analysis is well known in the art. In one embodiment, the melamine derivative mixture has a TGA temperature for 3% weight loss which is 300°C or higher under N_2

atmosphere. In a preferred embodiment, the melamine derivative mixture has a TGA temperature for 3% weight loss which is 330°C or higher under N₂ atmosphere. Generally, the heating rate of the TGA analysis is 10°C per min.

[0028] According to yet another aspect of the present invention, there is provided a polymer composition [Composition (P)] comprising at least one polymer and a melamine derivative mixture as afore-described.

[0029] Typically, the at least one polymer in the Composition (P) is selected from the group consisting of polyphenylene ethers, polyamides such as PA66, PA6, PA610, or high-temperature polyamides (PPA/ PA4.6/ PA9T/ PA66.6T/ PA10T/ PA6.6T and blends of polyamides, such as PA/ PET, PA/ ABS or PA/PP), polyesters, polycarbonates, epoxy resins; phenolic resins; acrylonitrile butadiene styrene (ABS); styrene acrylonitrile (SAN); mixtures of high impact polystyrene (HIPS) and polyphenylene ethers (such as PPO/HIPS); Styrene Butadiene Rubber and lattices (SBR and SB); and Halogenated polymers such as polyvinylchloride (PVC), and mixtures and blends of these polymers, expandable Polystyrene (EPS), and polybutylene terephthalate (PBT).

[0030] Moreover, the Composition (P) may further comprise one or more additional flame retardant additives, which could enhance its flame retardancy properties such as endothermic degradation, thermal shielding, dilution of gas phase, dilution of combustible portion, and radical quenching.

[0031] The additional flame retardant additive in the Composition (P) are notably described in US 6344158 , US 6365071 , US 6211402 , and US 6255371 .

[0032] Preferably, the additional flame retardant additive(s) used in the Composition (P) is selected from the group comprising:

A) Phosphorous containing flame retardant additives, such as:

- phosphine oxide such as for example triphenylphosphine oxide, tri-(3-hydroxypropyl) phosphine oxide and tri-(3-hydroxy-2-methylpropyl) phosphine oxide;
- phosphonic acids and their salts, and phosphinic acids and their salts, such as for example phosphinic acid of zinc, magnesium,

calcium, aluminium or manganese, notably aluminium salt of diethylphosphinic acid, aluminium salt of dimethylphosphinic acid, or zinc salt of dimethylphosphinic acid;

- cyclic phosphonates, such as diphosphate cyclic esters that is for example Antiblaze 1045;
- organic phosphates such as triphenylphosphate;
- inorganic phosphates such as ammonium polyphosphates and sodium polyphosphates; and
- red phosphorous, that can may be found under several shapes such as stabilized, coated, as a powder,

B) Nitrogen containing flame retardant additives, such as: triazines, cyanuric acid and/or isocyanuric acid, melamine or its derivatives such as cyanurate, oxalate, phthalate, borate, sulfate, phosphate, polyphosphate and/or pyrophosphate, condensed products of melamine such as melem, melam, melon, tris(hydroxyethyl) isocyanurate, benzoguanamine, guanidine, allantoin and glycoluril,

C) Halogen containing flame retardant additives, such as:

- Bromine containing flame retardant additives, such as polybromodiphenyloxydes (PBDPO), brominated polystyrene (BrPS), poly(pentabromobenzylacrylate), brominated indane, tetradecabromodiphenoxybenzene (Saytex 120), ethane-1,2-bis(pentabromophenyl) or Saytex 8010 of Albemarle, tetrabromobisphenol A and brominated epoxy oligomers. Notably can be used the following compounds: PDBS-80 from Chemtura, Saytex HP 3010 from Albemarle or FR-803P from Dea Sea Bromine Group, FR-1210 from Dea Sea Bromine Group, octabromodiphenylether (OBPE), FR-245 from Dead Sea Bromine Group, FR-1025 from Dead Sea Bromine Group and F-2300 or F2400 from Dead Sea Bromine Group; and

- Chlorine containing flame retardant additives, such as Dechlorane plus® from OxyChem (CAS 13560-89-9), and

D) Inorganic flame retardant additives, such as antimony trioxide, aluminium hydroxide, magnesium hydroxide, cerium oxide, boron containing compounds such as calcium borate.

- [0033] These above-listed flame retardant additive compounds may be used alone or in combination in the Composition (P). Charring agents and charring catalysts may also be added if necessary.
- [0034] Furthermore, the Composition (P) may further comprise fillers and reinforcing materials and/or other additives, such as lubricants (e.g. stearic acid or stearate salts such as calcium stearate), glass fibers, or antidripping agents such as poly(tetrafluoroethylene), e.g. PTFE SN3306.
- [0035] Additionally, the Composition (P) may also comprise additives normally used for the manufacture of polymer compositions, such as plasticizers, nucleating agents, catalysts, light and/or thermal stabilizers, antioxidants, antistatic agents, colorants, pigments, matting agents, conductive agents such as carbon black, molding additives or the like.
- [0036] For the preparation of the Composition (P), the fillers and additives may be added by any conventional means, e.g. during the polymerization or as a molten mixture. Preferably, the additives are added to the polymer in a melt process, such as during a melt extrusion step. Alternatively, the additives can be added to the polymer in a solid process, in a mechanical mixer, to produce a solid mixture that is subsequently melted, for example by extrusion process.
- [0037] The Composition (P) may be used as raw material in the field of plastics processing, such as for the preparation of articles formed by injection molding, by injection/ blow-molding, by extrusion or by extrusion/blow-molding. According to one customary embodiment, the Composition (P) is extruded in the form of rods, for example in a twin-screw extrusion device, said rods then being chopped into granules. The molded components are then prepared by melting the granules produced above and feeding the molten composition into injection-molding devices.
- [0038] As articles made from the Composition (P), examples include vehicle parts such as tubes, tanks, bodywork components, or components under the engine hood, as well as articles for the electrical and electronics applications, such as connectors.
- [0039] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of

the present application to the extent that it may render a term unclear, the present description shall take precedence.

[0040] The present invention will be further illustrated with reference to the following examples.

Description of embodiments

[0041] Materials

PA 66: an aliphatic polyamide obtained from Solvay Advanced Polymers;

PBT 1200: a polybutylene terephthalate resin obtained from Taiwan Changchun Ltd;

Exolit OP1230: aluminium phosphinate from Clariant GmbH

MPP (Melapur-200): from BASF

[0042] Example 1

78g H_3PO_3 was added to a mixture of 70.86g $\text{Ca}(\text{OH})_2$ and 400g H_2O under stirring. Subsequently, the resulting mixture was stirred at 40°C for 2.5h, then filtrated to obtain a solid mixture comprising calcium phosphite. The solid mixture was washed by using Di water and dried at 105°C for 3h.

[0043] A 250 mL reactor equipped with mechanical stirrer was charged with 120 g water and 30.46g of a calcium phosphite mixture obtained as mentioned above. Under stirring, 53.3g of a 85% orthophosphate acid solution was added into the resulting mixture at room temperature. After addition, the mixture was stirred for half an hour and then was filtered to remove unsolvable solid to get a clean solution. Then 58g melamine was slowly added into the filtrate with stirring for another 1 hour reaction. After that, this mixture was evaporated to remove all water to obtain a white solid. This white solid was heated at 330°C for 3 hours, with a weight loss of 22%, to convert into a calcium melamine phosphorous salt. The thus obtained calcium melamine phosphorous salt, by elemental analysis using a gas chromatographic system, contained 27.68% of N, 12.24% of C, 2.40% of H, 19.68% of P%, and 7.09% of Ca by weight. The percentage of remaining oxygen element, by calculation, is 30.91% by weight in the calcium melamine phosphorous salt. Accordingly, based on the overall valence balance, the valence of the phosphorous element in the calcium

melamine phosphorous salt can be calculated by the following formula (a):

$$\frac{(2 \times O\%)/16 + (3 \times N\%)/14 - (4 \times C\%)/14 - (1 \times H\%)/1 - (2 \times Ca\%)/40}{P\% \times 31}$$

(a),

to be 4.66. From this valence value, the P(III) molar percentage in the phosphorus species of the calcium melamine phosphorous salt can be calculated to be 17%.

[0044] Further analysis revealed that, a 10wt% aqueous slurry of the calcium melamine phosphorous salt had a pH of 5.4, and the 10wt% aqueous solution of MPP had a pH measured to be 5.0. Thus, compared to MPP, the calcium phosphorous salt obtained in this Example is less acidic and thus gives a better resin matrix compatibility. Moreover, TGA analysis of the salt product of this Example indicated that there was 3% weight losing at 383°C under N₂ atmosphere.

[0045] Example 2

A 500 mL reactor equipped with mechanical stirrer was charged with 400g water and 60g of a calcium phosphite mixture. Under stirring, 91.34g of a 38% hydrochloride acid solution was added into the resulting mixture at room temperature. After addition, the mixture was stirred for half an hour and then was filtered to remove unsolvable solid to get a clean solution. Then 144g melamine was slowly added into the filtrate with stirring for another 1 hour reaction. After that, this reaction mixture was filtered to remove aqueous solution and obtained a white solid. This white solid was then heated at 330°C for 3 hours, with a weight loss of 23%, to convert into a calcium melamine phosphorous salt. The thus obtained calcium melamine phosphorous salt, by elemental analysis, contained 41.55% of N, 7.27% of P%, and 7.98% of Ca. The percentage of remaining oxygen element, by calculation, is 23.67% by weight in the calcium melamine phosphorous salt. Accordingly, based on the formula (a) above, this salt product has a phosphorous valence of 4.41, corresponding to a P(III) percentage of 29.5% in its phosphorus species.

[0046] Further analysis revealed that, a 10wt% aqueous slurry of the calcium melamine phosphorous salt obtained in this Example had a pH of 5.2, notably less acidic than a 10wt% aqueous solution of MPP and thus offers a comparatively better compatibility in resin matrix. Moreover, TGA analysis of the salt product indicated that there was 3% weight losing at 369°C under N₂ atmosphere.

[0047] **Example 3**

A 500 mL reactor equipped with mechanical stirrer was charged with 400 g water and 65.5g of a calcium phosphite mixture. Under stirring, 91.34g of a 38% hydrochloride acid solution was added into the resulting mixture at room temperature. After addition, the mixture was stirred for half an hour and then was filtered to remove unsolvable solid to get a clean solution. Then 144g melamine was added slowly into the filtrate with stirring for another one hour reaction. After that, this mixture was filtered to remove aqueous solution to obtain a white solid. This white solid was heated at 330°C for 3 hour to produce a calcium melamine phosphorous salt, with 23% weight loss during heating. The thus obtained calcium melamine phosphorous salt, by elemental analysis, contained 31.5% N, 16.0% C, 2.60% H, 14.2% P% and 7.98% Ca. The percentage of remaining oxygen element, by calculation, is 27.72% by weight in the calcium melamine phosphorous salt. Accordingly, based on the formula (a) above, this salt product has a phosphorous valence of 4.11, corresponding to a P(III) percentage of 44.5% in its phosphorus species.

[0048] Further analysis revealed that, a 10wt% aqueous slurry of the calcium melamine phosphorous salt obtained in the above procedure also had a pH greater than 5, notably less acidic than a 10wt% aqueous solution of MPP and thus offers a comparatively better compatibility in resin matrix. Moreover, TGA analysis of this salt product indicated that there was 3% weight losing at 335°C under N₂ atmosphere.

[0049] **Example 4**

- [0050] A 500 mL reactor equipped with mechanical stirrer was charged with 400g water and 65.5g of a calcium phosphite mixture. Under stirring, 66 g of a 67% nitrate acid solution was added into the resulting mixture at room temperature. After addition, the mixture was stirred for half an hour and then was filtered to remove unsolvable solid to get a clean solution. Then 106g melamine was slowly added into the filtrate with stirring for another one hour reaction. After that, this mixture was filtered to remove all aqueous solution to obtain a white solid. This white solid was heated at 330°C for 3 hours to produce a calcium melamine phosphorous salt, with 21% weight loss during heating. The thus obtained calcium melamine phosphorous salt, by elemental analysis, contained 27.68% N, 13.21% C, 2.39 H%, 18.55% P% and 7.89% Ca. The percentage of remaining oxygen element, by calculation, is 30.28% by weight in the calcium melamine phosphorous salt. Accordingly, based on the formula (a) above, this salt product has a phosphorous valence of 4.23, corresponding to a P(III) percentage of 38.5% in its phosphorus species.
- [0051] Further analysis revealed that, a 10wt% aqueous slurry of the calcium melamine phosphorous salt obtained in the above procedure also had a pH greater than 5, notably less acidic than a 10wt% aqueous solution of MPP and thus offers a comparatively better compatibility in resin matrix. Moreover, TGA analysis of this salt product indicated that there was 3% weight losing at 400°C under N₂ atmosphere.
- [0052] **Test Example 1: Determination of the Flame Retardant Capacity of Examples 1-4**
- [0053] The calcium melamine phosphorous salts obtained from Examples 1-4 were each tested as flame retardants for epoxy resins. Specifically, various resin samples were prepared by mixing the calcium melamine phosphorous salts with glass fiber and selected monomer (see Table 1), in the injection moulding machine, subsequently cured and then extruded in granulate form. For comparison, additional two resin samples were prepared in the same manner, only without addition of the calcium melamine phosphorous salts according to the invention (see CE 1 and CE

2 in Table 1). The flame retardancy performance of these resin samples were tested according to the UL94 vertical burning test procedure, using a sample thickness of both 1.6 mm and 0.8 mm.

Table 1

Trail No.	1	2	3	4	5	6
Melamine Calcium phosphorous salt	Ex. 1	Ex. 2	Ex. 3	Ex.4	CE1	CE2
<i>Resin formulation (wt%)</i>						
PA66 (26A)	45	40			70	
PBT (1200)/%			45	40		70
Glass fibers/%	30	30	30	30	30	30
Melamine Calcium phosphorous salt/%	25	30	25	30		
<i>Flame Retardancy Test (UL-94 rating)</i>						
for 1.6mm-thick resin	v0	v0	v0	v0	HB	HB
for 0.8mm-thick resin	v0	v0	v0	v0	HB	HB

[0054] As seen from Table 1, the resin samples incorporating calcium melamine phosphorous salts of Examples 1-4 each achieved V0 rating in the UL94 vertical burning test procedure, showing a satisfactory fire protection level and much improved fire retardancy compared to the resins without salt addition (i.e. CE1 and CE2).

[0055] **Test Example 2: Comparison of the Flame Retardant Capacity of Example 1 and MPP**

[0056] For comparison, resin samples containing a given amount of MPP or the calcium melamine phosphorous salt of Example 1 were tested for flame retardancy. Specifically, two resin samples were prepared by mixing MPP (melapur-200) or the salt product of Example 1 into a combination of glass fiber, selected monomers (see below) and $Zn_3(BO_3)_2$, with an equivalent weight percentage of each component, subsequently cured and extruded in a granulate form. The flame retardancy performance and the physical

properties of both resin samples were tested and the results are indicated in the Table 2 below.

[0057]

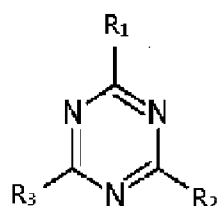
Table 2

Trail No.	7	8
<i>Resin Formulation (wt%)</i>		
PA66 (26A)	52	52
Glass fibers	30	30
Exolit OP1230	11.6	11.6
Melamine Calcium phosphorous salt (Ex. 1)	5.8	
MPP (Melapur-200)		5.8
Zn ₃ (BO ₃) ₂	0.6	0.6
<i>Flame Retardancy Test (UL-94 rating)</i>		
for 1.6mm-thick resin	v0	v0
for 0.8mm-thick resin	v0	v0
<i>Resin Properties</i>		
Tensile strength (Mpa)	153	130
Elongation (%)	2.70	2.30
Notched Charpy impact strength (KJ/m ²)	8.78	6
Charpy impact strength (KJ/m ²)	63.38	55

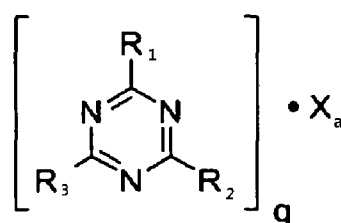
[0058] As seen from Table 2, the resin sample incorporating the calcium melamine phosphorous salt of Example 1 achieved equally good fire retardancy as the MPP-added sample, and notably improved physical properties than the latter.

Claims

1. A process for manufacturing a melamine derivative mixture, comprising at least the following steps:
 - (i) providing an aqueous solution of a metallic phosphite or hydrogen phosphite salt [Solution (S)] with a pH of between 1 and 7;
 - (ii) mixing the Solution (S) with at least one nitrogen-containing compound [Compound (N)] at a temperature between 5°C and 100°C, to obtain a reaction mixture;
 - (iii) separating the reaction mixture obtained in step (ii) by a solid-liquid separation method to obtain a solid phase; and,
 - (iv) heating the solid phase obtained in step (iii), at a temperature between 150°C and 500°C in the presence of an oxidant, to obtain the melamine derivative mixture,
 wherein the Compound (N) is a compound of formula (I) or formula (II)



(I)



(II)

wherein: R_1 , R_2 , and R_3 are independently hydrogen, hydroxyl, amino, or mono- or di- C_1 - C_8 alkyl amino; or C_1 - C_8 alkyl, C_5 - C_{16} cycloalkyl, -alkylcycloalkyl, each being optionally substituted by a hydroxyl or a C_1 - C_4 hydroxyalkyl, C_2 - C_8 alkenyl, C_1 - C_8 alkoxy, -acyl, -acyloxy, C_6 - C_{12} aryl, -OR₁ and -N(R₁)R₂; or are N-alicyclic or N-aromatic, where N-alicyclic denotes cyclic nitrogen containing compounds such as pyrrolidine, piperidine, imidazolidine, piperazine and N-aromatic denotes nitrogen containing heteroaromatic ring compounds such as

pyrrole, pyridine, imidazole and pyrazine; X is phosphoric acid or pyrophosphoric acid, q is 1, 2, 3, or 4, and a is 1, 2, 3, or 4; provided that at least one of R₁, R₂, and R₃ has an amino end-group;

and wherein the metallic phosphite or hydrogen phosphite salt refers to a salt containing a metallic cation and one anion of HPO₃²⁻ or H₂PO₃⁻.

2. The process of claim 1, wherein the metallic phosphite or hydrogen phosphite salt is selected from a group consisting of Li₂HPO₃, LiH₂PO₃, Na₂HPO₃, NaH₂PO₃, K₂HPO₃, KH₂PO₃, CaHPO₃, Ca(H₂PO₃)₂, ZnHPO₃, Zn(H₂PO₃)₂, MgHPO₃, Mg(H₂PO₃)₂, Al₂(HPO₃)₃, and Al(H₂PO₃)₃.
3. The process of claim 2, wherein the metallic phosphite is CaHPO₃.
4. The process of any one of the preceding claims, wherein the Compound (N) is selected from a group consisting of: melamine, melamine cyanurate, melamine phosphate compounds, dimelamine phosphate compounds, melamine pyrophosphate compounds, melem, melam, melon, ammeline, and ammelide.
5. The process of claim 4, wherein the Compound (N) is melamine.
6. The process of any one of the preceding claims, wherein in step (i), the Solution (S) is acidic and has a PH value between 1.0 to 6.0, preferably between 1.5 and 4.5.
7. The process of any one of the preceding claims, wherein in step (ii), the molar ratio of Compound (N) to the phosphite and/or hydrogen phosphite salt in the Solution (S) is within the range of 1:5 to 5:1, preferably 1:2 to 2:1, and more preferably 1.1:1 to 1:1.1.
8. The process of any one of the preceding claims, wherein in step (iv), the heating temperature is between 200°C and 400°C, and preferably between 300°C and 380°C.
9. The process of any one of the preceding claims, wherein in step (iv), the oxidant used is selected from air, oxygen, nitrogen (N_xO_y) and ozone.
10. The process of any one of the preceding claims, wherein in step (iv), the heating time is from 1 to 8 hours, preferably between 2 to 4 hours, to obtain a dry loss between 10 and 40% wt, based on the weight of the solid phase separated from step (iii).
11. A product susceptible to be obtained by the process of any one of the preceding claims.

12. Use of a reaction between at least one Compound (N) and a metallic phosphite or hydrogen phosphite salt in an aqueous solution to produce a flame retardant, wherein the Compound (N) and metallic phosphite or hydrogen phosphite salt are as defined in claim 1.
13. A melamine derivative mixture characterized by:
 - (i) containing metal element in a range between 1 to 20 wt%, phosphorus element in a range between 5 and 25 wt%, and nitrogen element in a range between 15 and 40 wt%, based on the total weight of the melamine derivative mixture; and
 - (ii) having a mixture of phosphorus species containing P(III) species in a molar percentage between 5 and 100%.
14. The melamine derivative mixture according to claim 13, wherein the melamine derivative mixture has a TGA temperature for 3% weight loss which is 300°C or higher under N₂ atmosphere.
15. A polymer composition [Composition (P)] comprising at least one polymer and a melamine derivative mixture obtained by any one of claims 1 to 10.
16. A polymer composition [Composition (P)] comprising at least one polymer and a melamine derivative mixture of claim 13 or 14.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/084589

A. CLASSIFICATION OF SUBJECT MATTER

C08K 5/51(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08K5/49, C08K5/51

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPLEPODOC,CA,CNPAT,CNKI: melamine, phosphite, oxidant, reaction, heating, CaHPO_3 , oxygen, nitrogen, ozone

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4879327 A (ATOCHEM) 07 November 1989 (1989-11-07) Example 2	1-16

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

15 October 2014

Date of mailing of the international search report

19 November 2014

Name and mailing address of the ISA/CN

**STATE INTELLECTUAL PROPERTY OFFICE OF THE
P.R.CHINA(ISA/CN)
6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088 China**

Authorized officer

REN, Weihua

Facsimile No. (86-10)62019451

Telephone No. (86-10)82246917

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2014/084589

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	4879327	A	07 November 1989	IE	880961	L	30 September 1988
				JP	S63277651	A	15 November 1988
				DE	3878960	D1	15 April 1993
				JP	2804917	B2	30 September 1998
				DK	176188	D0	30 March 1988
				DK	172305	B1	09 March 1998
				FR	2620119	B1	24 April 1992
				EP	0286478	A1	12 October 1988
				ES	2054839	T3	16 August 1994
				DE	3878960	T2	30 June 1994
				PT	87132	A	01 April 1988
				PT	87132	B	31 July 1992
				DK	176188	A	01 December 1988
				IE	63370	B1	19 April 1995
				CA	1334093	C	24 January 1995
				JP	2544315	B2	16 October 1996
				JP	H08245598	A	24 September 1996
				FR	2620119	A1	10 March 1989
				EP	0286478	B1	10 March 1993