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(54) Title: GLYCEROL ESTER AND BROMINATED POLYMER IN STYRENIC POLYMER

(57) Abstract: A polymer composition contains a polymer component containing at least 50 weight-percent styrenic polymer based on polymer component weight, a brominated vinyl aromatic/butadiene copolymer and glycerol ester. The polymer composition can be a polymeric foam.



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GLYCEROL ESTER AND BROMINATED POLYMER IN STYRENIC POLYMER

BACKGROUND OF THE INVENTION

Field of the Invention

5 This invention relates to styrenic polymeric compositions comprising glycerol ester and a brominated vinyl aromatic/butadiene copolymer, polymeric foams containing such compositions and a process for preparing such foam.

Introduction

10 To make a styrenic polymer foam, conventional low molecular weight brominated compound such as hexabromocyclododecane (HBCD) is typically used as a flame retardant. However, HBCD is facing governmental regulation over environmental concerns. Therefore, there is a need for an alternative flame retardant for use in styrenic foam.

 US patent application US2008/0287559A discloses the use of a brominated vinyl
15 aromatic/butadiene copolymer as an alternative flame retardant to HBCD in styrenic foam. A challenge with using the brominated vinyl aromatic/butadiene copolymer is that it tends to nucleate cell growth during foaming to a larger degree than HBCD due to the dispersed particulate nature of the brominated vinyl aromatic/butadiene copolymer in the polystyrene matrix. As a result an undesired amount of nucleation can occur in polystyrene foam, which
20 produces a greater number of cells, smaller cells and a higher density foam than foam made using HBCD. In addition, under thermal processing conditions typical used for styrenic polymers when preparing masterbatches of flame retardant in styrenic resins, the brominated vinyl/aromatic butadiene copolymer can degrade and produce bromine, which causes the masterbatch composition comprising the brominated vinyl/aromatic butadiene copolymer to
25 develop a yellow coloration. A yellow masterbatch concentrate can cause undesirable discoloration in foam, resulting in an undesirably off-white foam composition.

 US patent US5776389 discloses glycerol monoester as a cell size enlarger of an alkenyl aromatic resin. However, there is no suggestion that glycerol monoester is able to
effectively work to produce larger cells in the presence of particulates by counteract the
30 nucleating effect of the particulates (such as brominated vinyl aromatic/butadiene copolymer particulates) during the formation of a styrenic polymer foam. Nor does US5776389

mention anything about yellowing of polymer compositions due to degradation of brominated flame retardants.

It is desirable to find an additive that would allow preparation of HBCD-free styrenic polymer foam comprising brominated vinyl aromatic/butadiene copolymer that has a larger cell size and lower density than comparable styrenic polymer foam prepared in the absence of the additive. It is particularly desirable to prepare such foam where the cell size is at least as large as comparable HBCD-containing styrenic polymer foam and the density is at least as low as comparable HBCD-containing styrenic polymer foam. It is further desirable to minimize or eliminate yellowing resulting from decomposition of the brominated copolymer in polymeric masterbatch formulations useful for preparing foam.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a solution to the problem of finding an additive that would allow preparation of HBCD-free styrenic polymer foam comprising brominated vinyl aromatic/butadiene copolymer that has a larger cell size and lower density than comparable styrenic polymer foam prepared in the absence of the additive. Moreover, the present invention is capable further solving the problems of preparing such foam where the cell size is at least as large as comparative HBCD-containing styrenic polymer foam and the density is at least as low as comparable HBCD-containing styrenic polymer foam. Even more, the present invention is capable of minimizing or eliminating yellowing of polymer compositions resulting from decomposition of brominated flame retardant.

The present invention is a result of surprisingly discovering that glycerol esters can counteract the nucleating effect of brominated vinyl aromatic/butadiene copolymer particles in a thermoplastic foam during the process of manufacturing the foam and can further inhibit or eliminate yellowing caused by decomposition of the brominated copolymer during preparation of masterbatches containing the flame retardant, which are used to incorporate flame retardant into foam during manufacture.

In a first aspect, the present invention is a polymer composition comprising a polymer component comprising styrenic polymer at a concentration of at least 50 weight-percent of the polymer component weight, a brominated vinyl aromatic/butadiene copolymer and a glycerol ester. In a desirably embodiment, the polymer composition is a polymeric foam where the polymer component has cells defined therein.

In a second aspect, the present invention is a process for preparing the composition of the first aspect, the process comprising melt blending together the polymer component, the brominated vinyl aromatic/butadiene copolymer and glycerol ester. The process of the second aspect can further comprise melt blending into the composition a blowing agent to
5 form a foamable polymer composition and expanding the foamable polymer composition into a polymeric foam.

The process of the second aspect is useful for preparing the polymeric foam of the first aspect. The foam of the first aspect is useful, for example, as thermal insulation.

10 DETAILED DESCRIPTION OF THE INVENTION

Test methods refer to the most recent test method as of the priority date of this document when a date is not indicated with the test method number. References to test methods contain both a reference to the testing society and the test method number. The following test method abbreviations and identifies apply herein: ASTM refers to ASTM
15 International (formerly known as American Society for Testing and Materials); EN refers to European Norm, DIN refers Deutches Institute fur Normung; and ISO refers to International Organization for Standards.

“Multiple” means two or more. “And/or” means “and, or as an alternative”. All ranges include endpoints unless otherwise indicated.

20 “Majority” and “major” indicate more than half.

Two foams are “comparable” when they are made from the same foamable polymer composition and in a similar process.

“Copolymer” refers to any combination of more than one monomer co-reacted to form a polymer. Copolymers can be random copolymers or block copolymers. Block
25 copolymers can be of any type including diblock and triblock copolymers.

The polymer composition and polymeric foam of the present invention comprise a polymer component comprising styrenic polymer, a brominated vinyl aromatic/butadiene copolymer and a glycerol ester. The polymer component consists of all of the non-halogenated polymer in the polymer composition. Desirably, the only halogenated polymer
30 in the polymer composition is brominated vinyl aromatic/butadiene copolymer; so, the polymer component desirably consists of all polymer in the polymer composition except

brominated aromatic/butadiene copolymer. Desirably, the polymer composition of the present invention is free of HBCD.

(A) Styrenic Polymer

Styrenic polymer can be any one or more than one polymer selected from
5 homopolymers of styrenic monomers and copolymers containing a majority of
copolymerized styrenic monomer. Polystyrene homopolymer is the most preferable
styrenic polymer for use in the present invention.

Examples of monomers that can be copolymerized with styrenic monomers to form
copolymers that are suitable styrenic polymers for use in the present invention include any
10 one or combination of more than one monomer selected from: styrene derivatives such as
methyl styrene, di-methyl styrene, ethyl styrene, di-ethyl styrene, iso-propyl styrene, bromo
styrene, di-bromo styrene, tri-bromo styrene, chloro styrene, dichloro styrene or tri chloro
styrene; vinyl compounds such as vinyl toluene, vinyl xylene or di-vinyl benzene;
unsaturated compound such as acrylic acid, methacrylic acid, methyl acrylate, methyl
15 methacrylate, ethyl acrylate, ethyl methacrylate, butadiene or acrylonitrile or derivative
thereof; maleic anhydride and itaconic anhydride.

The styrenic polymer desirably is more than 50 weight-percent (wt%), preferably 75
wt% or more and can be 90 wt% or more, 95 wt% or more and even 100 wt% based on the
polymer component weight.

20 (B) Brominated Vinyl Aromatic/Butadiene Copolymer

The flame retardant used in the present invention is brominated vinyl
aromatic/butadiene copolymer. Preferably, the brominated vinyl aromatic/butadiene
copolymer is brominated styrene/butadiene copolymer because flame retardant effect of the
brominated vinyl aromatic/butadiene copolymer is greater. The brominated
25 styrene/butadiene copolymer includes brominated styrene/butadiene block copolymer,
brominated random styrene/butadiene copolymer and brominated styrene/butadiene graft
copolymer. Brominated tri-block brominated vinyl aromatic/butadiene copolymer such as
brominated styrene/butadiene/styrene block copolymer is more preferable. The brominated
vinyl aromatic/butadiene copolymer is desirably one or more brominated butadiene/vinyl
30 aromatic copolymer selected from those described and/or claimed in EP1957544B1.

The concentration of brominated vinyl aromatic/butadiene copolymer is desirably
0.25 wt% or more and generally 70 wt% or less based on weight of polymer component. At

concentrations below 0.25 wt% the brominated vinyl aromatic/butadiene copolymer is generally not present at a high enough concentration to improve flame retardant properties of the polymer composition to a desirable extent. At concentrations above 70 wt% , the brominated vinyl aromatic/butadiene copolymer is at such a high concentration so as to often make processing difficult.

When the polymer composition is a masterbatch concentrate, the concentration of brominated vinyl aromatic/butadiene copolymer is desirably 0.25 wt% or more, preferably 5 wt% or more, still more preferably 10 wt% or more, yet more preferably 25 wt% or more and can be 30 wt% or more, 40 wt% or more, 50 wt% or more, 60 wt% or more and even 70 wt% or more based on weight of polymer component. At the same time, the concentration of brominated vinyl aromatic/butadiene copolymer is typically 70 wt% or less based on total weight of polymer component. Masterbatch concentrate is often used to incorporate additives (such as brominated vinyl aromatic/butadiene copolymer) into additional polymer in a process such as is useful for preparing polymeric foam. Hence, the concentration of brominated vinyl aromatic/butadiene copolymer in a masterbatch concentrate is typically higher than the concentration of brominated vinyl aromatic/butadiene copolymer in polymeric foam.

When the polymer composition is in the form of polymeric foam, the concentration of brominated vinyl aromatic/butadiene copolymer is desirably 0.25 wt% or more, preferably 0.5 wt% or more and more preferably one wt% or more at the same time desirably is 10 wt% or less, preferably 5 wt% or less, and more preferably 4 wt% or less based on weight of polymer component.

(C) Glycerol ester

The glycerol ester of the present invention is desirably a glycerol monoester, preferably a glycerol monoester of glycerin and alkyl carbonic acid. The glycerol ester includes glycerol monopalmitate, glycerol monostearate and glycerol monobehenate. The preferable glycerol monoester is glycerol monostearate.

The concentration of glycerol ester in the polymer composition typically is 0.02 wt% or more and 8 wt% or less based on weight of polymer component. At concentrations below 0.02 wt%, the glycerol ester is generally not present to a sufficient extent so as to influence properties. At concentrations above 8 wt%, the glycerol ester tends to over plasticize the polymer composition and cause undesirable softening. As with the

brominated styrene/butadiene copolymer, the concentration of glycerol ester is typically higher in a masterbatch concentrate than in a polymeric foam. The concentration of glycerol ester in the polymer composition, when the polymer composition is a masterbatch concentrate, is generally 0.02 wt% or more, preferably 0.1 wt% or more, still more preferably one wt% or more, yet more preferably two wt% or more and can be three wt% or more, four wt% or more five wt% or more, six wt% or more, seven wt% or more and even eight wt% or more based on polymer component weight. At the same time, the concentration of glycerol ester is desirably eight wt% or less. The concentration of glycerol ester in the polymer composition, when the polymer composition is a polymeric foam, is desirably 0.02 wt% or more, preferably 0.03 wt% or more and at the same time is desirably 5.0 wt% or less and preferably is 3 wt% or less based on weight of the polymer component.

(D) Additional additives

The polymeric composition can further comprise additional additives. Additional additives include stabilizer, flame retardant synergists (such as dicumyl peroxide), extrusion aids, pigments, inorganic fillers, and infrared attenuating agents (such as carbon black, graphite and titanium dioxide). Example of stabilizer includes magnesium oxide, epoxy resin and phosphite. Example of extrusion aids includes metal salts of stearic acid such as barium stearate.

The polymer composition of the present invention surprisingly experiences less yellowing than a similar polymer composition that does not include the glycerol ester. Moreover, the polymeric foam form of the present invention surprisingly has a cell size that is larger than a comparable foam without the glycerol ester. Yet more, the polymeric foam of the present invention tends to have a cell size equal to or greater than a comparable foam comprising an equal amount HBCD instead of brominated alkyl aromatic/butadiene copolymer. The polymeric foam of the present invention desirably has an average cell size ("cell size") that is 0.1 millimeters (mm) or more and at the same time that is desirably 4.0 mm or less, preferably one mm or less, still more preferably 0.8 mm or less. Determine cell size according to ASTM method D-3576-04.

The polymeric foam can be either an open cell foam or a closed cell foam. Desirably, the styrenic polymer foam has an open cell content of 30 percent (%) or less, preferably 10% or less, still more preferably 5% or less, even more preferably one % or less

and can be zero %. Determine open cell content according to ASTM method D6226-05. Open cell foams can contain greater than 30% open cell content.

Desirably, the polymeric foam has a density of 24 kilograms per cubic meter (kg/m^3) or more and at the same time desirably has a density of 80 kilograms per cubic meter (kg/m^3) or less, preferably 48 kg/m^3 or less. Determine density of the styrenic polymer according to ASTM method D35-75-93, Suffix W, Method A. It is desirable to have a density of 24 kg/m^3 or more in order to ensure structural integrity. It is desirably to have a density of 80 kg/m^3 or less, especially 48 kg/m^3 or less for optimal thermal insulating properties.

Prepare the polymeric composition of the present invention by melt blending glycerol ester and brominated vinyl aromatic/butadiene copolymer together in a polymer component.

Prepare the polymeric foam form of the present invention by any foaming method suitable for preparing polymeric foam. In general the process for preparing the polymeric foam comprises: (a) melt blending the polymeric component with the brominated vinyl aromatic/butadiene copolymer, glycerol ester and a blowing agent to form a foamable polymer composition; and (b) expanding the foamable polymer composition into polymeric foam. When additional additives are present, they are typically melt blended in to form the foamable polymer composition in step (a).

Foaming process can be either batch or continuous processes. An example of a batch process is an expanded bead foam process. In an expanded bead foam process the foamable polymer composition is cooled below the softening temperature of the polymer components and processed into expandable polymer pellets. The expandable polymer pellets are placed in a mold and then heated above the softening temperature of the polymer components, thereby causing the expandable polymer pellets to foam and fuse together filling the mold space. The resulting polymeric foam comprises multiple fused expanded polymer pellets (or "beads") and has a characteristic network of polymer film extending throughout and surrounding groups of cells. The film is the skin of each bead that has fused to the skin of a neighboring bead. That network of skins can detrimentally provide thermal shorts throughout the foam thereby inhibiting the thermal insulation properties of the resulting foam

The process of the present invention is desirably a continuous process such as an extrusion process. In an extrusion process the foamable polymer composition is formed within an extruder at an initial pressure and then extruded through a die into an atmosphere at a pressure lower than the initial pressure. At the lower pressure the blowing agent expands the foamable polymer composition into a polymeric foam. Polymeric foam prepared by an extrusion process is "extruded polymeric foam" and has distinct characteristics from batch processes such as expanded bead foam process. Unlike foam made by an expanded bed foam process an extruded polymeric foam is free of a continuous network of polymer film or skin that surrounds groups of cells within the foam. Therefore, extruded thermoplastic polymer foam can be a better thermal insulating material than expanded bead foam. The polymeric foam form of the polymer composition of the present invention is desirably an extruded polymeric foam.

The blowing agent is typically selected from organic blowing agents, inorganic blowing agents and chemical blowing agents. Desirably, the blowing agent comprises or consists of one or more than one saturated hydrocarbon having 3 to 5 carbon atoms.

Examples of saturated hydrocarbon having 3 to 5 of carbon atoms are: propane, normal-butane, iso-butane, industrial butane (mixture of normal-butane and iso-butane), normal-pentane, iso-pentane, cyclopentane and neopentane. Preferable hydrocarbon having 3 to 5 carbon atoms is normal-butane or iso-butane because of blowing effect and insulating effect of obtained foam. The most preferable hydrocarbon having 3 to 5 carbon atoms is iso-butane. The concentration of saturated hydrocarbon having 3 to 5 carbon atoms is preferably 1 to 10 parts by weight based on 100 parts by weight of styrenic polymer, more preferably, 1.5 to 5 parts by weight based on 100 parts styrenic polymer in order to obtain both quality insulating effect and flame retardant effect.

Examples of other organic blowing agents include: alkyl chlorides such as methyl chloride or ethyl chloride; ethers such as dimethyl ether, diethyl ether, methyl ethyl ether, isopropyl ether, normal butyl ether, di-isopropyl ether, furan, furfural, 2-methyl furan, tetrahydro furan or tetrahydro pyran; ketones such as dimethyl ketone, methyl ethyl ketone, diethyl ketone, methyl normal-propyl ketone, methyl normal-butyl ketone, methyl iso-butyl ketone, methyl normal-amyl ketone, methyl normal-hexyl ketone, ethyl normal-propyl ketone or ethyl normal-butyl ketone; alcohols such as methanol, ethanol, normal-propanol, iso-propanol, normal-butanol, iso-butanol or tertiary-butanol; and carbonic esters such as

methyl formate, ethyl formate, propyl formate, butyl formate, amyl formate, methyl propionate or ethyl propionate.

Examples of inorganic blowing agents include carbon dioxide and water. Example of chemical blowing agents include azo compound. These blowing agents could be used alone or as a mixture of more than two blowing agents. Suitable other blowing agents include methyl chloride, ethyl chloride and dimethyl ether.

The total concentration of blowing agents is preferably, 0.5 to 20 wt% based on polymer component weight.

10 EXAMPLES

Example 1 and Comparative Examples A and B: *Effect on Average Cell Size*

Prepare Example 1 and Comparative Examples A and B by an extrusion foaming process. The polymer composition is polystyrene homopolymer (weight average molecular weight of 210,000, such as PS680 available from Styron Corp. LLC). The glycerol ester is glycerol monostearate (for example ATMER™ 129, ATMER is a trademark of Uniqema Americas, LLC). The brominated alkyl aromatic/butadiene copolymer is a brominated styrene/butadiene/styrene block copolymer that is 64 wt% bromine and that has a softening point of 120 degrees Celsius (°C), molecular weight of 100,000-160,000 grams per mole and a 5% weight loss temperature by thermogravimetric analysis of 262°C (for example, EMERALD INNOVATION™ 3000, EMERALD INNOVATION is a trademark of Chemtura Corporation).

For Example (Ex) 1 and Comparative Example (Comp Ex) A, use the brominated alkyl aromatic/butadiene copolymer as a flame retardant additive at a concentration of 2.85 wt% relative to polystyrene homopolymer weight.

25 For Ex 1, further include 2 wt% glycerol monostearate based on polystyrene homopolymer weight.

For Comp Ex B, include 2.5 wt% hexabromocyclododecane (HBCD) as a flame retardant additive at 2.5 wt% relative to polystyrene homopolymer weight in place of the brominated alkyl aromatic/butadiene copolymer and do not include any glycerol monostearate.

30 Prepare Example (Ex) 1 by preparing a flame retardant masterbatch concentration and a glycerol monostearate (GMS) masterbatch concentrate. The flame retardant

masterbatch concentration contains 50 wt% polystyrene (168,000 g/mol Mw, for example PS610 from American Styrenics), 37 wt% Br-SBC, 6.2 wt% epoxy creosol novalac (Araldite ECN 1280 from Huntsman), 3.7 wt% pentaerythritol diphosphite (DOVERPHOS™ S9228, DOVERPHOS is a trademark of Dover Chemical Corporation) and 3.1 wt% epoxidized soybean oil (Plascheck 775 from Ferro). Feed these components into a Farrel CP250 continuous mixer that feeds into a single screw extruder, which is followed by an underwater pelletizing unit and produce a pelletized concentrate using the parameters in Table 1.

Table 1

Diverter Valve Temperature	199°C	FCM Speed	80% of max ^a
Die Temperature	218°C	Orifice Setting	50% open
Water Temperature	66°C	Extruder Speed	28 RPM*
Screen Changer Temps	199°C	Pelletizer Speed	2600 RPM*
Extruder + Mixer Hopper Temps	66°C	Die Size/# of Open Holes	2.4 millimeters/6
Extruder Barrel Zone 1 Temp	182°C	Water Flow	37.8 liters/min
Extruder Barrel Zone 2 Temp	182°C	Feed Rate	90.7 kilograms/hr
Extruder + Mixer Screw Temp	60°C	Mixer Chamber Temp.	166°C

*revolutions per minute (RPM)

^aspeed is expressed in RPM as a percent of maximum RPM for this device.

Prepare the GMS masterbatch concentrate in like manner as the flame retardant concentration but with 95 wt% polystyrene (same as in flame retardant concentrate) and 5 wt% GMS (ATMER 129, ATMER is a trademark of UNIQEMA AMERICAS LLC). For processing parameters use the values in Table 2.

Table 2.

Diverter Valve Temperature	232°C	FCM Speed	80 of max ^a
Die Temperature	260°C	Orifice Setting	32% open
Water Temperature	60°C	Extruder Speed	30 RPM*
Screen Changer Temps	232°C	Pelletizer Speed	2950 RPM*
Extruder + Mixer Hopper Temps	71°C	Die Size/# of Open Holes	2.4 millimeters/3
Extruder Barrel Zone 1 Temp	221°C	Water Flow	38 liters per minute
Extruder Barrel Zone 2 Temp	229°C	Feed Rate	91 kg/hr
Extruder + Mixer Screw Temp	57°C	Mixer Chamber Temp	177°C

*revolutions per minute (RPM)

^aspeed is expressed in RPM as a percent of maximum RPM for this device.

Feed the two masterbatch concentrates and polystyrene (weight average molecular weight of 210,000 grams per mole (g/mol), such as PS680 available from Styron Corp. LLC) along with remaining additives as identified in Table 3 into a 25 mm single screw extruder with five heating zones, a blowing agent mixing section, cooler sections and adjustable slit die. Feed the components at the following rates: 36.3 kilograms per hour (kg/hr) GMS masterbatch concentrate, 7.0 kg/hr flame retardant masterbatch concentrate, 0.1 kg/hr barium stearate, 0.24 kg/hr linear low density polyethylene (DOWLEX™ 2247G, DOWLEX is a trademark of The Dow Chemical Company), 0.045 kg/hr blue concentrate (40 wt% phthalocyanine blue in polystyrene resin), 15.4 kg/hr polystyrene and 31.75 kg/hr of a recycle composition comprising each of the aforementioned components in the ratio shown in Table 3. The total feed rate is 90.7 kg/hr.

Melt blend the components in the extruder with the five heating zones set at 95°C, 145°C, 180°C, 200°C and 200°C, respectively. Inject a blowing agent composition (carbon dioxide, 35/65 mix of isobutane/normal butane, and ethyl chloride at ratios in Table 3) into the mixture in the blowing agent mixing section at a pressure of 170 bar to form a foamable polymer composition. Mix the foamable polymer composition for four minutes at 210°C and feed into the cooler section. Cool the foamable polymer composition to 109°C and extrude through a slit die (2.5 millimeter gap height by 76.2 millimeter width) into atmospheric pressure (760 bar) and allow to expand into polymeric foam. The resulting foam was conditioned 25°C for seven days at atmospheric pressure to obtain Example 1.

Prepare Comparative Example (Comp Ex) A in like manner as Example 1 except do not include the glycerol monostearate masterbatch when preparing the polymer foam.

Prepare Comp Ex B in like manner as Example 1 except do not include either of the two masterbatch concentrates and instead feed in hexabromocyclododecane (HBCD) at a rate of 11.02 kg/hr to achieve a final concentration in the foam of 2.5 wt% relative to polymer composition weight. Also feed into the extruder a magnesium oxide (an acid scavenger) additive in the form of a 75 wt%/25 wt% blend of barium stearate with magnesium oxide (available as BM75 from Sun Ace Corporation) at a feed rate of 1.01 kg/hr to achieve a final concentration of magnesium oxide in the foam of 0.06 wt% relative to total polymer composition weight.

The composition (in wt% relative to polystyrene) and resulting polymeric foam characteristics for Ex 1 and Comp Exs A and B are in Table 3. The foam characteristics

reveal that GMS effectively counteracted the nucleating effect of Br-SBC (compare Ex 1 to Comp Ex A) and to such an effect as to even produce a foam having a larger cell size than foam made using HBCD (compare Ex 1 to Comp Ex B).

Table 3

Component		Ex 1	Comp Ex A	Comp Ex B
Flame retardant	Br-SBC	2.85	2.85	-
	HBCD	-	-	2.5
Cell size enlarger	GMS	2	-	-
Foaming agents	Carbon dioxide	3	3	3
	Ethyl chloride	4.3	4.3	4.3
	Industrial butane (mixture of iso butane and normal butane)	2	2	2
Other additives	Barium stearate	0.17	0.17	0.17
	Magnesium oxide	-	-	0.06
	Pigment (Phthalocyanine copper)	0.05	0.05	0.05
	Polyethylene	0.4	0.4	0.25
Characteristics				
Cell size (millimeters) per ASTM D3576-04		0.75	0.29	0.60
Density without skins (kg/m ³) per ASTM D 2575-93, Suffix W, Method A		26.87	37	35

5

The flame retardant test was conducted according to JIS A 9511. For each of the examples and comparative examples, the flame of the sample was extinguished within 3 seconds and combustion was not continued exceeding the combustion limiting line without embers was determined as pass the test. Therefore, Ex 1 illustrates that the GMS additive serves as an effective cell size enlarger even in the presence of brominated styrene/butadiene copolymer and that the GMS does not inhibit passage of the critical JIS A 9511 flame retardancy test.

10

Examples 2, 3 and Comparative Example C: Effect on Masterbatch Concentrate

15

Yellowness

Decomposition of brominated flame retardant can result in yellowing of a masterbatch concentrate containing the brominated flame retardant. It has been discovered that combining a glycerol ester with a brominated styrene/butadiene copolymer flame

retardant in a masterbatch concentrate results in reduced or eliminated yellowing. This result is evident in comparing yellowing characteristics of the following Exs 2 and 3 with that of Comp Ex C.

The Master Batch Concentrate of Example (Ex) 2 is a flame retardant masterbatch concentrate containing Br-SBC , glycerol monostearate (GMS), and additional additives. The flame retardant masterbatch concentrate contains 50 wt% polystyrene (168,000 g/mol Mw, for example PS610 from American Styrenics), 31.25 wt% Br-SBC, 7.81 wt% GMS (ATMER 129, ATMER is a trademark of UNIQEMA AMERICAS LLC), 5.24 wt% epoxy creosol novalac (Araldite ECN 1280 from Huntsman), 3.13 wt% pentaerythritol diphosphite (Doverphos S9228 from Dover Chemical) and 2.62 wt% epoxidized soybean oil (Plascheck 775 from Ferro). Feed these components into a Farrel CP250 continuous mixer that feeds into a single screw extruder, which is followed by an underwater pelletizing unit and produce a pelletized concentrate using the parameters in Table 4.

Table 4

Diverter Valve Temperature	178°C	FCM Speed	55% of max ^a
Die Temperature	218°C	Orifice Setting	40% open
Water Temperature	60°C	Extruder Speed	27RPM*
Screen Changer Temps	199°C	Pelletizer Speed	1800 RPM*
Extruder + Mixer Hopper Temps	71°C	Die Size/# of Open Holes	2.4 millimeters/3
Extruder Barrel Zone 1 Temp	210°C	Water Flow	37.8 liters/min
Extruder Barrel Zone 2 Temp	210°C	Feed Rate	90.7 kilograms/hr
Extruder + Mixer Screw Temp	71°C	Mixer Chamber Temp.	159°C

*revolutions per minute (RPM)

^aspeed is expressed in RPM as a percent of maximum RPM for this device.

Prepare masterbatch concentrate Ex 3 in like manner as for Ex 2 except adjust the concentrations of the following components to: 32.97 wt% Br-SBC, 5.49 wt% GMS (ATMER 129, ATMER is a trademark of UNIQEMA AMERICAS LLC), 5.52 wt% epoxy creosol novalac (Araldite ECN 1280 from Huntsman), 3.3 wt% pentaerythritol diphosphite (Doverphos S9228 from Dover Chemical) and 2.76 wt% epoxidized soybean oil (Plascheck 775 from Ferro). Prepare masterbatch concentrate Comp Ex C as described for the flame retardant masterbatch concentrate for Ex 1.

Characterize the color of masterbatch concentrates of Ex 2, Ex 3 and Comp Ex C according to the method of ASTM E313-00 Yellowness Index Standard using Color iTM7

Benchtop Spectrophotometer (available from X-Rite) using a test plaque of each masterbatch concentrate. Prepare a test plaque of masterbatch concentrate by pre-melting a sample of the masterbatch concentrate and then pressing the molten sample for 15 seconds under 12 tons of pressure using a Wabash Press model G302H-12-BC to produce a plaque of masterbatch concentrate that is 47-48 millimeters thick. Report the characterization as a yellowing index (YI) value. Higher YI values correspond to a more yellow color.

YI index values for Exs 2 and 3 and Comp Ex C are as follows: YI (Ex 2) = 12.59; YI (Ex 3) = 12.53; YI(Comp Ex C) = 25. Inclusion of glycerol ester with the Br-SBC in a masterbatch concentrate results in a reduction in yellowing by almost a factor of two. These results are included in a summary of Exs 2 and 3 and Comp Ex C in Table 5.

Use the masterbatch concentrates of Exs 2 and 3 and Comp Ex C to prepare polymeric foam. Use the foaming procedure of Ex 1 to produce polymeric foams of Exs 2, 3 and Comp Ex C.

Table 5

	Ex 2	Ex 3	Comp Ex C
YI for master batch	12.59	12.53	25.14
Cell size (mm)	0.60	0.57	0.42
Density without skins (kg/m ³)	33.8	36.2	37.6
JIS Fire Test (sec.)	1.4	1.6	1.7
	PASS	PASS	PASS

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The flame retardant test was conducted according to JIS A 9511. For each of the examples and comparative examples, the flame of the sample was extinguished within 3 seconds and combustion was not continued exceeding the combustion limiting line without embers was determined as pass the test. Exs 2 and 3 illustrate that the GMS additive serves as an effective cell size enlarger in the presence of brominated styrene/butadiene copolymer and that the GMS does not inhibit passage of the critical JIS A 9511 flame retardancy test.

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CLAIMS:

1. A polymer composition comprising a polymer component comprising non-halogenated styrenic polymer at a concentration of at least 50 weight-percent of the polymer component weight, a brominated vinyl aromatic/butadiene copolymer and a glycerol ester;
5 where the polymer component consists of all non-halogenated polymers in the polymer composition.

2. The composition of Claim 1, wherein the brominated vinyl aromatic/butadiene copolymer is a brominated styrene/butadiene/styrene triblock copolymer.

3. The composition of Claim 1 or Claim 2, wherein the styrenic polymer
10 comprises polystyrene.

4. The composition of any of Claims 1-3, wherein the glycerol ester is glycerol monostearate.

5. The composition of any of Claims 1-4, wherein the polymeric foam is an extruded polymeric foam.

15 6. The composition of any of Claim 1-5, wherein glycerol ester is present at a concentration of 0.02 weight-percent or more and 5.0 weight-percent or less based on styrenic polymer.

7. The composition of any of Claims 1-6, wherein the composition is in the form of a polymeric foam wherein the polymer component has cells defined therein.

20 8. A process for preparing the composition of Claim 1, the process comprising melt blending together the polymer component, the brominated vinyl aromatic/butadiene copolymer and glycerol ester.

9. The process of Claim 8, further comprising melt blending into the composition a blowing agent to form a foamable polymer composition and expanding the
25 foamable polymer composition into a polymeric foam.

10. The process of Claim 9, further characterized by forming the foamable polymer composition in an extruder at an initial pressure and then extruding the foamable polymer composition through a die into an atmosphere at a pressure lower than the initial pressure.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/064904

A. CLASSIFICATION OF SUBJECT MATTER INV. C08L25/06 C08L53/02 C08K5/103 C08J9/16 ADD.		
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) C08J C08L C08K		
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) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/016906 A1 (BASF SE [DE]; BELLIN INGO [DE]; HAHN KLAUS [DE]; HAVERKEMPER GREGOR [D] 9 February 2012 (2012-02-09) page 9, line 28 - line 30; claims 17,18 page 10, line 40 - page 41 page 11, line 9 example 8; table 2 -----	1-10
X	US 2012/252914 A1 (HAHN KLAUS [DE] ET AL) 4 October 2012 (2012-10-04) paragraphs [0068], [0073]; claim 26 examples 2-4; table 1 -----	1-10
X,P	WO 2013/081958 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 6 June 2013 (2013-06-06) claim 7 -----	1-10
☐ 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 12 March 2014		Date of mailing of the international search report 18/03/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Friebe, Lars

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/064904

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