The invention relates to a liquid flame retardant formulation useful for flexible foams in flame lamination applications.
This invention relates to a liquid flame retardant formulation for use in flexible foam applications. More particularly this invention relates to a liquid flame retardant formulation useful for flexible foams in flame lamination applications.

BACKGROUND

Polyurethane foams are used in many applications such as furniture, (chairs, couches, mattresses, pillows), automobiles, (car seats, head and arm rests, roof liniers, dashboards), carpet liniers, filtration media, insulation, etc. Like all carbon based products, polyurethane foams have the potential to burn, but polyurethane foams are especially susceptible because they have a very large surface area by weight and being open celled allows ready access to oxygen required for combustion. Much research has been done on providing flame retardancy to these foams. However, the art is always striving for suitable flame retardants compositions that outperform or have more favorable characteristics than those currently available.

Examples of areas in which flexible foams are used include automotive interiors, seating, and furniture applications. In one application, flexible foams are attached or adhered to textiles by flame lamination. Flame lamination is a term used for a process for the bonding of textiles and foams by using a flame for incipient melting of one side of a foam sheet and then immediately pressing a textile web onto this side. The requirements for this application is that the resulting textile have good flame retardant properties, good adhesion between the textile and foam, and for some customers good scorch and low fogging/volatile organic carbon (VOC) emissions.

SUMMARY OF THE INVENTION

The present invention relates to a liquid flame retardant composition useful for flexible polyurethane foams in a flame lamination application comprising:

(a) a liquid flame retardant;

(b) an aromatic polyester polyol;

(c) a low molecular weight diol;
(d) a cyclic phosphonate flame retardants; and
(e) an optional alkylated diphenylamine or hindered phenol antioxidant.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Fig. 1 illustrates the Scorch Test data in Table 2 comparing inventive Example 1 with Comparative Examples 2 to 5 and 12.

**DETAILED DESCRIPTION OF THE INVENTION**

The present invention relates to a liquid flame retardant composition comprising: a liquid flame retardant, an aromatic polyester polyol, a low molecular weight diol, a cyclic phosphonate flame retardants, and an optional hindered phenol antioxidant.

The liquid flame retardant may be any suitable liquid flame retardant used in the industry. Preferably, the liquid flame retardant is a phosphorus flame retardant or a halogenated phosphorus flame retardant. For example, the phosphorus flame retardant that may be used is a chloroalkyl phosphate or phosphonate flame retardant.

Examples of such liquid flame retardants include, but are not limited to, bis(2-chloroethyl) 2-chloroethyl phosphonate, tris(monochloropropyl) phosphate, tri(1,3-dichloroisopropyl) phosphate, 2,2-bis(chloromethyl)trimethylene bis(bis(2-chloroethyl)phosphate), bisphenol A bis-(diphenyl phosphate), isopropylated phenol phosphate (IPPP), dimethyl methyl phosphonate, diethylethyl phosphonate, or mixtures thereof.

The amount of the liquid flame retardant that may be used may range from about 1 wt % to about 90 wt% or more particularly about 7.5 wt% to about 80 wt%, or most especially about 15 wt% to about 70 wt% based on the total weight of the composition.

The aromatic polyester polyol is formed by reaction between (a) an aromatic acid based material (e.g., a phthalic acid based material), (b) an hydroxylated material and optional (c) an hydrophobic material.

The term "aromatic polyester polyol" as used herein means a polyol having ester linkages and an aromatic component. The aromatic polyester polyols advantageously have an average functionality of from about 1.5 to 8.0, preferably from about 1.6 to 6.0, and more preferably from about 1.8 to 4.0. Their average hydroxyl number values generally fall within a range of about 50 to about 400 or about 100 to about 325 or about 150 to about 250. "Hydroxyl number" refers to the concentration of hydroxyl groups, per unit weight of the
polyol, that are able to react with the isocyanate groups. Hydroxyl number is reported as mg KOH/g, and is measured according to the standard ASTM D 1638.

The viscosity of the aromatic polyester polyol ranges from about 300 to about 25,000 centipoise at a temperature of about 25° C.

The aromatic component of the aromatic polyester polyol composition can be, for example, phthalic acid based components such as phthalic acid, terephthalic acid, isophthalic acid, phthalic anhydride, pyromellitic anhydride, dimethyl terephthalate, polyethylene terephthalate, trimellitic anhydride, bottom residues, derivatives thereof, and combinations thereof. By phthalic acid based material as used herein is meant phthalic acid or a derivative of phthalic acid. A preferred phthalic acid based material for use in the preparation of the aromatic polyester polyols is ortho or terephthalic anhydride.

The aromatic component of the aromatic polyester polyol can comprise, for example, from about 20% to about 70% by weight of the aromatic polyester polyol composition, alternatively between about 30% to about 60% by weight.

The hydroxylated component of the aromatic polyester polyol composition of the present technology can be, for example, at least one aliphatic diol, at least one derivative thereof, or combinations thereof.

The hydroxylated component may be an aliphatic diol of generic formula (1):

\[ \text{HO-R}^1-\text{OH} \]

where \( \text{R}^1 \) is a divalent radical selected from the group consisting of

(a) alkylene radicals each containing from 2 through 18 carbon atoms, and

(b) radicals of the formula (2): \(-\text{(R}^2\text{O)}\text{n-R}^2\)- where \( \text{R}^2 \) is an alkylene radical containing from 2 through 3 carbon atoms, and \( \text{n} \) is an integer of from 1 through 3, and

(c) mixtures thereof.

Examples of suitable aliphatic diols of formula (1) include ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, trimethylene glycol, butylene glycols, 1,2-cyclohexanediol, poly (oxyalkylene) polyols each containing from two to four alkylene radicals derived by the condensation of ethylene oxide, propylene oxide, or any combination thereof, and the like. As those skilled in the art will appreciate, in the preparation of mixed poly(oxyethylene-oxypropylene) polyols, the ethylene and propylene oxides may be added to a starting hydroxyl-containing reactant either in admixture or sequentially. Mixtures of such diols can be employed, if desired. A presently most preferred aliphatic diol of formula (I) is diethylene glycol. Additionally, amine-based aliphatic hydroxylated materials (i.e., hydroxylated amines) may be utilized, such as for example, monoethanolamine, diethanolamine, and triethanolamine.
Optionally, and for example, mixtures of diols can incorporate low molecular weight polyols (that is, compounds which contain less than 7 carbon atoms per molecule but which contain at least three hydroxyl groups per molecule) in an amount generally ranging from greater than 0 up to 100 percent of the total hydroxylated material. Such polyols comprise, for example, glycerol, 1,1,1-trimethylolpropane, 1,1,1-trimethylol ethane, 2,2-dimethyl-1,3-propane diol, pentaerythritol, mixtures thereof, and the like.

The hydroxylated component of the aromatic polyester polyol composition can comprise, for example, from about 30% to about 80% based on the total weight of the aromatic polyester polyol composition. Alternatively, the hydroxylated component of the aromatic polyester polyol can be from about 30-65% by weight, based on the total weight of the aromatic polyester polyol. Alternatively, the hydroxylated material in the polyester polyol is from about 40-60% by weight, based on the total weight of the aromatic polyester polyol.

Optionally, the aromatic polyester polyol may contain a hydrophobic component. Example of such hydrophobic components, include, but are not limited to: carboxylic acids (especially fatty acids), lower alkanol esters of carboxylic acids (especially fatty acid methyl esters) fatty acid alkanolamides, and natural oils (e.g., triglycerides (especially fats and oils)) derived from renewable resources. The natural oils may be unmodified (e.g., do not contain a hydroxyl functional group), functionalized (natural oil polyols) or a combination thereof. Suitable natural oils for practice of the present technology include, for example, triglyceride oils, coconut oil, cochin oil, corn oil, cottonseed oil, linseed oil, olive oil, palm oil, palm kernel oil, peanut oil, soybean oil, sunflower oil, tall oils, tallow, lesquerella oil, tung oil, whale oil, tea seed oil, sesame seed oil, safflower oil, rapeseed oil, fish oils, derivatives thereof, and combinations thereof. Suitable derivatives thereof of natural oils include, but are not limited to, carboxylic acids (e.g., fatty acids, lower alkanol esters (e.g., fatty acid methyl esters) and fatty acid alkanolamides. Examples of fatty acids include, but are not limited to, caproic, caprylic, capric, lauric, myristic, palmitic, stearic, oleic, linoleic, linolenic, ricinoleic, and mixtures thereof. Another suitable acid is 2-ethylhexanoic acid. Examples of fatty acid methyl esters include, but are not limited to, methyl caproate, methyl caprylate, methyl caprate, methyl laurate, methyl myristate, methyl palmitate, methyl oleate, methyl stearate, methyl linoleate, methyl linolenate, and mixtures thereof. Examples of fatty alkanolamides include, but are not limited to, tall oil fatty acid diethanol amide, lauric acid diethanolamide, and oleic acid monoethanolamide. These suitable natural oils can be functionalized by expoxidizing and/or hydroxylating reactions.
In some embodiments of the aromatic polyester polyol blend, the hydrophobic material is about 1% to about 40% of the total weight of the aromatic polyester polyol, alternatively about 5% to about 20%. Suitably, the hydrophobic material is a natural oil component.

The aromatic acid based polyester polyol reaction product is formed by the reaction of the aromatic acid based material (e.g., phthalic acid), the hydroxylated material, and optional hydrophobic material. The reaction typically occurs at a temperature of about 180°C to about 220°C, although other temperatures can satisfactorily enable the desired reaction.

Examples of commercial aromatic polyester polyols that may be used are those under the product names Terate® (available from Invista), Terol® (available from Oxid), and Stepanpol® (available from Stepan Chemical Corporation).

The amount of the aromatic polyester polyol that may be used may range from about 10 wt% to about 80 wt% or about 20 wt% to about 70 wt%, or about 25 wt% to about 50 wt%, based on the total weight of the composition.

The low molecular weight diol that may be used will typically have a molecular weight less than about 200, or less than about 175 or less than about 150. Examples of low molecular weight diols that may be used include, but are not limited to ethylene glycol, propylene glycol, butylene glycol, pentylene, glycol, hexylene glycol, octylene glycol, diethylene glycol, dipropylene glycol, dihexylene glycol, trimethylene glycol, butylene glycols, 1,2-cyclohexanediol or mixtures thereof.

The amount of the low molecular weight diol that may be used may range from about 0.5 wt% to about 10 wt% or about 1 wt% to about 7 wt%, about 1 wt% to about 5 wt%, based on the total weight of the composition.

Cyclic phosphonate flame retardants are known in the industry. In one embodiment of a cyclic phosphonate flame retardant, there are two P-alkylphosphonic acid diesters. One diester has one (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl ester group, and the other diester has two (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl ester groups. In the P-alkylphosphonic moiety of the P-alkylphosphonic acid diesters, the alkyl group has one to about six carbon atoms. Examples of suitable alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, penty1, hexyl, and the like. Preferred alkyl groups for the P-alkylphosphonic moiety include methyl and ethyl (so the P-alkylphosphonic moiety is P-methylphosphonic or P-ethylphosphonic), with methyl being more preferred. For the diester which has one (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl ester group, the alkyl ester group has one to about six carbon atoms.
atoms. Suitable alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, pentyl, hexyl, and the like. Preferred alkyl groups for the alkyl ester include methyl and ethyl, with methyl being more preferred. Particularly preferred P-alkylphosphonic acid diesters in the practice of this invention are the (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl methyl ester of P-methylphosphonic acid (CAS No. 41203-81-0) and the bis[(5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl]ester of P-methylphosphonic acid (CAS No. 42595-45-9).

Proportions of the P-alkylphosphonic acid diester having one (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl ester group to P-alkylphosphonic acid diester having two (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl ester groups can be in the range of about 25:1 to about 1:5, or about 10:1 to about 1:1, or about 5:1 to about 2:1. In the practice of this invention, a particularly preferred ratio of P-alkylphosphonic acid diester having one (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl ester group to P-alkylphosphonic acid diester having two (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl ester groups is about 3.35:3.55:1.

One commercial example of a cyclic phosphonate flame retardants is Amguard™ CU, which is a mixture of the (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl ester of P-methylphosphonic acid (~3.5 parts) and bis[(5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl]ester of P-methylphosphonic acid (~1 part).

Alternative nomenclature for the components in Amguard CU are Phosphonic acid, methyl-, (5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl) methyl methyl ester, P-oxide (Cas # 41203-81-0) and Phosphonic acid, methyl-, bis[(5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl) methyl ester, P,P'-dioxide (Cas # 42595-45-9).

The amount of the cyclic phosphonate flame retardant that may be used may range from about 0.1 wt% to about 10 wt% or about 0.25 wt% to about 7.5 wt%, or about 0.5 wt% to about 5 wt%, based on the total weight of the composition.

Optionally, the composition may also contain an antioxidant such as an alkylated diphenylamine or a hindered phenol antioxidant.

Alkylated diphenylamine has the general formula: \( R_a^\text{-NH-R_b} \), wherein \( R_a \) and \( R_b \) each independently represents a substituted or unsubstituted phenyl group. Substituents on the phenyl rings may include but are not limited to alkyl groups having from 1 to 20 carbon atoms, alkylaryl groups, hydroxy, carboxy and nitro groups. In one embodiment of the invention, one or both of the phenyl groups are substituted with an alkyl. In yet another embodiment of the invention, both phenyl groups are alkyl substituted.
Examples of alkylated diphenylamines which can be used in the present invention include 3-hydroxydiphenylamine, N-phenyl-1,2-phenylenediamine, N-phenyl-1,4-phenylenediamine, butyldiphenylamine, dibutylidiphenylamine, octyldiphenylamine, dioctydiphenylamine, di-tert-octyldiphenylamine, nonyldiphenylamine, dinonyldiphenylamine, heptyldiphenylamine, diheptyldiphenylamine, methylstyryldiphenylamine, mixed butyl/octyl alkylated diphenylamines, mixed butyl/styryl alkylated diphenylamines, mixed ethyl/nonyl alkylated diphenylamines, mixed octyl/styryl alkylated diphenylamines, and combinations of these of varying degrees of purity that are commonly used in the petroleum industry.

Hindered phenol compounds preferably contain at least one group of the formula:

![Chemical Structure](image)

in which \( R^3 \) is hydrogen, methyl or tert-butyl and \( R^4 \) is substituted or unsubstituted alkyl or substituted or unsubstituted thioether and \( \sim \sim \sim \) means that the phenol is bonded to another group.

Examples of such sterically hindered phenols are:

- 2,6-di-tert-butyl-4-methylphenol
- 2-tert-butyl-4,6-dimethylphenol
- 2,6-di-tert-butyl-4-ethylphenol
- 2,6-di-tert-butyl-4-n-butylphenol
- 2,6-di-tert-butyl-4-i-butylphenol
- 2,6-dicyclopentyl-4-methylphenol
- 2-(a -methylcyclohexyl)-4,6dimethylphenol
- 2,6-dioctadecyl-4-methylphenol
- 2,4,6-tricyclohexylphenol
- 2,6-di-tert-butyl4-methoxymethylphenol
- 2,6-dinonyl-4-methylphenol
- 2,6-di-tert-butyl-4-methoxyphenol
- 2,5-di-tert-butylhydroquinone
- 2,5-di-tert-amylhydroquinone
- 2,6-diphenyl4-octa-decylxoyphenol
- 2,2'-thiobis(6-tert-butyl-4-methylphenol)
- 2,2'-thiobis(4-octylphenol)
- 4,4'-thiobis(6-tert-butyl-3-methylphenol)
- 4,4'-thiobis(6-tert-butyl-2-methylphenol)
- 2,2'-methylenebis(6-tert-butyl-4-methylphenol)
- 2,2'-methylenebis[4-methyl-6-(a.-methylcyclohexyl)phenol]
- 2,2'-methylenebis(4-methyl-6-cyclohexylphenol)
- 2,2'-methylenebis(6-tert-butyl-4-ethylphenol)
- 2,2'-methylenebis[4-methyl-6-(a.-methylberi2yl)-4-nonylphenol]
dimethylbenzyl)-4-nonyl-phenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1'-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-do-decylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis[3-tert-butyl-4-hydroxy-5-methylphenyl]dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethyl benzene, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithiophthalate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate and the calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, p-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid and of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with monohydric or polyhydric alcohols, for example with methanol, octadecanol, 1,6-hexanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, and the amides of these acids, for example N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl-propionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl-propionyl)trimethylenediamine and N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl-propionyl)hydrazine or mixtures thereof.

The amount of the alkylated diphenylamine or hindered phenol antioxidant that may be used may range from 0 wt % to about 10 wt% or about 0.01 wt% to about 5 wt%, or about 0.1 wt% to about 3 wt%, based on the total weight of the composition.

Another embodiment of this invention is a method of producing a polyurethane foam composition. The method comprises combining the liquid flame retardant composition of the present invention with a polymerization formulation comprised of isocyanate and polyl along with at least one surfactant, at least one blowing agent, at least one catalyst, and optionally other additives such as anti-stat agents, anti-microbial agents, and pigments and reacting the mixture to form a flexible polyurethane foam.

To provide flame retardancy to polyurethane foams, the liquid flame retardant composition is typically included as one the components employed in the polyurethane foam formation process. The polyurethane foam is usually formed under normal polyurethane foam formation conditions and normal polyurethane foam formation methods/processes. For

Flexible polyurethane foams are typically formed by bringing together at least two liquids - isocyanates and polyols. The polyols can be polyether or polyester polyols, natural oil-based polyols, or copolymer polyols. The reaction readily occurs at room temperature in the presence of a blowing agent such as water, a volatile hydrocarbon, halocarbon, or halohydrocarbon, or mixtures of two or more such materials. Catalysts used in effecting the reaction include amine catalysts, tin-based catalysts, bismuth-based catalysts or other organometallic catalysts. Surfactants such as substituted silicone compounds are often used in order to provide for cell nucleation or to maintain homogeneity of the cells in the polymerization system. Preferred catalysts include triethylenediamine (33%) in dipropylene glycol, and stannous octoate.

The polyol or polyols used in forming the polyurethane foams in the practice of this invention, in addition to those used in the liquid flame retardant composition, may be any polyl that can be used to produce flexible polyurethane foams. When flexible polyurethane foam is being formed, the polyl usually is a polyl or mixture of polyols having hydroxyl numbers up to about 150 mg KOH/g, preferably in the range of 0 to about 100 mg KOH/g, and more preferably in the range of about 10 to about 100 mg KOH/g. Suitable polyols for flexible polyurethane foams include polyether polyols. In the practice of this invention, preferred polyols for forming flexible polyurethane foams include Voronol® 3010 polyl, (a polyl ether polyl having a molecular weight of about 3000 and a hydroxyl number of about 56 mg KOH/g; The Dow Chemical Company, Midland, MI), Pluracol® 1718 polyl (a polyl ether polyl having a molecular weight of about 3000 and a hydroxyl number of about 58 mg KOH/g; BASF Corporation, Florham Park, NJ), and Pluracol® 1388 polyl (a polyl ether triol having a molecular weight of about 3100; BASF Corporation, Florham Park, NJ).

In the practice of this invention, when forming flexible polyurethane foams, the isocyanate can be any isocyanate that is normally used to produce flexible polyurethane foams. Generally, the isocyanate has at least one isocyanate group, more preferably two
isocyanate groups, and molecules having more than two isocyanate groups can be utilized. Preferably, diisocyanates are used. The isocyanates used herein can be aliphatic or aromatic isocyanates. Examples of isocyanates that can be used for forming flexible polyurethane foams in the practice of this invention include, but are not limited to, 1,4-tetramethylene diisocyanate, 1,5-pentamethylene diisocyanate, 2-methyl-1,5-pentamethylene diisocyanate, 1,6-hexamethylene diisocyanate (HMDI), 1,7-heptamethylene diisocyanate, 1,10-decamethylene diisocyanate, cyclohexylene diisocyanate, isophorone diisocyanate (IPDI), 2,2,4-trimethylhexamethylene diisocyanate, 2,4,4-trimethylhexamethylene diisocyanate, 4,4'-methylenebis(cyclohexylisocyanate), phenylene diisocyanate, toluene diisocyanate (TDI), xylene diisocyanate, other alkylated benzene diisocyanates, 1,5-naphthalene diisocyanate, diphenylmethane diisocyanate (MDI, sometimes called methylene diisocyanate), and mixture of any two or more of these. Preferred isocyanates for flexible polyurethane foams include toluene diisocyanate and diphenylmethane diisocyanate.

Flexible polyurethane foams can be prepared by the one-shot process, the quasi- or semi-prepolymer process, or the prepolymer process. Further, the flexible polyurethane foams may be used to form articles such as molded foams, slabstock foams, and may be used as cushioning material in furniture and automotive seating, in mattresses, as carpet backing, as hydrophilic foam in diapers, and as packaging foam.

In the forming the polyurethane foams of the invention, a flame retardant amount of the liquid flame retardant composition is used. By a flame retardant amount is meant that amount of the liquid flame retardant composition needed to obtain the desired level of flame retardancy. At least for flexible polyurethane foams, a flame retardant amount is typically in the range of about 1 php to about 45 php, preferably is in the range of about 3 php to about 35 php, and more preferably is in the range of about 3 php to about 25 php, where "php" means parts flame retardant per hundred parts polyol used in the polyurethane formulation.

Suitable blowing agents in the practice of this invention when forming flexible polyurethane foams include water, a volatile hydrocarbon, halohydrocarbon, or halocarbon, or mixtures of any two or more of these. Preferred blowing agents for flexible polyurethane foams include combinations of water with methylene chloride, Freon 11, or acetone, in a weight ratio of water to the other component of the combination in the range of about 1:2 to about 2:1; water and methylene chloride are a preferred combination.

Catalyst systems for forming flexible polyurethane foams include amine catalysts such as dimethylethyl amine, triethylene diamine, and bis(dimethylaminoethyl) ether. A preferred catalyst system is a combination or blend of amine catalysts such as a blend of
dimethylethyl amine, triethylene diamine, and bis(dimethylaminoethyl) ether. The catalysts are usually used in amounts of about 0.001 to about 2 parts by weight per 100 parts by weight of the polyl(s).

One or more optional additives can be included when forming either a flexible polyurethane foam. Such optional additives include surfactants, antioxidants, diluents, chain extenders or cross-linkers, synergists (preferably melamine), stabilizers, coloring agents, fillers, antistatic agents and cell openers.

Cell openers, a particular type of surfactant, are typically polyalkylene oxides. Suitable polyalkylene oxide cell openers in the practice of this invention include polyethylene glycol monoallyl ether, polyethylene glycol allyl methyl diether, polyethylene glycol monoallyl ether acetate, polyethylene glycol monomethyl ether, polyethylene glycol glycerol ether, polyethylene-polypropylene glycol monoallyl ether, polyethylene-polypropylene glycol monoallyl monomethyl diether, and polyethylene-polypropylene glycol allyl ether acetate. Preferred cell openers include Tegostab® B 8239, Evonik Industries AG, Essen, Germany and Tegostab® B 8229, Evonik Industries, Essen, Germany).

Surfactants can be used in forming flexible or semi-flexible polyurethane foams as well, if desired. They serve as a surface-active substance in order to improve the compatibility of the various components of the formulation and to control the cell structure. Examples of suitable surfactants are emulsifiers such as sodium salts of castor oil sulfates or fatty acids; fatty acid salts with amines, e.g., diethylamine oleate and diethanolamine stearate; salts of sulfonic acids, e.g., alkali metal or ammonium salts of dodecylbenzenedisulfonic acid and ricinoleic acid; foam stabilizers such as siloxaneoxyalkylene copolymers and other organopolysiloxanes, ethoxylated alkylphenols, ethoxylated fatty alcohols and castor oil.

These surface-active substances are usually used in amounts of from 0.01 to 5 parts by weight based on 100 parts by weight of polyl blend.

The following Examples illustrate the present invention. It is to be understood, however, that the invention as fully described herein, and as recited in the claims, is not intended to be limited by the details of the following Examples.
EXAMPLES

EXAMPLE 1 AND COMPARATIVE EXAMPLES 2-5

FOAM FORMULATIONS

In foam formulation Example 1 and Comparative Examples 2 to 5, the following ingredients were additional added to the formulations to produce a block polyurethane foam: 100 parts of polyether polyol (KONIX GP-3001 from Korea Polyol), 3.5 parts water, 1 part silicone stabilizer (Tegostab® B8239 from TH. Goldschmidt AG), 0.16 parts triethylenediamine catalyst (Dabco® 33LV from Air Products, GMBH), 0.28 parts of tin octate (Dabxco® T-9 from Air Products), 4 parts methylene chloride as blowing agent (obtained from Reagent & H.V. Chemical); 105 parts toluene diisocyanate (TDI-80 from BASF) and a variable amount (from 3.5 - 10 parts) of the liquid flame retardant composition of Examples 1 and Comparative examples 2 to 5 below. (All concentrations are phr - parts ingredients per 100 parts polyether polyol).

The polyol, surfactant, flame retardant formulation, water and triethylenediamine catalyst were weighed into a half-gallon container in the amounts indicated above and in the Tables 1 below. The mixtures were then pre-blended with a bow tie agitator at 2000 rpm for 60 seconds or until the mix was homogenous with no visible phase separation. Once mixed, the rpm's were reduced to 500, the timer was started and the blend was mixed for 40 seconds, at which time the TDI (isocyanate) was added. At 50 seconds, the stannous octoate was added and mixing continued until cream time (reaction time) was noted. The mixture was then poured into a 14x14x14-in. cardboard box and rise time was recorded. Times are from the start of mixing to point of observation. For this system, the typical reactivity profile was 35 sec for cream time, 1 min 5 sec for gel time, 1 min 35 sec for tack free time, and 2 min 5 sec for free rise time.

The block foam materials were tested using Federal Motor Vehicle Safety Standard (FMVSS) Flame Retardant Test 302. This test has 4 possible classifications self-extinguishing ("SE") > no burn rate ("NBR") > Pass > Fail.

The bond strength of the laminates obtained was determined in accordance with the following procedure. First, the foam was prepared based on the desired formulation. After curing (ageing the foam at room temperature for 24 hours), the foam was cut into 40X40X30mm dimension specimens. Five specimens were needed for each test. The fabric, a cotton bed sheet material with density of about 126±22g/m², was cut into 60X60mm dimension pieces. The flame of the burner was adjusted to 55mm high, and propane was
used as the flammable gas. The specimens were put over the burner and the lower side (40*40mm side) of the specimen was kept at about 40mm above the top of the burner. The specimens were exposed to the flame for 3 seconds, which partially melted the foam surface. The fabric was immediately pressed into the foam with a steel plate and held for 3 seconds. After flame lamination, age the specimens at room temperature for 24 hours and then test the bond strength through a Universal testing machine.

The testing procedure for the bond strength test was to first calibrate the Universal testing machine using a 1KN load. Pneumatic grips were used in the testing and the load was tared. The foam was attached to the down grip and the cotton fabric was attached to the up grip. A preload of 1N with a pulling speed of 5mm/min was used, then the load was tared automatically and the test was continued with a pulling speed of 50mm/min until the foam was fully peeled off from the fabric. The bond strength was calculated as Bond strength=Maximum load (N)/Width of the foam (40mm).

The foam specimens without FR were processed slightly differently because the foam was still burning after exposure to the open flame. In those specimens, the foam was exposed to the flame for only 2 seconds, and the fabric was immediately pressed into the foam. Results of the FMVSS flame retardant and bond strength test for the examples are shown in Table 1 below.

Table 1. Results Of The FMVSS Flame Retardant And Bond Strength Test

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Example 1</th>
<th>Comparative Example 2</th>
<th>Comparative Example 3</th>
<th>Comparative Example 4</th>
<th>Comparative Example 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic Polyester Polyol</td>
<td>3.5</td>
<td>3.5</td>
<td>--</td>
<td>--</td>
<td>3.5</td>
</tr>
<tr>
<td>Liquid FR</td>
<td>6</td>
<td>--</td>
<td>6</td>
<td>6</td>
<td>--</td>
</tr>
<tr>
<td>Cyclic Phosphonate</td>
<td>0.1</td>
<td>--</td>
<td>0.1</td>
<td>--</td>
<td>0.1</td>
</tr>
<tr>
<td>Low MW Diol (DEG)</td>
<td>0.3</td>
<td>--</td>
<td>0.3</td>
<td>--</td>
<td>0.3</td>
</tr>
<tr>
<td>Diphenylamine Anti-oxidant</td>
<td>0.1</td>
<td>--</td>
<td>0.1</td>
<td>--</td>
<td>0.1</td>
</tr>
<tr>
<td>FMVSS 302</td>
<td>NBR</td>
<td>Fail</td>
<td>NBR</td>
<td>Pass</td>
<td>Fail</td>
</tr>
<tr>
<td>Bond Strength kN/M</td>
<td>0.58</td>
<td>0.057</td>
<td>0.433</td>
<td>0.295</td>
<td>0.117</td>
</tr>
</tbody>
</table>

1 Stepanol® PS1752 aromatic polyester polyol (Stepan Chemical Corporation)
2 Antiblaze® 195 tri(1,3-dichloroisopropyl) phosphate (Albemarle Corp)
3 Amgard CU
4 Irganox® 5157 from Ciba® (now part of BASF).
In foam formulation Example 6 and Comparative Examples 7 to 10, the foams of Example 1 and Comparative Examples 2 to 5 were repeated except that the foam formulation contained 6.5 parts water, 110 parts TDI and a variable amount (from 10 to 22.5 parts) of the liquid flame retardant composition of Example 1 and comparative Examples 2 to 5. A 14X14X14 inch foam was prepared according to the process described above and were put into a 25°C oven for ageing for 24 hrs. After ageing, the foam was cut into 70 mm X 70 mm X 50 mm smaller foam rectangles along the center of the larger foam for scorch testing.

Yellowness Index (YI) was measured in accordance to ASTM D1925. The results are shown below in Table 2 below.

**Table 2 - Scorch Test - Yellow Index Across Center Of Foam For Different Formulations**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Foam Across Center - Yellow Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Example 1</td>
<td>-1.73</td>
</tr>
<tr>
<td>Comparative Example 2</td>
<td>-1.39</td>
</tr>
<tr>
<td>Comparative Example 3</td>
<td>-1.70</td>
</tr>
<tr>
<td>Comparative Example 4</td>
<td>-1.72</td>
</tr>
<tr>
<td>Comparative Example 5</td>
<td>-1.58</td>
</tr>
<tr>
<td>Comparative Example 12 (see below)</td>
<td>-1.36</td>
</tr>
</tbody>
</table>

**EXAMPLE 11 AND COMPARATIVE EXAMPLE 12 FOAM FORMULATIONS**

In foam formulation Example 11 and Comparative Examples 12, the following ingredients were used to produce the liquid flame retardant composition.
Table 3. Liquid Flame Retardant Composition For Example 11 And Comp. Example 12

<table>
<thead>
<tr>
<th>Example</th>
<th>Aromatic polyester polyl</th>
<th>Liquid FR²</th>
<th>Cyclic phosphonate³</th>
<th>DEG</th>
<th>Diphenylamine Antioxidant⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 11</td>
<td>35 wt%</td>
<td>60 wt%</td>
<td>1 wt%</td>
<td>3 wt%</td>
<td>1 wt%</td>
</tr>
<tr>
<td>Comparative</td>
<td>35 wt%</td>
<td>62 wt%</td>
<td>--</td>
<td>5 wt%</td>
<td>1 wt%</td>
</tr>
<tr>
<td>Example 12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Stepanpol® PS1752 aromatic polyester polyl (Stepan Chemical Corporation)
2 Antiblaze® 195 tri(l,3-dichloroisopropyl) phosphate (Albemarle Corp)
3 Amgard CU
4 Irganox® 5157 from Ciba® (now part of BASF).

The liquid flame retardant compositions of Example 11 and Comparative Example 12 were admixed with other polyurethane foam ingredients according to Table 4 below to produce a polyurethane foam using the same procedure described in Example 1 above.

Table 4. Foam Formulation And Results For Example 11 And Comparative Example 12

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Parts /100 parts polyether polyl (GP-3001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 11</td>
<td>10</td>
</tr>
<tr>
<td>Comparative</td>
<td>10</td>
</tr>
<tr>
<td>Example 12</td>
<td>10</td>
</tr>
<tr>
<td>GP-3001</td>
<td>100</td>
</tr>
<tr>
<td>Water</td>
<td>4</td>
</tr>
<tr>
<td>Niax A1</td>
<td>0.08</td>
</tr>
<tr>
<td>T9</td>
<td>0.20</td>
</tr>
<tr>
<td>L5770</td>
<td>1.1</td>
</tr>
<tr>
<td>TDI Index</td>
<td>105</td>
</tr>
<tr>
<td>Foam Density</td>
<td>27.25</td>
</tr>
<tr>
<td>Bond strength</td>
<td>0.716</td>
</tr>
<tr>
<td>N/mm</td>
<td>SE</td>
</tr>
<tr>
<td>FMVSS 302</td>
<td>NBR</td>
</tr>
</tbody>
</table>

The results show a superior bond strength and/or flame retardancy with inventive Example 11 as compared to Comparative Example 12.

Components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., another component, a solvent, or etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution as such changes, transformations, and/or reactions are the natural result of bringing the specified components together under the conditions called for pursuant to this disclosure. Thus the
components are identified as ingredients to be brought together in connection with performing a desired operation or in forming a desired composition. Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, blending or mixing operations, if conducted in accordance with this disclosure and with ordinary skill of a chemist, is thus of no practical concern.

The invention described and claimed herein is not to be limited in scope by the specific examples and embodiments herein disclosed, since these examples and embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.
CLAIMS

1. A liquid flame retardant composition comprising:
   (a) a liquid flame retardant;
   (b) an aromatic polyester polyol;
   (c) a low molecular weight diol;
   (d) a cyclic phosphonate flame retardants; and
   (e) an optional alkylated diphenylamine or hindered phenol antioxidant.

2. The composition of claim 1, wherein said liquid flame retardant is a phosphorus flame retardant or a halogenated phosphorus flame retardant.

3. The composition of clam 1, wherein said liquid flame retardant is bis(2-chloroethyl) 2-chloroethyl phosphonate, tris(monochloropropyl) phosphate, tri(1,3-dichloroisopropyl) phosphate, 2,2-bis(chloromethyl)trimethylene, bis(bis(2-chloroethyl)phosphate), bisphenol A bis-(diphenyl phosphate), isopropylated phenol phosphate (IPP), dimethyl methyl phosphonate, diethylethyl phosphonate or mixtures thereof.

4. The composition of clam 1, wherein the aromatic polyester polyol contains an aromatic component based on phthalic acid or a derivative of phthalic acid.

5. The composition of clam 1, wherein the aromatic polyester polyol contains a hydroxylated component, wherein said hydroxylated component is aliphatic diol of generic formula HO-R'-OH where R' is a divalent radical selected from the group consisting of:
   (a) alkylene radicals each containing from 2 through 18 carbon atoms, and
   (b) radicals of the formula (2): -(R2)n-R2- where R2 is an alkylene radical containing from 2 through 3 carbon atoms, and n is an integer of from 1 through 3, and
   (c) mixtures thereof.

6. The composition of clam 5, wherein said hydroxylated component is ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, trimethylene glycol, butylene glycol, 1,2-cyclohexanediol, poly (oxyalkylene) polyols each containing from two to four alkylene radicals derived by the condensation of ethylene oxide, propylene oxide, or mixtures thereof.
7. The composition of clam 1, wherein said low molecular weight diol is ethylene glycol, propylene glycol, butylene glycol, pentylene, glycol, hexylene glycol, octylene glycol, diethylene glycol, dipropylene glycol, dihexylene glycol, trimethylene glycol, butylene glycols, 1,2-cyclohexanediol or mixtures thereof.

8. The composition of claim 1 wherein said two diesters of P-alkylphosphonic acid are diesters of P-methylphosphonic acid.

9. The composition of claim 1, wherein said cyclic phosphonate flame retardant is (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl methyl ester of P-alkylphosphonic acid (Cas # 41203-81-0), and bis[(5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl] ester of P-alkylphosphonic acid (Cas # 42595-45-9).

10. The composition of claim 9 wherein the cyclic phosphonate flame retardant contains in the range of from about 60 wt.% to about 90 wt.% (5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl methyl ester of P-alkylphosphonic acid (monomer), and in the range of from about 10 wt.% to about 40 wt.% bis[(5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphorinan-5-yl)methyl] ester of P-alkylphosphonic acid (dimer), based on the total weight of the monomer and dimer.

11. The composition of claim 1, wherein a hindered phenol antioxidant is present.

12. The composition of any of claims 1 to 11, wherein the amount of said liquid flame retardant may range from about 1 wt % to about 90 wt%; the amount of said aromatic polyester polyol may range from about 10 wt % to about 80 wt%; the amount of said low molecular weight diol may range from about 0.5 wt % to about 10 wt%; the amount of said cyclic phosphonate flame retardants may range from about 0.1 wt % to about 10 wt %; and the amount of said optional hinder phenol antioxidant may range from 0 wt% to about 10 wt%.
13. A process for producing a polyurethane foam comprising contacting the liquid flame retardant composition of claim 1 with:

(i) an isocyanate or polyisocyanate;
(ii) a polyol;
(iii) a blowing agent; and
(iv) a catalyst;

and reacting the mixture to form a polyurethane foam.

14. A polyurethane foam composition comprising:

(i) the liquid flame retardant composition of claim 1;
(ii) an isocyanate or polyisocyanate;
(ii) a polyol;
(iv) a blowing agent; and
(v) a catalyst.

15. An article comprising the polyurethane foam of claim 14 and a textile.

16. The article of claim 15, wherein said foam is attached to said textile by flame lamination.
INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/031208

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J9/00 C09K21/14

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 C09K 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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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"Z" document member of the same patent family

Date of the actual completion of the international search

5 July 2011

Date of mailing of the international search report

13/07/2011

Name and mailing address of the ISA:
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Authorized officer

Martinez Marcos, V
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