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(54) Title: NON-HALOGENATED FLAME RETARDANT POLYCARBONATE COMPOUNDS

(57) Abstract: A flame retardant polycarbonate compound is disclosed. The compound comprises a polycarbonate and non-halogenated bisphosphate ester as a flame retardant, along with talc, and acrylic modified polytetrafluoroethylene, and optionally, polyphosphazene and/or a potassium salt of perfluorobutane sulfonic acid. The compound can achieve a UL 94 rating of V-0 at two different thicknesses of less than 1 mm.

NON-HALOGENATED FLAME RETARDANT
POLYCARBONATE COMPOUNDS

CLAIM OF PRIORITY

[0001] This application claims priority from U.S. Provisional Patent Application Serial Number 61/675,545 bearing Attorney Docket Number 12012011 and filed on July 25, 2012, which is incorporated by reference.

FIELD OF THE INVENTION

[0002] This invention concerns thermoplastic polymer compounds which are flame retardant using non-halogenated ingredients.

BACKGROUND OF THE INVENTION

[0003] Thermoplastic compounds, unlike wood, metal, or glass, do not rot, rust, or shatter. For that reason, the world in the past seventy years has seen a revolution in material science arising from the combination of a thermoplastic resin and one or more functional additives to provide specific properties to the resin.

[0004] Unlike wood but like metal and glass, at a given temperature, a thermoplastic resin can melt. Its processing versatility benefits from its capacity to mix with the functional additives while in a molten state.

[0005] But in use, the exposure of a fully formed thermoplastic article to excessive heat or flame can be quite detrimental to property and person.

[0006] Flame retardants, drip suppressants, mineral fillers, and char formers are functional additives which can be used to help the thermoplastic compound to retard the effects of heat or flame from melting or even burning. Flame retardant thermoplastic compounds are particularly needed when the plastic article is used in any confined space where persons might be present during any condition, planned or emergency, which might expose the plastic article to such excessive heat or flame.

[0007] Non-halogenated flame retardants have recently become popular because they minimize the release of halogenated chemicals if the plastic article would begin to degrade, melt, or burn.

SUMMARY OF THE INVENTION

[0008] What the art needs is a non-halogenated thermoplastic compound capable of passing the Underwriters' Laboratories Test No. 94 (UL 94 test) by achieving a V-0 rating.

[0009] Even with the variety of functional additives commercially available, it is not a predictable pathway for a person having ordinary skill in the art to find a particular combination of ingredients which, together, can achieve a V-0 rating in a UL 94 test.

[00010] The present invention has found a particular combination of known ingredients which, together, achieve a V-0 rating in a UL 94 test, at thicknesses ranging from about 0.4 mm to 0.7 mm, less than the thickness of one American dime (\$0.10) coin, a task very difficult and unpredictable to achieve.

[00011] Starting with polycarbonate as the thermoplastic resin chosen for its physical properties, a non-halogenated flame retardant is combined with other functional ingredients to achieve that coveted V-0 rating.

[00012] One aspect of the present invention is a flame retardant polycarbonate compound, comprising polycarbonate, bisphosphate ester, talc, and acrylic modified polytetrafluoroethylene, wherein the bisphosphate ester is present in the compound at a weight percent from 7 to about 15, and wherein the compound injected molded and tested at a thickness of 0.75 mm has a UL 94 rating of V-0.

[00013] Features of the invention will be explored below.

EMBODIMENTS OF THE INVENTION

[00014] Polycarbonate

[00015] Any polycarbonate is a candidate for use in the compound, whether obtained from petrochemical or bio-derived sources, whether virginal or recycled.

[00016] Polycarbonates can be branched or linear, a mixture of them being preferred in this invention. Polycarbonates can be aliphatic or aromatic, with the latter being preferred in this invention. Without undue experimentation, one of ordinary skill in the art can select a polycarbonate matrix based on considerations of cost, manufacturing technique, physical properties, chemical properties, etc.

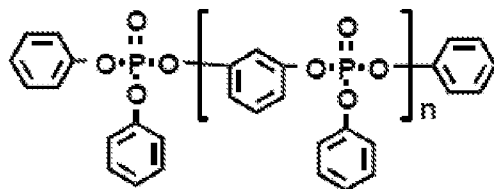
[00017] Unpredictably, it has been found that a combination of branched and linear polycarbonate in compounds of the present invention performs better than only either branched polycarbonate or linear polycarbonate. Linear polycarbonate has a higher melt flow index than branched polycarbonate, and it is believed that the linear polycarbonate assists in the melt processing of the compound while the branched polycarbonate assists in the flame retardant performance.

[00018] Commercial manufacturers of polycarbonate are Sabic, Bayer, Teijin, Dow, and others.

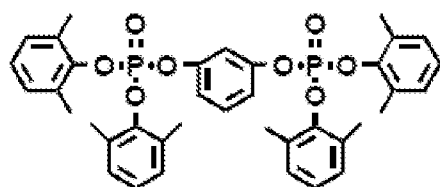
[00019] Non-Halogenated Bisphosphate Esters

[00020] Bisphosphate esters as candidates for use in this invention contain no halogen atoms, which characterizes them as non-halogenated. One reason for using non-halogenated bisphosphate esters is that they are more economical as compared with other non-halogenated phosphorus-containing flame retardants.

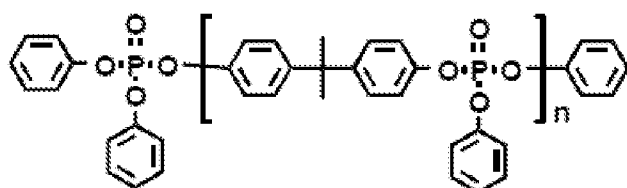
[00021] Bisphosphate esters are commercially available and known as non-halogenated flame retardants. Specific examples of commercially available bisphosphate esters have the following structures and CAS Numbers:



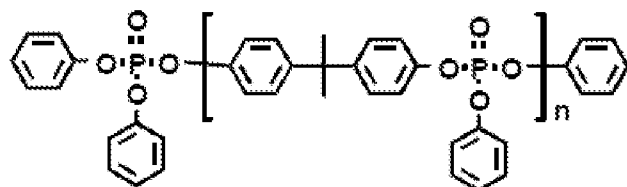
[57583-54-7]



[139189-30-3]

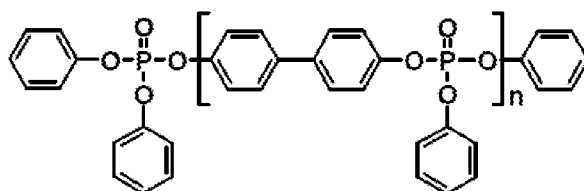


[181028-79-5]



[181028-79-5]

n (average) < 1.1



1003300-73-9

[00022] The foregoing examples of the non-halogenated bisphosphate esters can be used either alone or in combination. Of those examples listed above, all are pale yellow liquids except the second one, CAS No. 139189-30-3 and the last one, CAS No. 1003300-73-9, which are white granules. Granules are preferred for melt compounding because of easier solid material handling and processing. But liquid-based bisphosphate esters can also be used in the invention if suitable liquid material handling equipment such as dosing equipment is available for batch or continuous melt mixing with the polycarbonate and other solid ingredients.

[00023] Commercially available bisphosphate esters can be purchased from Adeka Palmarole of Saint Louis, France or Zhejiang Wangsheng Co., Ltd of Linhai City, Zhejiang Province, China. Presently preferred is WSFR-PX220 bisphosphate ester from Zhejiang Wangsheng Co. Ltd, because it is a white solid in granule form and has a melting point greater than 90°C; a water content of less than 0.1 weight percent; and good compatibility with polycarbonate.

[00024] Talc

[00025] Talc is used in thermoplastic compounds as a mineral filler. In flame retardant thermoplastic compounds, talc can assist in flame retardance by being a barrier to oxygen and increasing viscosity of the molten polymer matrix during combustion.

[00026] Talc can have a particle size ranging about 0.5 μm to about 10 μm and preferably from about 0.5 μm to about 0.9 μm.

[00027] Talc is commercially available from a number of manufacturers. Presently preferred is Ultra Talc 609 from Specialty Minerals Company, which has a particle size of from about 0.5 μm to about 0.9 μm .

[00028] PTFE

[00029] Polytetrafluoroethylene is known to be useful as a drip suppressant because it tends fibrillate and elongate during injection molding. Fibrils shrink upon exposure to heat from a flame and hence retard dripping of the matrix in which the fibrils reside.

[00030] PTFE can have a particle size ranging from about 5 μm to about 25 μm with the possibility of aggregation and agglomeration.

[00031] PTFE is commercially available from a number of manufacturers, but the best known is Teflon™ brand from DuPont which invented the polymer.

[00032] PTFE also can be supplied with modification, such as an acrylic-modified PTFE which is advertised to improve dispersibility of the PTFE into the thermoplastic compound. Metablen A-3800 acrylic-modified PTFE is commercially available from Mitsubishi Rayon America, Inc. and is presently preferred because of that improved dispersibility.

[00033] Though PTFE is fluorinated, its presence in the compound is not regarded by those having skill in the art of flame retardant compounds as compromising the non-halogenated characteristics of the flame retardant itself because the amount of PTFE present is very minor. Therefore, the use of a fluorinated drip suppressant in the amounts identified in this invention does not disqualify the compound from being considered a non-halogenated flame retarded thermoplastic compound according to the course of conduct in the thermoplastic compound industry.

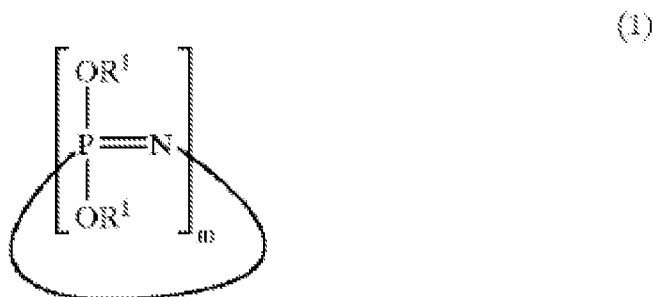
[00034] Optional Polyphosphazene

[00035] In the event that a second type of non-halogenated flame retardant is desired, one can include polyphosphazene flame retardants in the

thermoplastic compounds of the invention because polyphosphazene flame retardants have excellent hydrolytic stability, better than bisphosphate esters.

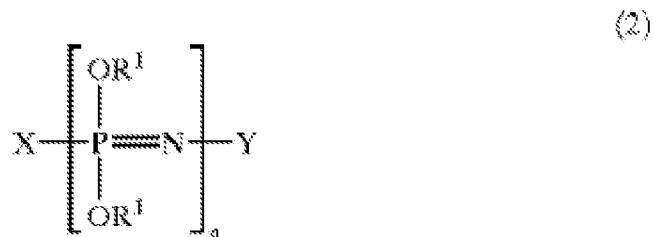
[00036] U.S. Pat. No. 6,518,336 (Yabuhara et al.) and U.S. Pat. No. 6,743,841 (Shimizu et al.), both of which are incorporated by reference herein, disclose non-halogenated polyphosphazenes which are candidates for use in this invention. Briefly, U.S. Pat. No. 6,518,336 discloses four types of polyphosphazenes.

[00037] (1) Cyclic polyphosphazenes represented by the Formula (1)



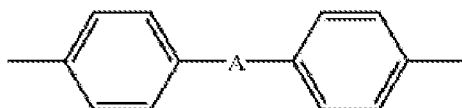
[00038] wherein m is an integer of 3 to 25, two R^1 groups are the same or different and each represents a phenyl group substituted with at least one group selected from the class consisting of alkyl groups having 1 to 6 carbon atoms and an allyl group or an unsubstituted phenyl group.

[00039] (2) Straight-chain polyphosphazenes represented by the Formula (2)



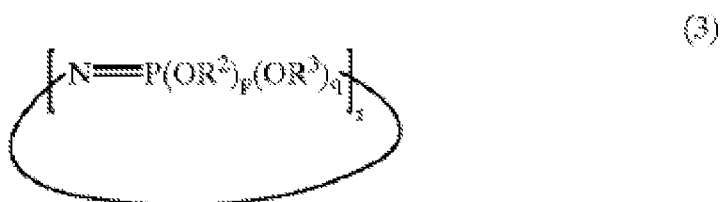
[00040] wherein n is an integer of 3 to 1000, R^1 is as defined above, X represents a group $—N=P(OR^1)_3$ or a group $—N=P(O)OR^1$, and Y represents a group $—P(OR^1)_4$ or a group $—P(O)(OR^1)_2$.

[00041] (3) Crosslinked polyphosphazenes wherein at least one of the foregoing phosphazenes (1) and (2) is crosslinked with at least one crosslinking group selected from the group consisting of o-phenylene, m-phenylene, p-phenylene, biphenylene, and a group represented by



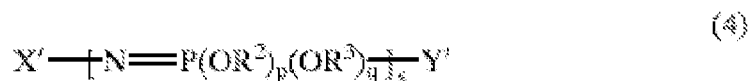
[00042] wherein A is a group $—SO_2—$, a group $—S—$, a group $—O—$ or a group $—C(CH_3)_2—$, each of said crosslinking groups being interposed between the two oxygen atoms left after the elimination of group R^1 from the phosphazene (1) or (2), and the number of the R^1 groups in the crosslinked phosphazene being 50 to 99.9% based on the total number of R^1 groups in the phosphazene prior to the crosslinking.

[00043] (4) At least one polyphosphazene selected from the group consisting of cyclic polyphosphazenes represented by formula (3)



[00044] wherein R^2 is a cyano-substituted phenyl group; R^3 is an alkyl group having 1 to 18 carbon atoms or an aryl group having 6 to 10 carbon atoms; these groups may be substituted with at least one group selected from alkyl groups having 1 to 10 carbon atoms, allyl group and aryl groups; when two or more R^3 groups exist, the R^3 groups may be the same or different; p and q

are numbers which fulfill the requirements that $p > 0$, $q = 0$, and $p + q = 2$; and r is an integer of 3 to 25, and a straight-chain polyphosphazene represented by the formula (4)



[00045] wherein R^2 , R^3 , p and q are as defined above; r is an integer of 3 to 1000; X' is a group $-\text{P}(\text{OR}^2)_1$, a group $-\text{P}(\text{OR}^2)_3(\text{OR}^3)$, a group $-\text{P}(\text{OR}^2)_2(\text{OR}^3)_2$, a group $-\text{P}(\text{OR}^2)(\text{OR}^3)_3$, a group $-\text{P}(\text{OR}^3)_4$, a group $-\text{P}(\text{O})(\text{OR}^2)_2$, a group $-\text{P}(\text{O})(\text{OR}^2)(\text{OR}^3)$, or a group $-\text{P}(\text{O})(\text{OR}^3)_2$; and Y' is a group $-\text{N}=\text{P}(\text{OR}^2)_3$, a group $-\text{N}=\text{P}(\text{OR}^2)_2(\text{OR}^3)$, a group $-\text{N}=\text{P}(\text{OR}^2)(\text{OR}^3)_2$, a group $-\text{N}=\text{P}(\text{OR}^3)_3$, a group $-\text{N}=\text{P}(\text{O})\text{OR}^2$ or a group $-\text{N}=\text{P}(\text{O})\text{OR}^3$.

[00046] The foregoing examples of the non-halogenated polyphosphazenes can be used either alone or in combination.

[00047] Specific examples of the cyclic polyphosphazene (1) and the straight-chain polyphosphazene (2) include a mixture of phosphazenes in which phenoxy groups and/or alkoxy groups are introduced as substituents and which are obtainable from a mixture of cyclic and straight-chain chlorophosphazenes, e.g., hexachlorocyclotriphosphazene, octachlorocyclotetra-phosphazene and the like, prepared by reacting ammonium chloride and phosphorus pentachloride at about 120 to about 130° C; and hexaphenoxycyclotriphosphazene, octaphenoxycyclotetraphosphazene, decaphenoxycyclopentaphosphazene, hexaalkoxycyclotriphosphazene, octaalkoxycyclotetraphosphazene, decaalkoxycyclopenta-phosphazene and like cyclic phosphazenes obtained by isolating, from the above mixture of chlorophosphazenes, hexachlorocyclotriphosphazene, octachlorocyclotetraphosphazene, decachlorocyclopenta-phosphazene or like single substances, followed by substitution with a phenoxy group and/or an alkoxy group.

[00048] Specific examples of the straight-chain polyphosphazenes (2) include those obtained by heating (at 220 to 250° C.) hexachlorocyclotriphosphazene for ring-opening polymerization to give dichlorophosphazene, followed by substitution with a phenoxy group and/or an alkoxy group.

[00049] Specific examples of the crosslinked polyphosphazenes (3) are phenoxyphosphazene having 4,4'-sulfonyldiphenylene(bisphenol-S residue) group-crosslinked structure, phenoxyphosphazene having 2,2-(4,4'-diphenylene)isopropylidene group-crosslinked structure, phenoxyphosphazene having 4,4'-oxydiphenylene group-crosslinked structure, phenoxyphosphazene having 4,4'-thiodiphenylene group-crosslinked structure, phenoxyphosphazene having 4,4'-diphenylene group-crosslinked structure, etc.

[00050] Specific examples of the polyphosphazenes (4) are monocyanophenoxyphenoxycyclotriphosphazene, dicyanophenoxytetraphenoxyphenoxycyclotriphosphazene, tricyanophenoxytriphenoxycyclotriphosphazene, tetracyanophenoxydiphenoxycyclotriphosphazene, pentacyanophenoxyphenoxycyclotriphosphazene and like cyclotriphosphazene compounds; monocyanophenoxyheptaphenoxyphenoxycyclotetraphosphazene, dicyanophenoxyhexaphenoxyphenoxycyclotetraphosphazene, tricyanophenoxyphenoxycyclotetraphosphazene, tetracyanophenoxytetraphenoxyphenoxycyclotetraphosphazene, pentacyanophenoxytriphenoxycyclotetraphosphazene, hexacyanophenoxydiphenoxycyclotetraphosphazene, heptacyanophenoxyphenoxycyclotetraphosphazene and like cyclotetraphosphazenes; cyclopentaphosphazenes having both cyanophenoxy and phenoxy groups as substituents; and like cyclic phosphazenes; and straight-chain phosphazenes having both cyanophenoxy and phenoxy groups as substituents.

[00051] Among these polymers, preferred are a mixture of polyphenoxyphosphazenes which have phenoxy groups as substituents and which are obtainable from a mixture of cyclic and straight-chain chlorophosphazenes, phenoxyphosphazene having 4,4'-sulfonyldiphenylene-crosslinked structure; phenoxyphosphazene having 2,2-(4,4'-diphenylene)-isopropylidene group-crosslinked structure; and polyphosphazenes having both cyanophenoxy and phenoxy groups as substituents.

[00052] Commercially available polyphosphazenes can be purchased from Otsuka Chemical Co., Ltd. of Osaka, Japan. Presently preferred as an optional second flame retardant is SPB 100 polyphosphazene from Otsuka.

[00053] Optional Char Former

[00054] Flame retardant thermoplastic compounds can benefit from the presence of char formers, chemicals which assist in the retention of the original shape of the plastic article by the formation of char from the compound.

[00055] One known char former is perfluorobutane sulfonic acid, potassium salt, which is sold as neat powder or as pellets of a masterbatch, with the latter being preferred for processing efficiency. The char former is considered optional for use in the compound of this invention because, as the Examples demonstrated, the compound does not need this particular functional additive to achieve a UL 94 V-0 rating.

[00056] Perfluorobutane sulfonic acid, potassium salt is commercially available as Bayowet C4 MB masterbatch (6% salt (CAS No. 029420-49-3) in polycarbonate pellets) or Bayowet C4 powder (CAS No. 029420-49-3) from Lanxess Deutschland GmbH.

[00057] Optional Other Additives

[00058] The compound of the present invention can include conventional plastics additives in an amount that is sufficient to obtain a desired processing or performance property for the compound. The amount should not be wasteful of the additive nor detrimental to the processing or performance of the

compound. Those skilled in the art of thermoplastics compounding, without undue experimentation but with reference to such treatises as Plastics Additives Database (2004) from Plastics Design Library (www.elsevier.com), can select from many different types of additives for inclusion into the compounds of the present invention.

[00059] Non-limiting examples of optional additives include adhesion promoters; biocides (antibacterials, fungicides, and mildewcides), anti-fogging agents; anti-static agents; bonding, blowing and foaming agents; dispersants; fillers and extenders; smoke suppressants; impact modifiers; initiators; lubricants; micas; pigments, colorants and dyes; plasticizers, such as core/shell impact modifiers; processing aids; release agents; silanes, titanates and zirconates; slip and anti-blocking agents; stabilizers; stearates; ultraviolet light absorbers; viscosity regulators; waxes; catalyst deactivators, and combinations of them.

[00060] Ingredients

[00061] Table 1 shows the acceptable, desirable, and preferred amounts of each of the ingredients discussed above, recognizing that the optional ingredients need not be present at all. The compound can comprise the ingredients, consist essentially of the ingredients, or consist of the ingredients. All amounts are expressed in weight percent of the total compound.

[00062] All ingredients other than the polycarbonate matrix can be added individually to the matrix or any two or more of them can be added together.

Table 1			
Range of Ingredients			
(Weight Percent)			
	Acceptable	Desirable	Preferable
Polycarbonate Matrix	80-90	82-88	85-87
Bisphosphate Ester	7-15	7-12	7-10
Talc	2-9	3-8	4-6
Acrylic Modified Polytetrafluoroethylene	0.1 -0.8	0.3-0.7	0.4-0.6
Optional Polyphosphazene	0-7	0-5	0-3.5
Optional Potassium salt of perfluorobutane sulfonic acid	0-0.2	0-0.1	0-0.01
Optional Other Additives	0-5	0-3	0-2

[00063] Processing

[00064] The preparation of compounds of the present invention is uncomplicated. The compound of the present can be made in batch or continuous operations.

[00065] Mixing in a continuous process typically occurs in a single or twin screw extruder that is elevated to a temperature that is sufficient to melt the polymer matrix with addition of other ingredients either at the head of the extruder or downstream in the extruder. Extruder speeds can range from about 50 to about 500 revolutions per minute (rpm), and preferably from about 350 to about 450 rpm. Typically, the output from the extruder is pelletized for later extrusion or molding into polymeric articles.

[00066] Mixing in a batch process typically occurs in a Banbury mixer that is capable of operating at a temperature that is sufficient to melt the polymer matrix to permit addition of the solid ingredient additives. The mixing speeds range from 60 to 1000 rpm. Also, the output from the mixer is chopped into smaller sizes for later extrusion or molding into polymeric articles.

[00067] Subsequent extrusion or molding techniques are well known to those skilled in the art of thermoplastics polymer engineering. Without undue experimentation but with such references as "Extrusion, The Definitive Processing Guide and Handbook"; "Handbook of Molded Part Shrinkage and Warpage"; "Specialized Molding Techniques"; "Rotational Molding Technology"; and "Handbook of Mold, Tool and Die Repair Welding", all published by Plastics Design Library (www.elsevier.com), one can make articles of any conceivable shape and appearance using compounds of the present invention.

USEFULNESS OF THE INVENTION

[00068] Thermoplastic compounds can be shaped by extrusion, molding, calendaring, thermoforming, or other means of shaping into any plastic article usable in an interior or confined space where fire can cause personal injury or property damage. The compounds resist melting and dripping.

[00069] Literally any plastic article useful in a human-occupied space such as a building, a vehicle, or a tunnel can benefit from the flame retardancy of this polycarbonate compound.

[00070] Because the physical properties of polycarbonate compounds are known, which are believed to not be deleteriously affected by the addition of the bisphosphate ester, the talc, and the acrylic modified PTFE, and optionally the polyphosphazene and/or the sulfonic acid salt char former, any plastic article which is currently made from a polycarbonate compound can now be made from the non-halogenated flame retardant compound of this invention.

[00071] Polycarbonate itself has superior flame retardant properties when compared to other polymer resins, such as polyolefins. The inherent flame retardant properties of polycarbonate assisted in achieving the UL 94 V-0 rating at very thin dimensions after the addition of the bisphosphate ester, the talc, the acrylic modified PTFE, and optionally, the polyphosphazene and/or the sulfonic acid salt char former.

[00072] By achieving a UL 94 V-0 rating at a thickness as thin as 0.4 mm, it is known that a plastic article having any larger thickness will also achieve a UL 94 V-0 rating.

[00073] Thermoplastic articles are sold into the following markets: appliance, building and construction, consumer, electrical and electronic, healthcare, industrial, packaging, textiles, transportation, and wire and cable. Compounds of this invention can be used in any of those markets regardless of thickness above 0.4 mm, 40% of the thickness of a United States dime (\$0.10) coin.

[00074] As stated repeatedly, Underwriters' Laboratories Test No. UL 94 serves as the litmus test for flame retardant thermoplastic compounds. As seen in Table 2, the V-0 rating is distinguished from V-1 and V-2 ratings, which are less acceptable if one is seeking the best flame retardance rating. For certain uses, V-1 is acceptable.

Table 2			
Criteria Conditions	V-0	V-1	V-2
Afterflame time for each individual specimen t_1 or t_2	$\leq 10s$	$\leq 30s$	$\leq 30s$
Total afterflame time for any condition set (t_1 plus t_2 for the 5 specimens)	$\leq 50s$	$\leq 250s$	$\leq 250s$
Afterflame plus afterglow time for each individual specimen after the second flame application ($t_2 + t_3$)	$\leq 30s$	$\leq 60s$	$\leq 60s$
Afterflame or afterglow of any specimen up to the holding clamp	No	No	No
Cotton indicator ignited by flaming particles or drops	No	No	Yes

[00075] Examples provide data for evaluation of the unpredictability of this invention.

EXAMPLES

[00076] Table 3 shows the ingredients chosen for Examples 1-4 and Comparative Examples A-E.

Ingredients	Details and Sources
Branched Polycarbonate	Branched Polycarbonate pellets, Makrolon 1239, from Bayer
Linear Polycarbonate	Linear Polycarbonate pellets, Makrolon 2658, from Bayer
Pigment	9019-BK-99 Carbon Black MB pellets, from PolyOne Shenzhen Color & Additive (China)
Bisphosphate Ester	WSFR-PX220-Bisphosphate ester Flame retardant from Wangsheng Co., Ltd (China)
Talc	Talc: Ultra Talc 609 powder from Specialty Minerals
Acrylic Modified PTFE	Metablen A-3800 from Mitsubishi Rayon America
Stabilizer	Irganox 1010 Stabilizer Package powder from BASF
Antioxidant	Ultranox 627A, antioxidant powder from Chemtura
Mold Release Wax	Licowax E powder, ester of montanic acids, from Clariant

[00077] Table 4 shows the mixing conditions in a Leistritz ZSE-18HP (L/D=41) twin screw extruder with all raw materials in pellet form being pre-mixed and then fed at throat at Barrel 1 and with all raw materials in powder form being pre-mixed and also fed at the throat at Barrel 1. The temperature in all zones was set at 270°C, with the values reported as measured.

[00078] The extrudate was pelletized, while in a water bath, for later injection or compression molding.

Table 4 – Extruder Conditions						
	1	2	3	4	A	B
Zone 1 (°C)	256	245	247	255	253	255
Zone 2 (°C)	270	269	271	269	272	269
Zone 3 (°C)	270	269	270	270	274	269
Zone 4 (°C)	269	269	273	272	275	270
Zone 5 (°C)	271	270	270	267	272	270
Zone 6 (°C)	270	269	272	271	277	271
Zone 7 (°C)	278	275	274	280	280	275
Zone 8 - Die (°C)	272	250	256	268	260	260
RPM / Side screw RPM	400/ 209	400/ 209	400/ 209	400/ 209	400/ 209	400/ 209
% Torque	47	42	46	35	44	50
Die Press (psi)	675	699	780	590	728	780
Melt Temp (°C)	276	274	275	276	275	276
Feeder Rate #_1_ S / M (lbs./hr.) (Pellets)	87.20	87.20	87.20	87.20	89.20	88.20
Feeder Rate #_2_ S / M (lbs./hr.) (Powder)	12.80	12.80	12.80	12.80	10.80	11.80
Total Feed Rate (lbs./hr.)	15	15	15	15	15	15
Vacuum (Mbar)	185	185	185	185	185	185

Table 4 Continued			
	C	D	E
Zone 1 (°C)	250	250	256
Zone 2 (°C)	275	267	271
Zone 3 (°C)	274	68	269
Zone 4 (°C)	275	270	270
Zone 5 (°C)	274	273	270
Zone 6 (°C)	274	273	270
Zone 7 (°C)	280	280	272
Zone 8 -Die (°C)	269	268	278
RPM / Side screw RPM	400/ 209	400/ 209	400/ 209
% Torque	33	34	33
Die Press (psi)	610	675	621
Melt Temp (°C)	277	276	275
Feeder Rate #_1_ S / M (lbs./hr.) (Pellets)	92.20	87.70	92.70
Feeder Rate #_2_ S / M (lbs./hr.) (Powder)	7.80	12.30	7.30
Total Feed Rate (lbs./hr)	15	15	15
Vacuum (Mbar)	185	185	185

[00079] The extrudate was pelletized for later molding.

[00080] Before molding, the pellets were dried for more than 4 hours at 120°C to reduce moisture content to less than 0.02%.

[00081] Using a DeMag molding machine, Table 5 shows the settings used to mold test bars of each Example and Comparative Example having a thickness of 0.75 mm.

Table 5 – Injection Molding Conditions	
Temperatures:	
Nozzle (°C)	271
Zone 2 (°C)	271
Zone 3 (°C)	265
Zone 4 (°C)	265
Mold (°C)	77
Oil Temp (°C)	32
Speeds:	
Screw RPM	150
% Shot - Inj Vel (in/sec)	2~2.5
Pressures:	
Injection Pressure (psi)	1834
Hold Pressure (psi)	800
Back Pressure (psi)	50
Timers:	
Injection Hold (sec)	6
Cure/Cool Time (sec)	10
Fill Time (sec)	0.55
Cycle Time (sec)	28.1
Operation Settings:	
Shot Size (in)	0.85
Cushion (in)	0.18
Cut-off Position (in)	0.2
Decompression (in)	1.05

[00082] Samples of all Examples and Comparative Examples were also subjected to compression molding into films of 0.4 ~ 0.5 mm thickness. About 30 to 40 g of the material was placed between two Teflon™ coated trays, inserted into a PHI 40000 ton manual hydraulic press (model: P2150) preheated at 221°C (430 °F), then started slowly increasing pressure to 4.13-6.2 MPa (600-900 psi) over 2 minutes. After that, remove the plates from the press and cooled for 3-5 minutes to take out film with a thickness of about 0.4 ~ 0.5 mm. From those films, an Arbor fitted with a flexural die cut a flame bar sample shape out of the film for UL 94 testing.

[00083] Samples of all Examples and Comparative Examples were also subjected to extrusion into films of about 0.4 mm thickness. The materials were

extruded in a single-screw extruder (model: C.W.Brabender 2503 No. 1914) with L/D of 3:1 and diameter of 0.5", and passed through a die with 4" die width and 1.4 mm die slit to form a tape. The extruder barrel temperature was 260 - 270 °C for zone 1, zone 2, zone 3 and die. The extruded tapes were pulled off by a C.W. Brabender Univex Take-Off Roll (Model SFR-100-B. No.468). The thickness of films ranged from 0.43 to 0.35 mm. The thickness was adjusted by extruder rpm and the speed of the take-off roll. The extruder rpm was about 60 - 70 rpm. The speed ranging from 0 to 100 of the DC motor of the take-off roll was set about 12 to 30. From the films, an Arbor fitted with a flexural die cut a flame bar sample shape out of the film for UL 94 testing.

[00084] Table 6 shows the flame performance tested for each Example and Comparative Example.

Table 6 – Physical Properties						
Ingredients	1	2	3	4	Comp. A	Comp. B
	Formulation in Wt. %					
Branched Polycarbonate	66.2	43.1	86.2		68.2	67.2
Linear Polycarbonate	20	43.1		86.2	20	20
Pigment	1	1	1	1	1	1
Bisphosphate Ester	7	7	7	7	5	6
Talc	5	5	5	5	5	5
PTFE	0.5	0.5	0.5	0.5	0.5	0.5
Stabilizer	0.1	0.1	0.1	0.1	0.1	0.1
Antioxidant	0.1	0.1	0.1	0.1	0.1	0.1
Mold Release Wax	0.1	0.1	0.1	0.1	0.1	0.1
Total	100	100	100	100	100	100
Thickness of Sample	UL Flammability Rating (UL 94 Test harmonized with ISO 9772/9773)					
0.75 mm, injection molded flexural bar*	V-0	V-0	V-0	V-0	V-2	V-1
0.4-0.5 mm bar compression molded	V-2	V-2	V-2	V-2	V-2	V-2
0.4-0.5 mm extruded film	V-0	V-1	V-1	V-1	V-not	V-1

*Flame bar dimension: 5" x 1/2" (or 12.7 mm x 1.27 mm) with desired thickness

Table 6 Continued

Ingredients	Comp. C	Comp. D	Comp. E
Branched Polycarbonate	71.2	66.7	71.7
Linear Polycarbonate	20	20	20
Pigment	1	1	1
Bisphosphate Ester	7	7	7
Talc	0	5	0
PTFE	0.5	0	0
Stabilizer	0.1	0.1	0.1
Antioxidant	0.1	0.1	0.1
Mold Release Was	0.1	0.1	0.1
Total	100	100	100
Thickness of Sample	UL Flammability Rating (UL Test harmonized with ISO 9772/9773)		
0.75 mm, injection molded flexural bar**	V-2	V-2	V-2
0.4-0.5 mm bar compression molded	V-2	V-2	V-2
0.4-0.5 mm, extruded film	V-not	V-2	V-2

**Flame bar dimension: 5" x 1/2" (or 12.7 mm x 1.27 mm) with desired thickness

[00085] To the required ingredients of polycarbonate and bisphosphate ester flame retardant, two functional additives were evaluated, in of the three possible combinations because of the unpredictability of achieving a UL 94 V-0 test rating: polytetrafluoroethylene (PTFE) drip suppressant and talc mineral filler which serves as a viscosity enhancer.

[00086] Comparative Examples C-E demonstrate that, in order to achieve a UL 94 V-0 rating for either the 0.75 thickness (injection molded article such as Examples 1-4) or the 0.4-0.5 thickness (extruded film such as Example 1), both PTFE and talc are required in the compound.

[00087] Comparative Examples A and B demonstrated that even with both PTFE and talc present in the same amounts as in Examples 1-4, the UL 94 V-0 rating for either the 0.75 thickness (injection molded article) or the 0.4-0.5 thickness (extruded film) required at least 7 weight percent of bisphosphate ester. Five and six weight percent of bisphosphate ester were inadequate.

[00088] Of Examples 1-4, the use of branched or linear polycarbonate demonstrated that a combination of both branched and linear polycarbonate (Examples 1 and 2) had a better flame test result than either one or the other (Examples 3 and 4). And of Examples 1 and 2, the use of a superior amount of branched polycarbonate and an inferior amount of linear polycarbonate (Example 1) had better flame test performance than equal amounts (Example 2). Therefore, the formulation of Example 1 is preferred. Thus, the ratio of branched polycarbonate to linear polycarbonate can range from about 1.2:1 to about 3.6:1 and preferably from about 3.0:1 to about 3.4:1.

[00089] The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. A flame retardant polycarbonate compound, comprising:
 - (a) polycarbonate,
 - (b) bisphosphate ester,
 - (c) talc, and
 - (d) acrylic modified polytetrafluoroethylene,wherein the bisphosphate ester is present in the compound at a weight percent from 7 to about 15,
and wherein the compound injection molded and tested at a thickness of 0.75 mm has a UL 94 rating of V-0.
2. The compound of Claim 1, further comprising the potassium salt of perfluorobutane sulfonic acid.
3. The compound of Claim 1, further comprising polyphosphazene.
4. The compound of Claim 1 or Claim 2 or Claim 3, wherein the polycarbonate is a mixture of a branched polycarbonate of virginal source, recycled source, or both, and a linear polycarbonate of virginal source, recycled source, or both.
5. The compound of Claim 4, further comprising an additive selected from the group consisting of adhesion promoters; biocides; anti-fogging agents; anti-static agents; anti-oxidants; bonding, blowing and foaming agents; dispersants; fillers and extenders; smoke suppressants; impact modifiers; initiators; lubricants; micas; pigments, colorants and dyes; plasticizers; processing aids; release agents; silanes, titanates and zirconates; slip and anti-blocking agents; stabilizers; stearates; ultraviolet light absorbers; viscosity regulators; waxes; catalyst deactivators, and combinations of them.

6. The compound of any one of the above claims, wherein the compound has ingredients in amounts expressed in weight percent:

Polycarbonate Matrix	80-90
Bisphosphate ester	7-15
Talc	2-9
Acrylic modified Polytetrafluoroethylene	0.1 -0.8
Optional Polyphosphazene	0-7
Optional Potassium salt of perfluorobutane sulfonic acid	0-0.2
Optional Other Additives	0-5

7. The compound of any one of the above claims, wherein the compound has ingredients in amounts expressed in weight percent:

Polycarbonate Matrix	82-88
Bisphosphate ester	7-12
Talc	3-8
Acrylic Modified Polytetrafluoroethylene	0.3-0.7
Optional Polyphosphazene	0-5
Optional Potassium salt of perfluorobutane sulfonic acid	0-0.1
Optional Other Additives	0-3

8. The compound of any one of the above claims, wherein the compound has ingredients in amounts expressed in weight percent:

Polycarbonate Matrix	85-87
Bisphosphate ester	7-10
Talc	4-6
Acrylic modified Polytetrafluoroethylene	0.4-0.6
Optional Polyphosphazene	0-3.5
Optional Potassium salt of perfluorobutane sulfonic acid	0-0.01
Optional Other Additives	0-2

9. A molded article made from the compound of any one of Claims 1-8.
10. An extruded article made from the compound of any one of Claims 1-8.
11. A calendered article made from the compound of any one of Claims 1-8.
12. A thermoformed article made from the compound of any one of Claims 1-8.
13. A method of using the compound of Claim 1, comprising the step of shaping the compound into an article designed to resist combustion or molten dripping in the presence of flame.
14. The method of Claim 13, wherein the polycarbonate of the compound is a mixture of a branched polycarbonate of virginal source, recycled source, or both and a linear polycarbonate of virginal source, recycled source, or both.
15. The method of Claim 13, wherein the shaping comprises extruding, molding, calendering, or thermoforming.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/051887**A. CLASSIFICATION OF SUBJECT MATTER****C08L 69/00(2006.01)i, C08K 5/521(2006.01)i, C08K 3/34(2006.01)i, C08L 27/18(2006.01)i, C09K 21/12(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)

C08L 69/00; C08K 3/38; C09K 21/12; C08L 67/02; C08K 5/52; C08K 5/5399; C08K 5/523; C08K 5/521; C08K 5/41; B32B 27/00; C08K 3/34; C08L 27/18

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

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: flame retardant, polycarbonate, bisphosphate ester, talc, acrylic modified polytetrafluoroethylene, injection molding, UL 94 v-0

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2011-0052895 A1 (Li, Y. et al.) 03 March 2011 See claims 1, 4; paragraphs [0003], [0004], [0011], [0030], [0033], [0035], [0036], [0052]-[0056], [0059], [0063], [0065].	1-5, 13-15
Y	US 7985788 B2 (SHINAGAWA, H. et al.) 26 July 2011 See claim 1; column 3, lines 49-62; column 4, lines 40-58.	1-5, 13-15
A	US 2011-0124781 A1 (SON, S. M. et al.) 26 May 2011 See claims 1, 4, 7, 8, 10; paragraphs [0030]-[0032], [0034], [0038], [0039], [0047], [0053].	1-5, 13-15
A	US 5952408 A (LEE, K. et al.) 14 September 1999 See claims 1, 9, 16, 17; column 6, line 62-column 7, line 20.	1-5, 13-15
A	WO 01-81470 A1 (GENERAL ELECTRIC COMPANY) 01 November 2001 See claims 1, 6-8, 12-14.	1-5, 13-15
A	US 2010-0010128 A1 (LEVCHIK, S. V. et al.) 14 January 2010 See claims 1, 2, 4, 5, 13; paragraph [0027].	1-5, 13-15

 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 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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/051887

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0052895 A1	03/03/2011	CN 102471528 A EP 2470594 A1 JP 2013-503247 A KR 10-2012-0060208 A TW 201124468 A WO 2011-028511 A1	23/05/2012 04/07/2012 31/01/2013 11/06/2012 16/07/2011 10/03/2011
US 7985788 B2	26/07/2011	CN 102079854 A EP 2327742 A2 EP 2327742 A3 JP 2011-132506 A US 2011-0130498 A1	01/06/2011 01/06/2011 14/11/2012 07/07/2011 02/06/2011
US 2011-0124781 A1	26/05/2011	CN 101945948 A KR 10-0914666 B1 KR 10-2009-0072082 A TW 200940646 A WO 2009-104866 A2 WO 2009-104866 A3	12/01/2011 28/08/2009 02/07/2009 01/10/2009 27/08/2009 22/10/2009
US 5952408 A	14/09/1999	US 5322553 A	21/06/1994
WO 01-81470 A1	01/11/2001	DE 60111212 D1 DE 60111212 T2 EP 1276813 A1 EP 1276813 B1 JP 04886959 B2 JP 2004-510837 A	07/07/2005 23/03/2006 22/01/2003 01/06/2005 29/02/2012 08/04/2004
US 2010-0010128 A1	14/01/2010	CN 101389696 B CN101389696 A EP 1976913 A1 JP 2009-522433 A KR 10-2009-0006054 A US 8026303 B2 WO 2007-081904 A1	30/05/2012 18/03/2009 08/10/2008 11/06/2009 14/01/2009 27/09/2011 19/07/2007

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2013/051887

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: 6-12
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.