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(54) Title: FLAME RETARDANT POLYMER COMPOSITIONS

(57) Abstract: The instant invention relates to polymer compositions comprising a calcium hypophosphite, an aluminium inorganic salt and an additive improving the flame retardant properties of the composition other than the hypophosphite salts.

FLAME RETARDANT POLYMER COMPOSITIONS

Field Of The Invention

The instant invention relates to polymer compositions comprising a calcium hypophosphite, an aluminium inorganic salt and an additive improving the flame retardant properties of the composition other than the hypophosphite salts.

Background Of The Invention

Halogen free flame retardant additives are of increasing interest in reinforced and unreinforced polymers, more particularly thermoplastic polymers, for their ability to provide flame retardant properties while remaining environmentally benign. Among those halogen free flame retardants, hypophosphite salts or inorganic phosphinates are known as good flame retardant additives for polymers. However, phosphinic acid salts may cause the degradation of the polymer to which they are added as mentioned for example in WO 2009/010812.

Moreover, hypophosphite salts are known to have a tendency to generate phosphine at elevated temperatures at which they are processed, and phosphine is spontaneously flammable, highly toxic and strong irritant as mentioned for example in US 2007/0173572.

The proposed solution taught by US 2007/0173572 is to scavenge the generated phosphine by adding a phosphine suppressing additive which can be a specific polymer, an amide, imide, cyanurate, phosphazine among other products. The drawback of that method is that another additive is added to the polymer composition which can only neutralize the phosphine without preventing the generation of that phosphine.

Thus, there exists a constant need in the market of FR agents in having hypophosphites salts without the above drawbacks and that premature instability or at a much lower degree. There is a need to propose polymer compositions containing hypophosphite salts sufficiently stabilized in order not to generate a dangerous amount of phosphine.

Detailed Description Of The Invention

After extensive research and development work, the Applicant has surprisingly found out and developed a flame retardant composition at least comprising a calcium hypophosphite and an aluminium inorganic salt. These compounds are especially suitable for rendering polymers flame-retardant, in particular in association with some specific additives which lead to especially good properties in terms of fire retardant properties.

The current invention actually relates to a flame retardant (“FR”) polymer composition comprising at least one polymer and:

(a) a calcium hypophosphite,

(b) an aluminium inorganic salt, and

(c) an other additive improving the flame retardant properties of the composition.

Preferably, said polymer composition is comprising at least one polymer and:

(a) a calcium hypophosphite, wherein the hypophosphite salt is so heat stabilized that ,when it is heated during 3 hours at 298°C under a flow of argon flushing at rate 58 mL/mins, it generates less than 0.5 mL of phosphine per gram of hypophosphite salt;

(b) an aluminium inorganic salt, and

(c) an other additive improving the flame retardant properties of the composition.

The instant composition preferably provides a V0 rate with specimens of 1.6 mm according to UL94 standard.

Polymers

Polymers used in the compositions of the present invention are preferably thermoplastic polymers.

Typically, the polymer present in a flame retardant polymer composition of the invention is selected from the group consisting in polyphenylene ethers, polyamides, polyesters, polycarbonates, epoxy resins, phenolic resins, acrylonitrile butadiene styrene (ABS), styrene acrilonitrile (SAN), polystyrene such as high impact polystyrene (HIPS), polyphenylene ethers such as PPO, styrene butadiene rubber (SBR), halogenated polymers such as polyvinylchloride (PVC), and mixtures and blends of these polymers.

Polyamides are preferably PA66, PA6, PA11, PA12, PA6.10, high temperature polyamides such as PPA, PA4.6, PA9T, PA66.6T, PA10T, PA6.6T and blends of polyamides, such as PA/PET, PA/ABS or PA/PP.

Polyesters may be polyethylene terephthalate (PET) or polybutylene terephthalate (PBT).

The composition of the present invention may comprise from 30 to 80 % by weight of polymer, according to the total weight of the composition.

(a) Calcium hypophosphite salt

The calcium hypophosphite salt can be prepared by any manufacturing process. The calcium hypophosphite can be prepared for example from white phosphorus (P_4) reacted under alkaline conditions with calcium hydroxide or calcium oxide and water as taught by US 5,225,052. It is also possible to obtain calcium hypophosphite by reaction of a calcium salt or simply from lime as taught by Chinese patent CN101332982, with hypophosphorous acid.

For example the lime suspension is simply neutralized with hypophosphorous acid, the impurities are removed by filtration and the product isolated in a same way as previously described. It is also possible to obtain calcium hypophosphite from other metallic hypophosphites or the acid by ion exchange process. According to an interesting embodiment, the starting hypophosphite salt comes from the reaction of calcium oxide, water and hypophosphorous acid.

The calcium hypophosphite present in the compositions of the invention may be so heat stabilized that ,when it is heated during 3 hours at 298°C under a flow of argon flushing at rate 58 mL/min, it generates less than 0.5 mL of phosphine per gram of calcium hypophosphite. Preferably according to this test it generates less than 0.1, more preferably less than 0.05, particularly less than preferably less than 0.02 mL of phosphine per gram of calcium hypophosphite. The heat stability of the calcium hypophosphite salt at 298°C may especially be tested by using a Gastec tube to detect PH3, as illustrated in the appended examples.

Generally, a flame retardant polymer composition according to the invention comprises the calcium hypophosphite in an amount of 0.1 to 30 weight percent, preferably from 1 to 25 weight percent, for example from 5 to 20 weight percent, based on the total weight of the flame retardant polymer composition.

The heat stabilized calcium hypophosphite which is present in the flame retardant polymer composition according to the instant invention may especially be obtained from a starting calcium hypophosphite, by a process for stabilizing said hypophosphite salt, comprising the steps of:

a) washing the starting hypophosphite salt at least one time, preferably 2 or 3 times, under a controlled value of pH comprised between 4 and 11, preferably between 5 and 8, said hypophosphite salt being in an aqueous solution and/or in a solid state, and

b) drying the hypophosphite salt as obtained after the washing operation(s) of step (a) under reduced pressure to remove the volatiles.

Advantageously, the heat stabilized calcium hypophosphite which is present in the flame retardant polymer composition according to the instant invention is obtained according to a process including the above step (a) and (b) and which further comprise, after step a) (and generally before step b)) the step a1) of:

a1) washing at least one time the hypophosphite salt with an organic solvent miscible with water.

The organic solvent used in step a) described above is preferably selected from the group comprising acetone, methanol, isopropanol, tetrahydrofurane, and acetonitrile.

According to a first possible embodiment, the starting hypophosphite salt which is used in step a) can be in the form of an aqueous solution, charged in a reactor and mixed with a mineral or an organic acid to obtain a slurry whose pH is set at a value of between 4 and 6.5, preferably 5 and 6.

The acid used in this connection is preferably selected from the group comprising hypophosphorous acid, citric acid, maleic acid, acetic acid, chlorhydric acid and sulphuric acid and, more preferably, the acid is hypophosphorous acid.

According to another embodiment, the starting hypophosphite salt of step a) may alternatively be in the form of an aqueous solution, charged in a reactor and mixed with a mineral or an organic base to obtain a slurry whose pH is set at a value of between 7.5 and 11, preferably 8 and 10. In that case the base is preferably selected from the group comprising sodium hydroxide, potassium hydroxide, calcium hydroxide, calcium oxide, magnesium oxide and magnesium hydroxide, even more preferably, the base is calcium hydroxide and/or calcium oxide.

The process for stabilizing the starting hypophosphite salt which is useful for preparing the polymer composition of the invention can be batch, continuous or semi-continuous and be performed in a close or open system under inert atmosphere. That inert atmosphere can be for example carbon dioxide, argon, or nitrogen.

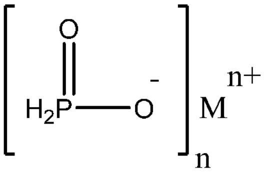
The process for stabilizing the starting hypophosphite salt can be performed under atmospheric pressure, under pressure or under vacuum.

Without linking the current invention to any theoretical rationale, it looks like most of the premature instability is due to the presence of problematic impurities. The quality of the calcium hypophosphite may be determined by detecting the remaining impurities using thermal analysis tools such as ARC (Adiabatic Reaction Calorimeter) and TGA (Thermal Gravimetric Analysis).

The test can be carried out at any stage during the heating process described before.

Another way to check the quality of the heat stabilized calcium hypophosphite used in the instant invention, is to perform a stability test at elevated temperature on the product, alone or mixed with plastic and measure the amount of phosphine generated during the test. It is also possible to measure the amount of phosphine generated when the product is compounded with plastics such as polyamide or polyester.

The calcium hypophosphite present in the composition according to the invention is preferably of the formula (1) below :



$$\left[H_2P(=O){-}O^- \right]_n M^{n+}$$

(1)

wherein :

n is 1, 2 or 3 ; and

M is a calcium.

Calcium hypophosphite may be surface coated by several compounds such as alkali-metal or alkali-earth hydrates; hydrotalcite or hydrotalcite-like compounds; and/or alkali-metal or alkali-earth organic acid salts, such as $Mg(OH)_2$, for example. Calcium hypophosphite can be preferably surface-coated by magnesium hydroxide, synthetic hydrotalcite, sodium benzoate, potassium benzoate, sodium stearate, and/or calcium stearate.

(b) Aluminium inorganic salt

The composition of the present invention also comprises an inorganic aluminum salt.

According to an embodiment of the invention, the aluminium salt is an inorganic salt, that may comprise at least a phosphorous or a sulfur atom.

Preferably, the inorganic aluminium salt is chosen in the group consisting of: aluminium ammonium sulphate, aluminium cerium oxide, aluminium cesium sulphate, aluminium hydroxide, aluminium metaphosphate, aluminium nitride, aluminium oxide, aluminium phosphate, aluminium hypophosphite, aluminium phosphate, aluminium potassium sulphate, aliuminium silicate, aluminium sulphate, aluminium sulfide and aluminium titanate.

Preferred aluminium inorganic salts of the present invention are chosen from: aluminium hypophosphite, aluminium phosphate, aluminium phosphite, aluminium sulfate.

The composition according to the invention may comprise an aluminium salt in an amount of 0.1 to 30 weight percent, preferably from 1 to 20 weight percent, for example from 5 to 20 weight percent, based on the total weight of the flame retardant polymer composition.

(c) Other FR additives

Different types of flame retardant additives may be used according to the invention. They can provide several mechanisms of function such as endothermic degradation, thermal shielding, dilution of gas phase, dilution of combustible portion, and radical quenching.

Flame retardant additives for polymer compositions are notably described in Plastics Additives, Gächter/Müller, Hansen, 1996, page 709 and passim. Useful Flame retardant additives are notably cited in the following patents: US6344158, US6365071, US6211402 and US6255371.

Flame retardant additives used in the composition of the instant invention are preferably chosen in 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.
- 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, phtalate, borate, sulfate, phosphate, polyphosphate and/or pyrophosphate, condensed products of melamine such as melem, melam, melon, tris(hydroxyethyl) isocyanurate, benzoguanamine, guanidine, allantoïne and glycoluril.

C) Halogen containing flame retardant additives, such as:

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

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

These compounds may be used alone or in combination. Charring agents and charring catalysts may also be used if necessary.

The composition according to the invention may comprise a additive c) in an amount of 0.1 to 30 weight percent, preferably from 1 to 20 weight percent, based on the total weight of the flame retardant polymer composition.

The composition according to the present invention may comprise 1 to 20 % by weight of melamine or melamine derivatives, such as melamine cyanurate, based on the total weight of the flame retardant polymer composition.

A composition according to the present invention may comprise 1 to 20 % by weight of a phosphinate salt, such as aluminium phosphinate, aluminium salt of diethylphosphinic acid and/or aluminium salt of dimethylphosphinic acid, based on the total weight of the flame retardant polymer composition.

Other additives & composition

In addition to the polymer and the heat stabilized hypophosphite salt, the compositions of the invention may further comprise fillers and reinforcing materials and/or other additives, such as plasticizers, nucleating agents, catalysts, light and/or thermal stabilizers, lubricants, antidriping agents, antioxidants, antistatic agents, colorants, pigments, matting agents, conductive agents, such as carbon black, molding additives or other conventional additives. Lubricants may be stearic acid or stearate salts such as calcium stearate. Antidriping agents may be poly(tetrafluoroethylene), notably PTFE SN3306 for example.

The composition of the invention preferably comprises reinforcing fibers such as glass fibers or carbon fibers. Notably the composition can comprise from 5 to 50 % by weight of reinforcing fibers, based on the total weight of the flame retardant polymer composition.

The composition of the present invention preferably comprises a polymer, notably polyester or polyamide and at least:

(a) 1-25 % by weight of a calcium hypophosphite, wherein the hypophosphite salt is so heat stabilized that ,when it is heated during 3 hours at 298°C under a flow of argon flushing at rate 58 mL/mins, it generates less than 0.5 mL of phosphine per gram of hypophosphite salt;

(b) 1-20 % by weight of an aluminium inorganic salt, and

(c) an other additive improving the flame retardant properties of the composition.

For the preparation of a polymer composition, the fillers and additives may be added to by any conventional means suitable, for instance during the polymerization or as a molten mixture. The additives are preferably added to the polymer in a melt process, in particular during a step of extrusion, or in a solid process in a mechanical mixer; the solid mixture may then be melted, for example by means of an extrusion process.

The compositions according to the invention may be used as raw material in the field of plastics processing, for example 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 modified polyamide 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.

As articles obtained from the composition according to the invention mention may, for example, be made of articles in the motor vehicle industry, such as components under the engine hood, bodywork components, tubes and tanks, or articles in the electrical and electronics field, such as connecters.

The invention will now be further illustrated by the following examples that refers to two distinct hypophosphite salts, namely : .

- CaHypo COM: calcium hypophosphite made from the commercial grade of calcium hypophosphite sourced from Shanghai lingfeng chemical reagent co., ltd.

- CaHypo HT : calcium hypophosphite so-called 'High Temperature' or 'HT', namely heat stabilized calcium hypophosphite according to the invention.

EXPERIMENTAL PART

EXAMPLE 1

CaHypo COM (102g) is charged in a reactor and mixed with water (161g). 50% hypophosphorous acid (34g) is then added slowly and the mixture is thoroughly stirred for 30 minutes and the pH is controlled between 4 and 6. Then, the slurry is filtered to afford 75g of solid. This solid is washed with water (40g) and then with acetone (75g). 57.8g of wet solid is thus obtained to finally afford 56g of dry CaHypo-HT after evaporation of the volatiles under reduced pressure overnight at room temperature.

EXAMPLE 2 Thermal aging test

2g of CaHypo COM and CaHypo HT from Example 1 are weighed and placed in separate glass vials. The vials are then placed into an oven pre-heated to 290°C under air. Pictures of the samples are then taken over time to compare the change of color. The pictures obtained, shown below, clearly indicate that CaHypo HT does not change color as quickly as the regular CaHypo commercial grade. The CaHypo COM material starts yellowing significantly between 1 to 5h while the CaHypo HT did not yellow before 8h. The yellowing of CaHypo is typically due to the formation of red phosphorus which is itself associated with the formation of phosphine.

The results are gathered in Table 1 below:

Table 1

Time	0h	1h	5h	8h	15h
Non-treated CaHypo	White	White	Pale yellow	Yellow	Dark yellow/orange
Stabilized CaHypo	White	White	White	Pale yellow	yellowish

EXAMPLE 3 Phosphine generation – Scrubber detection

For this experiment 2g of CaHypo (COM or HT from Example 1) are heated to 300°C for 30 minutes under a flow of argon. The out gases are bubbled through a 5% hydrogen peroxide solution to scrub phosphine that may be generated. The scrubber solution is then analyzed by Ion Chromatography (IC) to determine the level of phosphate. The phosphine generated is then calculated by assuming that all the phosphate detected is issued from phosphine. For CaHypo COM, a total of 555.8ppm of phosphine / g of CaHypo is detected while only 235ppm of phosphine / g of CaHypo is detected for CaHypo HT. Overall, under these conditions the amount of phosphine generated by CaHypo HT is reduced by about 60% compared to the commercial product.

EXAMPLE 4

For this experiment 2g of CaHypo (COM or HT from Example 1) are heated to 298°C under a flow of argon. The out gases are captured into gas bags and the concentration of phosphine is measured over time using Gastec tubes. The results (Table 2) clearly indicate that the amount of phosphine generated with CaHypo HT is up to 34 times lower which corresponds to a 97% reduction of the amount of phosphine generated compared to commercial CaHypo.

Table 2 – Phosphine generation

Time	Total Phosphine generated (mL) for 2g of CaHypo	
	CaHypo COM	CaHypo-HT (Example 1)
0.5 h	0.17	0.01
1.5 h	0.79	0.02
3.0 h	2.15	0.06

2 g sample heated to 298°C with argon flushing at rate 58 mL/mins

EXAMPLE 5 Water wash:

CaHypo COM (275g) is charged in 1L plastic bottle and mixed with water (119g) as well as ceramic balls (293g). The resulting mixture is rotated for 4h and the pH is controlled between 4-6. Then the balls are separated with wired filter. The white solid is washed with water (40g) and then three times with acetone to afford 242g of wet CaHypo-HT. The final product is dried under reduced pressure at room temperature to remove any volatile and afforded 240g of product.

EXAMPLE 6 Phosphine generation measuring PH_3 in gas

For this experiment 2g of CaHypo (COM or HT from Example 5) are heated to 298°C under a flow of argon. The out gases are captured into gas bags and the concentration of phosphine is measured over time using Gastec tubes. The results (Table 3) clearly indicated that the amount of phosphine generated with CaHypo HT is up to 140 times lower which corresponded to a 99.3% reduction of the amount of phosphine generated compared to commercial CaHypo.

Table 3 - Phosphine Generation

Time	Total Phosphine generated (mL)	
	CaHypo COM	CaHypo-HT (Example 5)
0.5 h	0.36	0.01
1.5 h	2.12	0.02
3.0 h	4.24	0.03

2 g sample heated to 298°C with argon flushing at rate 58 mL/mins.

EXAMPLE 7– Phosphine generation measuring PH_3 in gas – CaHypo + PA 6,6

In this experiment, 6g of PA6,6 are charged in a glass tube and heated to 298°C for 3h flushing with argon. Then 2g of CaHypo (COM or HT from Example 5) are added. After that, the out gases are captured into gas bags and the concentration of phosphine is measured over time using Gastec tubes. The results (Table 4) clearly indicate that the amount of phosphine generated with CaHypo HT is up to 74 times lower which corresponds to a 98.7% reduction of the amount of phosphine generated compared to the commercial CaHypo.

Table 4 - Phosphine generation with PA 6,6

Time	Total Phosphine generated (mL)	
	CaHypo COM	CaHypo-HT (Example 5)
0.5 h	0.18	0.02
1.5 h	1.06	0.05
3.0 h	7.42	0.10

2 g sample + 6g PA 6,6 heated to 298°C with argon flushing at rate 58 mL/mins.

EXAMPLE 8 Preparation of CaHypo-HT from CaO and HPA

Calcium oxide (39.2g, 0.7mol) is mixed with water (398g) under inert atmosphere. 50% hypophosphorous acid (129g, 0.98mol) is added slowly at room temperature while the pH is monitored. The pH is adjusted to 5-7 and the solution boiled for 3h. Then, the mixture is cooled down and a portion of it filtered to obtain 284g. This filtrate is pH adjusted to 6.5-7 and water is distilled off under reduced pressure to afford 252g of distillate. After cooling down the solution is filtered to afford 8.6g of CaHypo-HT. The product is dried under vacuum at 90°C overnight.

The product thus obtained is tested for phosphine generation by heating 2g of material to 298°C under argon while analyzing the off-gases for phosphine. The results indicated that after 30 minutes the total amount of phosphine generated is as low as 0.007mL which is 51 times lower that the amount detected for CaHypo COM in the same conditions. Overall, the phosphine generation is reduced by 98.1% compared to commercial CaHypo.

EXAMPLE 9– Recrystallization treatment:

CaHypo COM (418g) is dissolved in water (3012g) under inert atmosphere and heated to reflux. The pH of the solution is adjusted to 9-10 using lime and the mixture refluxed for 2h. After cooling down to room temperature the solution is filtered. The filtrate is then pH adjusted to between 6 and 7 using 50% hypophosphorous acid and then filtered again. The resulting solution is concentrated under reduced pressure until CaHypo precipitated. The solid thus obtained is filtered out at room temperature to afford 307g of wet material. After drying the product under reduced pressure at 120°C for 6h 297g of product is in hand.

EXAMPLE 10– Phosphine generation measuring PH_3 in gas

For this experiment 2g of CaHypo (COM or HT from Example 9) are heated to 298°C under a flow of argon. The out gases are captured into gas bags and the concentration of phosphine is measured over time using Gastec tubes. The results (Table 5) clearly indicate that the amount of phosphine generated with CaHypo HT is up to 70 times lower which corresponds to a 98.6% reduction of the amount of phosphine generated compared to the commercial CaHypo.

Table 5 – Phosphine generation

Time	Total Phosphine generated (mL)	
	CaHypo COM	CaHypo-HT (Example 10)
0.5 h	0.36	0.01
1.5 h	2.12	0.04
3.0 h	4.24	0.06

2 g sample heated to 298°C with argon flushing at rate 58 mL/mins.

EXAMPLE 11 Phosphine generation measuring PH_3 in gas – Grinded sample

CaHypo HT obtained in Example 9 is found to have a particle size superior to 100 microns. Some of this product is grinded using wet ball milling to reach a particle size inferior to 50 microns. The material thus obtained is then tested for phosphine evolution by heating 2g to 298°C under argon and by analyzing the off-gases for phosphine. The results are summarized in Table 6 and compared to the results obtained with CaHypo COM in the same conditions. The amount of phosphine generated is 35 times lower with CaHypo HT which corresponded to 97.3% reduction compared to the commercial product. This experiment shows that adjusting the particle size of CaHypo HT does not alter its performance.

Table 6 – Phosphine generation

Time	Total Phosphine generated (mL)	
	CaHypo COM	CaHypo-HT (Example 11)
0.5 h	0.36	0.02
1.5 h	2.12	0.05
3.0 h	4.24	0.12

2 g sample heated to 298°C with argon flushing at rate 58 mL/mins.

EXAMPLE 12 – Compounding using CaHypo HT

A sample of Example 11 (ground CaHypo HT) has been tested on an extruder and injection molding machine to verify that it is safe to compound. The product is compounded with polyester (PBT) as indicated in the table below with a processing temperature of 250°C. The formulations have been tested, and in all cases, the extrusion went well without any issues.

During the experiment, the out gases are captured into gas bags and the concentration of phosphine is measured over time using Gastec tubes. When samples of vent gases are analyzed no phosphine could be detected indicating that the level of phosphine is less than 0.05 ppm.

The formulations have then been injected into molded to prepare 0.8mm and 1.6mm specimens with a temperature of 260°C. The phosphine is also measured during this process and found to be less than 0.05ppm. The results are reported in the table 7 below, wherein the ratio of the compounds are expressed in parts by weight.

Table 7 : Compounding using CaHypo HT

TRIALS	C1	C2	C3	1	2
PBT	50	50	50	50	50
CaHyPo HT	20	10	-	5	10
Al Hypo	-	-	20	10	5
Glass fibers	30	30	30	30	30
MCA (melamine cyanurate)	-	10	-	5	5
Extrusion	OK	OK	KO	OK	OK
Injection	OK	OK	KO	OK	OK
UL94 1.6 mm	HB	V2	V1	V0	V0

What is claimed is:

1. A flame retardant polymer composition comprising at least one polymer and:

(a) a calcium hypophosphite,

(b) an aluminium inorganic salt, and

(c) an other additive improving the flame retardant properties of the composition.

2. Flame retardant polymer composition according to claim 1, in which calcium hypophosphite is so heat stabilized that ,when it is heated during 3 hours at 298°C under a flow of argon flushing at rate 58 mL/mins, it generates less than 0.5 mL of phosphine per gram of hypophosphite salt.

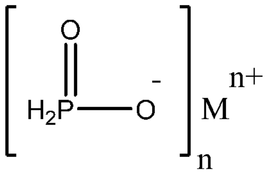
3. Flame retardant polymer composition according to claim 1 or 2, in which the composition provides a V0 rate with specimens of 1.6 mm according to UL94 standard.

4. Flame retardant polymer composition according anyone of claim 1 to 3, in which the polymer present in a flame retardant polymer composition is selected from the group consisting in polyphenylene ethers, polyamides, polyesters, polycarbonates, epoxy resins, phenolic resins, acrylonitrile butadiene styrene, styrene acrilonitrile, polystyrene such as high impact

polystyrene, polyphenylene ethers, styrene butadiene rubber, halogenated polymers, and mixtures and blends of these polymers.

5. Flame retardant polymer composition according anyone of claim 1 to 4, in which the composition comprises from 30 to 80 % by weight of polymer, according to the total weight of the composition.

6. Flame retardant polymer composition according anyone of claim 1 to 5, in which the calcium hypophosphite corresponds to the compound of formula (1):



$$\left[H_2P(=O)-O^{-}\right]_n M^{n+}$$

(1)

wherein :

n is 1, 2 or 3 ; and

M is a calcium.

7. Flame retardant polymer composition according anyone of claim 1 to 6, in which the calcium hypophosphite in an amount of 0.1 to 30 weight percent, based on the total weight of the flame retardant polymer composition.

8. Flame retardant polymer composition according anyone of claim 1 to 7, in

which the aluminium salt is an inorganic salt comprises at least a phosphorous or a sulfur atom.

9. Flame retardant polymer composition according anyone of claim 1 to 8, in which the inorganic aluminium salt is chosen in the group consisting of: aluminium ammonium sulphate, aluminium cerium oxide, aluminium cesium sulphate, aluminium hydroxide, aluminium metaphosphate, aluminium nitride, aluminium oxide, aluminium phosphate, aluminium hypophosphite, aluminium phosphate, aluminium potassium sulphate, aliuminium silicate, aluminium sulphate, aluminium sulfide and aluminium titanate.

10. Flame retardant polymer composition according anyone of claim 1 to 9, in which the composition comprises an aluminium salt in an amount of 0.1 to 30 weight percent, based on the total weight of the flame retardant polymer composition.

11. Flame retardant polymer composition according anyone of claim 1 to 10, in which the additive c) improving the flame retardant properties of the composition is selected from :

A) Phosphorous containing flame retardant additives, such as phosphine oxide, phosphonic acids and their salts, phosphinic acids and their salts, cyclic phosphonates, organic phosphates, inorganic phosphates, or red phosphorous ;

B) Nitrogen containing flame retardant additives, such as triazines, cyanuric acid and/or isocyanuric acid, melamine or its derivatives ;

C) Halogen containing flame retardant additives, such as Bromine containing flame retardant additives or Chlorine containing flame retardant additives ;

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

12. Flame retardant polymer composition according anyone of claim 1 to 11, in which the composition comprise aN additive c) in an amount of 0.1 to 30 weight percent, based on the total weight of the flame retardant polymer composition.

13. Flame retardant polymer composition according anyone of claim 1 to 12, in which the composition comprises a polymer, notably polyester or polyamide and at least:

(a) 1-25 % by weight of a calcium hypophosphite, wherein the hypophosphite salt is so heat stabilized that ,when it is heated during 3 hours at 298°C under a flow of argon flushing at rate 58 mL/mins, it generates less than 0.5 mL of phosphine per gram of hypophosphite salt;

(b) 1-20 % by weight of an aluminium inorganic salt, and

(c) an other additive improving the flame retardant properties of the composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/072605

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

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)

IPC: C08K3/-; C08L101/-

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)

CNTXT, WOTXT, VEN, CNKI; calcium, salt, aluminum, aluminium, Ca, Al, +hypophosphite

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN102171290A (STYRON EURO GMBH) 31 August 2011 (31.08.2011) claims 2, 9; examples 1-5	1-13
X	US2007082995A1(ITALMATCH CHEM SPA) 12 April 2007 (12.04.2007) claims 1-24	1-13
X	US2008214715A1(ITALMATCH CHEM SPA) 04 September 2008 (04.09.2008) claims 1-18	1-13

☐ 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 11 December 2012 (11.12.2012)	Date of mailing of the international search report **27 Dec. 2012 (27.12.2012)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer LI, Kaiyang Telephone No. (86-10)62084429

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2012/072605

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		EP1907473B1	10.02.2010
		DE602005019333E	25.03.2010

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/072605

CLASSIFICATION OF SUBJECT MATTER:

C08K 3/32 (2006.01) i
C08K 3/10 (2006.01) i
C08L 101/00 (2006.01) i