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(54) Title: BROMINATED FLAME RETARDANT AND ITS APPLICATION IN POLYURETHANE FOAMS

(57) Abstract: This invention provides polyurethane foams containing a brominated flame retardant. Also provided are formulations and methods for preparing polyurethane foams containing a brominated flame retardant.



BROMINATED FLAME RETARDANT AND ITS APPLICATION IN POLYURETHANE FOAMS

TECHNICAL FIELD

[0001] This invention relates to a brominated short-chain alcohol useful as a flame retardant in flexible and rigid polyurethane foams.

BACKGROUND

[0002] Fire resistance is an important property of polyurethane foams. Various compounds or mixtures thereof have been used effectively to meet applicable fire safety standards. Tris(1-chloro-2-propyl) phosphate (TCPP) is a flame retardant widely used in polyurethane foams. However, TCPP is a non-reactive compound in polyurethane foam formation and can thus leach or migrate from the foams. This results in health and environmental concerns.

[0003] A brominated isocyanate-reactive compound that has been disclosed as a flame retardant is 2,3-dibromobutene-1,4-diol (*e.g.*, U.S. Patent No. 4,002,580). However, 2,3-dibromobutene-1,4-diol (DBBD) is a solid with a high melting point and requires additional steps to pre-dissolve for it to be useful in polyurethane foam applications.

[0004] Thus, it would be desirable to have a flame retardant that is a liquid at processing conditions and has low viscosity to allow ease of processing (mixing and pumping). In addition to effectiveness as flame retardants, it is desired to provide compounds that are compatible with polyurethane foam manufacturing processes, and do not migrate out of the polyurethane foam over time, lessening the health and environmental impacts.

SUMMARY OF THE INVENTION

[0005] This invention provides formulations and processes for producing flame retardant polyurethane foams. More specifically, this invention provides an isocyanate-reactive brominated flame retardant compound that is useful in polyurethane forms. In particular, the invention relates to the application of 2,3-dibromo-2-propen-1-ol (2,3-dibromoallyl alcohol or DBAA) in polyurethane foams, including open-cell spray foams, closed-cell spray foams, rigid panel foams, and flexible foams.

[0006] An embodiment of this invention is a polyurethane foam formed from ingredients comprising DBAA.

[0007] Also provided are formulations that can be used to make flame retardant polyurethane foams.

[0008] Other embodiments of this invention include processes for forming polyurethane foams.

FURTHER DETAILED DESCRIPTION OF THE INVENTION

[0009] As used throughout this document, the phrase "reactive brominated flame retardant" has equivalent meaning to "isocyanate-reactive brominated flame retardant."

[0010] Polyurethane foams are typically produced by contacting two main liquid components, *viz.*, polyisocyanates (A side) and polyols (B side). It is desirable for the B side (here, the formulation of the invention), which contains all of the components other than the polyisocyanates, to be in the form of a liquid. As used herein, the term "liquid" means that the formulation is in the liquid state at the conditions at which the B side formulation is used. For more information regarding the formation of polyurethane foams, see for example U.S. Pat. Nos: 3,954,684; 4,209,609; 5,356,943; 5,563,180; and 6,121,338.

[0011] The present invention relates to polyurethane foams flame retarded with dibromoallyl alcohol (DBAA). These foams are formed from formulations comprising DBAA, at least one polyol, at least one blowing agent, at least one catalyst, and at least one surfactant, which formulations are contacted with a polyisocyanate.

[0012] An isocyanate-reactive brominated flame retardant contains at least one functional group which is available for, and capable of, reacting with another polyurethane-forming component during polyurethane formation so that the resultant polyurethane contains the reactive brominated flame retardant in chemically-bound form. It is believed that the functional groups of the reactive brominated flame retardant react with isocyanate groups during the preparation of polyurethane foam; usually, the functional (reactive) groups in the reactive brominated flame retardants are hydroxyl groups.

[0013] The isocyanate-reactive brominated flame retardant used in the practice of this invention, 2,3-dibromo-prop-2-en-1-ol, a known molecule (also referred to herein as dibromoallyl alcohol or DBAA), which has CAS[®] registry number 7228-11-7 (Chemical Abstracts Service). DBAA is not commercially available, but synthesis of DBAA from propargyl alcohol (2-propyn-1-ol) and elemental bromine (Br₂) at room temperature in a solvent is known. In the past, DBAA has been used as an intermediate to make phosphorus compounds (see U.S. Pat. No. 3,950,457).

[0014] DBAA can be used in forming both flexible polyurethane foams and rigid polyurethane foams. DBAA is a reactive component that becomes part of the

polyurethane foam. This provides the advantage that DBAA does not migrate out of the foam. Another advantage is that DBAA has a high bromine content (74 wt%). Other flame retardants that can be included in the polyurethane foams with DBAA include a mixed ester of tetrabromophthalic anhydride with diethylene glycol and propylene glycol, tris(1-chloro-2-propyl)phosphate, or both tris(1-chloro-2-propyl)phosphate and a mixed ester of tetrabromophthalic anhydride with diethylene glycol and propylene glycol.

[0015] Formulations of the invention, which can be used as the B side in processes for forming polyurethane foams, comprise DBAA, a polyol, a blowing agent, a catalyst, and a surfactant.

[0016] In forming polyurethane foams of the invention, a flame retardant amount of DBAA is used. By a flame retardant amount is meant that amount of DBAA needed to obtain the desired level of flame retardancy. A flame retardant amount is typically in the range of about 1 wt% to about 25 wt%, preferably about 3 wt% to about 20 wt%, more preferably about 3 wt% to about 18%, based on the total weight of the formulation (B side components).

[0017] The polyol or polyols used in forming the polyurethane foams in the practice of this invention can be any polyol that is typically used to produce flexible polyurethane foams or rigid polyurethane foams. Often, mixtures of polyols are used, with the particular polyols selected for their effect on the properties of the polyurethane foam being formed.

[0018] When flexible polyurethane foam is being formed, the polyol usually is a polyol or mixture of polyols having hydroxyl numbers up to about 150 mg KOH/g, preferably in the range of about 5 mg KOH/g to about 150 mg KOH/g, more preferably about 10 to about 100 mg KOH/g, even more preferably about 20 mg KOH/g to about 75 mg KOH/g. When polymeric polyols are used, they typically have molecular weights in the range of about 2,000 to about 10,000, preferably about 3,000 to about 8,000.

[0019] When rigid polyurethane foam is being formed, the polyol usually is a polyol or mixture of polyols having hydroxyl numbers in the range of about 100 to about 850 mg KOH/g, preferably in the range of about 110 to about 600 mg KOH/g. When polymeric polyols are used, they typically have molecular weights in the range of about 250 to about 5000, often about 400 to about 3000.

[0020] Suitable polyols for forming polyurethane foams include polyether polyols, polyester polyols, aliphatic polyols, and polyoxyalkylene glycols. Mixtures of two or

more polyols can be used. Preferred polyols for forming rigid polyurethane foams include polyester polyols.

[0021] Polyoxyalkylene glycols that can be used include polyoxyethylene glycol, polyoxypropylene glycol, and block and heteric polyoxyethylene-polyoxypropylene glycols.

[0022] The aliphatic polyols typically contain up to about 18 carbon atoms per molecule. Suitable aliphatic polyols include ethylene glycol, propylene glycol, the isomeric butylene glycols, diethylene glycol, 1,5-pentanediol, 1,6-hexanediol, triethylene glycol, glycerol, trimethylolethane, trimethylolpropane, 1,2,6-hexanetriol, pentaerythritol, tetraethylene glycol, dipentaerythritol, sorbitol, sucrose, and alpha-methylglycoside.

[0023] Polyether polyols are produced by reacting one or more alkylene oxides having 2 to about 8 carbons in the alkylene radical with an initiator molecule containing two or more hydroxyl groups. Suitable polyether polyols include sucrose/glycerine polyether polyol; sucrose polyether polyol based on glycerine, propylene oxide and ethylene oxide; glycerin-initiated polyether polyols, *e.g.*, glycerine/propylene oxide polyether polyol; and mannich-based polyether polyols.

[0024] Polyester polyols are produced by polymerizing polycarboxylic acids or their derivatives, for example their acid chlorides or anhydrides, with a polyol. Suitable polyester polyols include aromatic polyester polyols and diethylene glycol-phthalic anhydride polyester polyol.

[0025] For forming both flexible and rigid polyurethane foams, the amount of polyol typically ranges from about 40 wt% to about 80 wt%, and often from about 50 wt% to about 70 wt%, based on the total weight of the B side components (formulation). These amounts refer to the total amount of polyol in the formulation, when there is more than one polyol present.

[0026] Blowing agents that can be used in this invention for forming flexible and rigid polyurethane foams include water, volatile hydrocarbons, hydrocarbons such as n-pentane, isopentane, cyclopentane; halocarbons (fully halogenated chlorofluorocarbons), in particular trichlorofluoromethane (CFC-11); and halohydrocarbons (hydrogen-containing chlorofluorocarbons, or HCFC's) such as 1,1-dichloro-1-fluoroethane (HCFC-141b), 1-chloro-1,1-difluoroethane (HCFC-142b), chlorodifluoromethane (HCFC-22). Mixtures of any two or more blowing agents can be used. In some instances, DBAA permits formulations in which water is the only blowing agent.

[0027] Other suitable blowing agents in the practice of this invention when forming flexible polyurethane foams include dichloromethane (methylene chloride) and acetone. Preferred blowing agents for flexible polyurethane foams include water. The amount of blowing agent for forming flexible foams may range from about 0.5 wt% to about 20 wt%, preferably about 2.5 wt% to about 15 wt%, based on the total weight of the B side components (formulation).

[0028] For forming rigid polyurethane foams, blowing agents which can be used in the practice of this invention include partially fluorinated hydrocarbons (HFC's). Suitable blowing agents for rigid foams include *trans*-1-chloro-3,3,3-trifluoropropene (HFO-1233zd(E)), 1,1,1,3,3-pentafluoropropane (HFC-245fa), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,2,3,3,3-hexafluoropropane (HFC-236ea), 1,1,1,4,4,4-hexafluorobutane (HFC-356mffm), and 1,2-bis(trifluoromethyl)ethene; and hydrocarbons such as n-pentane, isopentane, and cyclopentane. Mixtures of any two or more blowing agents can be used.

[0029] Preferred blowing agents when forming rigid foams include water, 1,1,1,3,3-pentafluoropropane, *trans*-1-chloro-3,3,3-trifluoropropene, 1,2-bis(trifluoromethyl)ethene, and mixtures of water with 1,1,1,3,3-pentafluoropropane, *trans*-1-chloro-3,3,3-trifluoropropene, or 1,2-bis(trifluoromethyl)ethene. In some instances, 2,3-dibromoallyl alcohol permits formulations in which water is the only blowing agent. The amount of blowing agent for forming rigid foams may range from about 0.5 wt% to about 20 wt%, preferably about 2.5 wt% to about 15 wt%, based on the total weight of the B side components.

[0030] Various types of catalysts can be used in the practice of this invention when forming either flexible or rigid polyurethane foams, including tertiary amines, tin catalysts, typically an organic tin compound, bismuth catalysts, other organometallic catalysts, and potassium salts of organic carboxylic acids. Mixtures of catalysts of the same type and/or different types can be used in the practice of this invention.

[0031] In the amine catalysts, the groups on the amine are preferably alkyl groups; more preferably, the groups are oxygen-containing groups such as etheric or saturated alcoholic groups. Suitable amine catalysts include dimethylethyl amine, triethylenediamine, dimethylethylamine, dimethylcyclohexylamine, dimethylbenzylamine, tetramethyldipropylenetriamine, pentamethyldiethylenetriamine, tris(dimethylaminopropyl)-hydrotriazine, 1-methyl-4-(2-dimethylaminoethyl)piperazine,

1,4-diaza(2,2,2)bicyclooctane, 3-methoxy-N,N-dimethylpropylamine, N-methylmorpholine, N-ethylmorpholine, N-coccomorpholine, bis(dimethylaminoethyl) ether, and ethanol amine catalysts, such as dimethylethanolamine, 2-(2-dimethylaminoethoxy)ethanol, and N,N,N'-trimethylaminoethyl-ethanol amine. For flexible foams, preferred catalysts include 2-(2-dimethylaminoethoxy)ethanol. For rigid polyurethane foam, the amine catalyst is preferably a tertiary amine.

[0032] Types of tin compounds that can be used as catalysts include dialkyl(dialkylthio) stannanes, stannous(II) salts of organic carboxylic acids, and dialkyltin(IV) salts of carboxylic acids. Suitable tin catalysts in the practice of this invention include dibutylbis(dodecylthio) stannane, stannous(II) octoate, stannous(II) acetate, dibutyltin dilaurate, and dioctyltin diacetate.

[0033] Still another type of catalyst is one or more potassium salts of organic carboxylic acids. Suitable potassium salts include potassium acetate and potassium octoate.

[0034] The catalysts are usually used in a total amount of about 0.25 wt% to about 10 wt%, preferably about 1 wt% to about 8 wt%, based on the total weight of the formulation (B side components) for both the flexible and rigid polyurethane foams. These amounts refer to the total amount of catalyst in the formulation, when there is more than one catalyst present.

[0035] A surfactant is often needed for production of polyurethane foams, and surfactants are normally used when forming both flexible and rigid polyurethane foams.

[0036] For both flexible and rigid polyurethane foams, suitable silicone-based surfactants include silicone glycols, silicone glycol copolymers, polyether modified polysiloxanes, polyether modified dimethylpolysiloxanes such as a polyether polydimethylsiloxane copolymer, polysiloxane polyoxoalkylene copolymers, polysiloxane polyoxoalkylene copolymers, polysiloxane copolymers, and the like. Silicone-based surfactants are a preferred type of surfactant for forming both flexible and rigid polyurethane foams. Polyether modified dimethylpolysiloxanes and polysiloxane copolymers are preferred silicone-based surfactants.

[0037] Cell openers, typically polyalkylene oxides, are a preferred type of surfactant for flexible foams. 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.

[0038] Other surfactants that can be used when forming rigid polyurethane foams include 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 *e.g.*, dodecylbenzenedisulfonic acid and ricinoleic acid; ethoxylated alkylphenols, ethoxylated fatty alcohols; ether amine quaternary ammonia compounds; 2-hydroxypropyltrimethylammonium formate; sodium hydroxy-nonylphenyl-N-methylglycinate (the sodium salt of N-((2-hydroxy-5-nonylphenyl)methyl)-N-methyl-glycine), and castor oil.

[0039] For forming both flexible and rigid polyurethane foams, the surfactants are usually used in amounts of about 0.1 wt% to about 5 wt%, preferably about 0.5 wt% to about 5 wt%, based on the total weight of the B side components (formulation). These amounts refer to the total amount of surfactant in the formulation, when there is more than one surfactant present.

[0040] One or more optional additives which can be included in the formulation of the invention when forming either a flexible or a rigid polyurethane foam include antioxidants, diluents, chain extenders or cross-linkers, synergists (preferably melamine), stabilizers, fungistats, pigments, dyes, fillers, antistatic agents, and plasticizers.

[0041] The components of the formulation can be combined in any order; preferably, the blowing agent is the last ingredient added. More preferably, DBAA is combined with the polyol(s), followed by the surfactant, catalyst, and any optional ingredients, followed by the blowing agent.

[0042] The isocyanates or polyisocyanates (A-side component) used in forming the polyurethane foams in the practice of this invention can be any isocyanate or polyisocyanate that can be used to produce flexible polyurethane foams or rigid polyurethane foams, as appropriate. When a polymeric polyisocyanate is used, it preferably has an isocyanate (NCO) content of about 25 wt% to about 50 wt%, preferably about 25 wt% to about 40 wt%.

[0043] When forming flexible polyurethane foams, the isocyanate generally has at least two isocyanate groups. The isocyanates can be aliphatic or aromatic. When forming rigid polyurethane foams, polyisocyanates are used, and the polyisocyanate can be aromatic or aliphatic. Suitable polyisocyanates for both flexible and rigid 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), 4,4'-methylenedicyclohexyl diisocyanate (H12MDI), hexahydrotoluene diisocyanate and isomers thereof, 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, toluene diisocyanate, 1,5-naphthalene diisocyanate, diphenylmethane diisocyanate (MDI, sometimes called methylene diisocyanate), 1-methoxyphenyl-2,4-diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, mixtures of 4,4'- and 2,4'-diphenylmethane diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 4,4',4"-triphenylmethane triisocyanate, toluene 2,4,6-triisocyanate, 4,4'-dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate, polymeric polyisocyanates such as polymethylene polyphenylene polyisocyanate, and mixture of any two or more of the foregoing.

[0044] Polyisocyanates that can be used in forming both the flexible and rigid polyurethane foams of the present invention include those isocyanates commonly referred to as polymeric methylene diphenyl diisocyanate (MDI), polyisocyanate-based prepolymers, and mixtures thereof. Polymeric MDI contains varying amounts of isomeric diphenylmethane diisocyanates and three-ring, four-ring, and greater than four-ring oligomers. In general, any commercial polymeric MDI having an isocyanate content of about 25 wt% or more may be used. A preferred polymeric MDI has an isocyanate content of about 30 wt% or more. Other isocyanates may be present with the polymeric MDI in minor amounts, as long as the polyisocyanate mixture as whole remains liquid. Preferably, the polyisocyanate is a polymeric MDI.

[0045] The polyurethane foam compositions of this invention are formed from A side and B side components in which the A side is one or more isocyanates or polyisocyanates as described above, and the B side comprises a formulation of the invention. The polyurethane formation reaction generally occurs readily at room temperature; normally, the A side and the B side begin to react with each other as soon as they are in contact, and

continue to react (cure), forming a polyurethane foam. Often, the mixture of the A side and B side is sprayed or cast to form a polyurethane foam.

[0046] In the processes of the invention for forming polyurethane foams, A) at least one isocyanate and/or polyisocyanate is contacted with B) a formulation formed from 2,3-dibromoallyl alcohol, at least one polyol, at least one blowing agent, at least one catalyst, and at least one surfactant, to form a mixture; and the mixture is allowed to cure to form a polyurethane foam.

[0047] The amount of isocyanates and/or polyisocyanate may be defined in terms of the Isocyanate Index.

$$\text{Isocyanate Index} = \frac{\text{Actual equivalent amount of isocyanate used}}{\text{Theoretical equivalent amount of reactive hydrogens}} \times 100$$

[0048] The theoretical equivalent amount of isocyanate is equal to one equivalent of isocyanate per one equivalent of reactive hydrogens from the B side. In the processes of this invention, Isocyanate Index values typically range from 80 to 200 or about 90 to about 150. Rigid polyurethane foams are usually formed by bringing together polyisocyanates with compounds having isocyanate-reactive hydrogen atoms (e.g., hydroxyl groups) in amounts such that the Isocyanate Index is in the range of about 85 to about 1000, preferably from about 95 to about 400, more preferably about 95 to about 200.

[0049] To form polyurethane foams, the functionality (*i.e.*, average number of hydroxyl groups per molecule), of the formulation (B side) which is typically provided by the polyol or mixture of polyols, is usually about 2 or more, preferably about 2 to about 8; more preferably about 3 or more, especially about 3 to about 8, more especially about 3 to about 7. As a monoalcohol, DBAA has a functionality of one (*i.e.*, one hydroxyl group in the molecule), which is chain-terminating, so at least a portion of the polyols in the formulation have three or more hydroxyl groups per molecule to form polyurethane foams. DBAA is included in the calculation of the average functionality of the B side.

[0050] In the polyurethane foams, the 2,3-dibromoallyl alcohol is generally about 0.5 wt% to about 12.5 wt%, preferably about 1.5 wt% to about 10 wt%, more preferably about 1.5 wt% to about 9%, based on the total weight of the polyurethane foam. Polyols typically ranges from about 20 wt% to about 40 wt%, and often from about 25 wt% to about 35 wt%, based on the total weight of the polyurethane foam. Surfactants are present in amounts of about 0.05 wt% to about 2.5 wt%, preferably about 0.25 wt% to about 2.5 wt%, based on the total weight of the polyurethane foam. The catalysts are present in a

total amount of about 0.125 wt% to about 5 wt%, preferably about 0.5 wt% to about 4 wt%, based on the total weight of the polyurethane foam. These amounts refer to the total amount of each type of ingredient in the foam, when there is more than one of that type of ingredient present.

[0051] The rigid polyurethane foams formed in this invention have a density range that varies with the end use application. For open-cell insulation foams, the density range is generally about 0.4 lb/ft³ to about 1.2 lb/ft³ (6.3 kg/m³ to 18.9 kg/m³). For closed-cell insulation foams, the density range is typically about 1.6 lb/ft³ to about 3.5 lb/ft³ (25.6 kg/m³ to 56.1 kg/m³). For molded architectural foams, the density range is usually about 4.0 lb/ft³ to about 31 lb/ft³ (64.0 kg/m³ to 497 kg/m³).

[0052] The flexible polyurethane foams formed in this invention have a density range of about 0.5 to about 1.0 lb/ft³ (8 to 16 kg/m³). Flexible polyurethane foams are typically 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.

[0053] The following examples are presented for purposes of illustration, and are not intended to impose limitations on the scope of this invention. All percentages in the following examples are by weight unless otherwise noted.

EXAMPLES - GENERAL

[0054] In the Examples, some of the substances used are referred to by their trade names. More specifically:

DBAA: 2,3-dibromoallyl alcohol

Saytex[®] RB-79: a mixed ester of tetrabromophthalic anhydride with diethylene glycol and propylene glycol (Albemarle Corporation).

TCPP: tris(1-chloro-2-propyl)phosphate.

DE: diethylene glycol monoethyl ether.

Voranol[®] 280: a polyether polyol with a functionality of about 7.0, a hydroxyl number of about 280, and an average molecular weight of about 1400; **Voranol[®] 370:** a sucrose/glycerine polyether polyol with a functionality of 7.0; **Voranol[®] 490:** a sucrose/glycerine polyether polyol with a functionality of 4.3 (all Voranol[®] materials are products of Dow Chemical Company).

Vorasurf[®] 504 is a non-silicone organic surfactant (Dow Chemical Company).

Terate[®] HT 5503: an aromatic polyester polyol with a hydroxyl number in the range of 225 to 245, a functionality of 2, and an equivalent weight of 239; **Terate[®] HT 5349**: an aromatic polyester polyol with a functionality of about 2.45, and a hydroxyl number of 295 to 315 (all Terate[®] materials are products of Invista Corporation).

Stepanpol[®] PS-3152 is a diethylene glycol-phthalic anhydride polyester polyol with a functionality of 2 and a hydroxyl number of 315 (Stepan Chemical Company).

Carpol[®] GP-5171: glycerin-initiated polyether polyol with a functionality of about 3, a hydroxyl number of 35, and an average molecular weight of about 5000; **Carpol[®] GP-5015**: glycerin-initiated polyether polyol with a functionality of 3, a hydroxyl number of 34, and an average molecular weight of about 5000; **Carpol[®] GP-1500**: glycerin-initiated polyether polyol with a functionality of 3, a hydroxyl number of 112, and an average molecular weight of about 1500; **Carpol[®] GSP-280**: sucrose polyether polyol based on glycerine, propylene oxide and ethylene oxide with a functionality of 7, a hydroxyl value of 280, and an average molecular weight of about 1400; **Carpol[®] GSP-355**: glycerine/sucrose initiated polyether polyol with a functionality of 4.5, a hydroxyl value of 355; **Carpol[®] MX-470**: mannich-based polyether polyol with a functionality of about 4, a hydroxyl number of 470, and an average molecular weight of 480; **Carpol[®] GP-700**: glycerine and propylene oxide polyether polyol with a functionality of 3, a hydroxyl number of 240, and an average molecular weight of about 700 (all Carpol[®] materials are products of Carpenter Company).

Terol[®] 250 is an aromatic polyester polyol with a functionality of 2 and a hydroxyl number in the range of 235 to 255 (Huntsman Corporation).

Dabco[®] DC193: silicone glycol surfactant; **Dabco[®] T**: amine with hydroxyl groups; **Dabco[®] T-120**: dibutylbis(dodecylthio) stannane; **Dabco[®] PM-300**: 2-butoxyethanol; **Dabco[®] DC 5598**: silicone glycol copolymer surfactant; **Dabco[®] K-15**: potassium octoate; **Dabco[®] TMR**: 2-hydroxypropyltrimethylammonium formate (all Dabco[®] materials are products of Air Products and Chemicals, Inc.).

Polycat[®] 204: amine catalyst (Air Products and Chemicals, Inc.).

Tomamine[®] Q17-2 PG is an ether amine quaternary ammonia surfactant (75%) in isopropyl alcohol (Air Products and Chemicals, Inc.).

Tegostab[®] B 8871: polysiloxane copolymer; **Tegostab[®] B 8407**: polyether polydimethylsiloxane copolymer (both are products of Evonik Industries AG, Essen, Germany).

Jeffcat[®] ZR-70 is 2-(2-dimethylaminoethoxy)ethanol, an ethanol amine catalyst; **Jeffcat[®] Z-110** is N,N,N'-trimethylaminoethyl-ethanolamine; **Jeffcat[®] ZF-20** is bis-(2-dimethylaminoethyl)ether (all Jeffcat[®] materials are products of Huntsman Corp., The Woodlands, TX).

Pel-cat 9506 is a mixture of potassium octoate and potassium acetate; **Pel-cat 9858-A** is sodium hydroxy-nonylphenyl-N-methylglycinate (both are products of Elé Corporation).

Solstice[®] LBA: *trans*-1-chloro-3,3,3-trifluoropropene (Honeywell Inc.).

Genetron[®] 245fa: 1,1,1,3,3-pentafluoropropane (Honeywell Inc.).

Opteon[™] 1100: 1,2-bis(trifluoromethyl)ethene; also called Formacel[®] 1100 (The Chemours Company).

Papi[®] 27: polymeric diphenylmethane diisocyanate (MDI) with 31.4 wt% NCO, viscosity 150 to 225 cps at 25°C, and an isocyanate equivalent weight of 134 (Dow Chemical Company).

[0055] Cone calorimetry measurements were performed on a Fire Testing Technology Dual Cone Calorimeter according to ASTM E-1354. For all of the Examples, an incident heat flux of 40 kW/m² was used in the cone calorimetry tests for the Predicted Smoke Index calculations and an incident heat flux of 100 kW/m² was used in the cone calorimetry tests for the Predicted Flame Spread Index calculations. The Peak Heat Release Rate (PHRR), the maximum value of the heat released during combustion of the sample in the cone calorimeter, was measured. Values for the Peak Heat Release Rate are preferably less than 250. The ASTM E-84 burn profiles for predicted Smoke Index calculations and for predicted Flame Spread Index calculations were calculated from the cone calorimetry results. Using mathematical equations that were previously derived from a cone calorimeter and ASTM E-84 correlation study, the cone calorimeter results were converted into predicted numbers in the ASTM E-84. The target value for the Flame Spread Index was less than 25, preferably less than 20, and the target value for the Smoke Density Index was less than 450, preferably less than 200. The term "Smoke Index" is short for "smoke density developed", which is also referred to as "Smoke Developed Index" and "Smoke Density Index."

[0056] For some samples, the dimensional stability was determined; preferred volume changes in dimensional stability are ±15%. Some samples were subjected to a thermal conductivity test, and R values were calculated from the thermal conductivities. The R value (or R-value) is a measure of insulation efficiency or thermal resistance (the ability of

a material to slow down heat transfer within itself), and is often used in the building and construction industry. The higher the R-value, the more a material prevents heat transfer. R-values for polyurethane foams are preferably about 6.5 or more.

EXAMPLES 1-22

[0057] The reported results in Examples 1-16 are an average of three lots with 5 samples per lot (a total of 15 samples for each test). The volume ratio of the A side to the B side in each run was 1:1, unless otherwise noted. The polyurethane foams of Examples 1-16 were prepared according to Procedure 1 below. The polyurethane foams of Examples 17-19 were prepared according to Procedure 2 below. The polyurethane foams of Examples 20-22 were prepared according to Procedure 1 below; the A side was Papi[®] 27 in all runs of Examples 1-22.

[0058] Procedure 1: To form the B side, DBAA, polyols, surfactants, flame retardant, blowing agent and catalyst were weighed into a 0.5 gallon (1.9 L) reclosable container, and blended with a bow-tie agitator at 2000 rpm for 60 seconds or until a homogenous mixture with no visible phase separation was obtained. At a 450-g scale (total of A and B sides), the required amount of the B side mixture was weighed and added to a one-liter paper cup.

[0059] The polymeric MDI was wet-tared by weighing about 10% of its required amount into a 250-mL paper cup, pouring out the polymeric MDI within 3 seconds, re-taring the wet 250-mL cup and adding the full amount of the polymeric MDI. The polymeric MDI was then poured within a 3-second time span into the one-liter cup containing the B-side mixture, and the contents of the one liter paper cup were immediately mixed for 5 seconds at 2000 rpm. By this process, the amount of MDI used is within $\pm 1\%$ of the required amount.

[0060] While the foam was rising but before the foam reached the top of the one liter paper cup, the cup was inverted and held over a paper sheet. While the foam continued to rise, the cup was guided upwards without impeding the rising of the foam. Once the foam had sufficient strength to support itself and the cup, guiding of the cup was discontinued. After allowing the foam to sit for at least 24 hours, it was cut to generate specimens for cone calorimeter testing. Each specimen was weighed to determine the foam density.

[0061] Procedure 2: To prepare each polyurethane foam, blends of the B-side components other than the catalyst(s) (DBAA, polyols, surfactants, flame retardant, and blowing agent) were made. The polyisocyanate and the B-side formulation were weighed

into a 16 oz. (473 mL) paper cup and then mixed at 2000 rpm with a bow tie agitator for 15 seconds, at which point the catalyst(s) was injected into the mixture while the agitation continued. At the 20-second mark, the agitation was discontinued, and the reacting mixture was immediately poured into a 10-in x 10-in x 10-in (25.4 cm x 25.4 cm x 25.4 cm) wooden box mold that had been pre-lined with a polyethylene bag, and the box was closed. After 15 minutes, the cube-shaped foam encased in the polyethylene bag was removed from the mold. After allowing the foam to sit for at least 24 hours, it was cut to generate the specimens for cone calorimeter testing. Each specimen was weighed to determine the foam density. The catalyst was added after the A side and B side were brought into contact, which is related to handling and timing on the laboratory scale; at larger scales, the catalyst is included in the B side formulations.

[0062] In Examples 1-4, open-cell spray polyurethane foams were prepared. Examples 2 and 3 are comparative. Amounts of the components and process information are listed in Table 1; test results are summarized in Table 2. In Examples 1-4, water was the only blowing agent.

[0063] In Examples 5-10, closed-cell spray polyurethane foams were prepared. Examples 5, 6, 8, and 9 are comparative. In Example 9, the Saytex[®] RB-79 flame retardant was added as a solution in 2-butoxyethanol. Amounts of the components and process information are listed in Table 3; test results are summarized in Table 4.

[0064] In Examples 11-16, closed-cell spray polyurethane foams were prepared. Examples 12-16 are comparative. Amounts of the components and process information are listed in Table 5; test results are summarized in Table 6.

[0065] In Examples 17-19, panel polyurethane foams were prepared. Examples 17 and 18 are comparative. Amounts of the components and process information are listed in Table 7; test results are summarized in Table 8.

[0066] In Examples 20-22, closed-cell spray polyurethane foams were prepared. Run 1 of Example 21 and runs 1 and 2 of Example 22 are comparative. Amounts of the components and process information for Examples 20-22 are listed in Tables 9A-B, 11A-B, and 13A-C; test results for Examples 20-22 are summarized in Tables 10A-B, 12A-B, and 14A-C.

TABLE 1

Example	1	2	3	4
B side				
DBAA	5.45	--	--	5.50
Saytex [®] RB-79	--	8.67	--	--
TCPP	--	--	30.00	--
2-butoxyethanol	4.95	4.78	--	4.00
Sucrose in water (67%)	69.35	67.00	50.50	69.46
Carpol [®] GP-5171	4.95	4.78	5.00	5.00
Jeffcat [®] ZR-70	5.75	5.55	5.80	6.40
Tegostab [®] B 8407	1.85	1.77	1.85	1.85
Tegostab [®] B 8871	1.85	1.77	1.85	1.85
Tomamine [®] Q17-2 PG	0.93	0.90	--	0.94
Water	4.95	4.78	5.00	5.00
A-Side				
Papi [®] 27	100.00	100.00	100.00	100.00
Process				
A:B Weight Ratio	104.2:100	103.7:100	103.5:100	104.1:100
Isocyanate Index	27.3	28.0	35.1	27.2

TABLE 2

Example	1	2	3	4
Foam properties				
Density, lb/ft ³	0.81	0.70	0.60	0.62
Density, kg/m ³	13.0	11.2	9.6	9.9
Dimensional Stability* (% vol. change)	0.5	-0.5	-5.1	0.5
Predicted Flame Spread Index	24	24	23	24
Predicted Smoke Density Index	18	11	45	17
Predicted Fire Rating	Class 1	Class 1	Class 1	Class 1

* Dimensional stability was measured at 70°C for 14 days at 95% RH.

[0067] Tables 1 and 2 show that much lower amounts of DBAA can be used relative to TCPP and RB-79 in open cell foams to achieve a Class 1 flame retardant rating for the

foam. The polyurethane foams containing DBAA had a much better dimensional stability than the foams containing TCPP or Saytex[®] RB-79 flame retardant.

TABLE 3

Example	5	6	7	8	9	10
B-side						
DBAA	--	--	8.11	--	--	8.11
Saytex [®] RB-79	6.76	13.33	--	6.76		--
TCPP	8.26	--	--	8.26	--	--
2-butoxyethanol	--	--	--	--		--
Terate [®] HT 5503	40.00	39.26	41.94	38.00	25.75	41.94
Voranol [®] 490	28.47	30.01	32.06	30.52	12.00	32.08
Carpol [®] GSP-355	--	--	--	--	22.00	--
Dabco [®] DC193	2.00	2.00	2.00	2.00	2.00	2.00
Dabco [®] T	3.00	3.00	3.00	3.00	3.00	3.00
Dabco [®] PM-300	2.00	2.00	2.00	2.00	2.00	2.00
Water	2.07	1.90	1.80	2.02	1.85	1.76
Genetron [®] 245fa	7.44	8.5	9.10	--	--	--
Solstice [®] LBA	--	--	--	7.44	8.45	9.10
A-side						
Papi [®] 27	100.00	100.00	100.00	100.00	100.00	100.00
Process						
A:B Weight Ratio	1.044:1	1.027:1	1.035:1			
Isocyanate Index	110.1	105.9	106.2	109.9	110.1	106.6

TABLE 4

Example	5	6	7	8	9	10
Foam properties						
Density (lb/ft ³)	1.57	1.64	1.80	1.68	1.75	1.99
Density (kg/m ³)	25.1	26.3	28.8	26.6	28.0	31.9
Compressive Strength (kPa)	94.5	86.2	101.4	94.5	85.5	124.1
R-value (/inch)	6.34	6.35	6.74	6.8	6.7	7.1
R-value (m ² K/W)	1.117	1.118	1.187	1.98	1.80	1.250
Predicted Flame Spread Index	21.4	23	24	27	27	31
Predicted Smoke Density Index	101	185	49	304	105	56
Predicted Fire Rating	Class 1	Class 1	Class 1			

[0068] Tables 3 and 4 show that much lower amounts of DBAA can be used relative to RB-79 alone or combinations of TCPP and RB-79 in closed cell foams to achieve a Class 1 flame retardant rating for the foam. The polyurethane foams containing DBAA had

improved R-values as compared to the foams containing TCPP and/or Saytex[®] RB-79 flame retardant.

TABLE 5

Example	11	12	13	14	15	16
B-side						
DBAA	8.11	--	--	--	--	--
2,3-dibromo-2-butene-1,4-diol	--	9.23	4.44	9.23	--	--
Saytex [®] RB-79	--	--	--	--	12.00	6.75
TCPP	--	--	8.57	--	--	8.25
Terol [®] 250	46.60	45.93	32.21	42.21	43.58	43.58
Carpol [®] GSP-280	--	--	--	9.79	--	--
Carpol [®] MX-470	14.38	--	--	--	--	--
Carpol [®] GP-700	--	15.27	--	19.05	5.00	--
Voranol [®] 370	17.42	--	36.83	--	--	--
Voranol [®] 490	--	16.07	--	--	24.77	28.07
Diethylene glycol	--	--	--	--	--	1.7
Dabco [®] PM-300	2.00	2.00	2.30	2.00	3.00	--
Dabco [®] DC193	2.00	2.00	2.00	2.00	2.00	2.00
Diglycolamine	--	--	2.96	6.15	--	--
Dabco [®] T	2.00	2.00	3.00	2.00	2.00	2.00
Water	1.66	1.67	1.69	1.67	1.65	1.65
Solstice [®] LBA	5.83	5.83	6.00	5.90	6.00	6.00
A-side						
Papi [®] 27	100.00	100.00	100.00	100.00	100.00	100.00
Process						
A:B Weight Ratio	102:100	103:100	104.5:100	104.1:100	102.6:100	102.5:100
Isocyanate Index	109.9	109.9	111.6	107	110	110

TABLE 6

Example	11	12	13	14	15	16
Foam Properties						
Density (lb/ft ³)	2.06	1.98	2.01	2.33	1.82	1.82
Density (kg/m ³)	33.0	31.7	32.2	37.3	29.2	29.2
Compressive Strength (kPa)	117.2	109.6	--	84.8	66.9	91.0
R-value (/inch)	6.45	--	--	6.50	6.62	6.84
R-value (m ² K/W)	1.136	--	--	1.145	1.662	1.205
Predicted Flame Spread Index	21.9	22.4	17.5	19.2	22.2	20.4
Predicted Smoke Density Index	33	31	123	47	15	55
Predicted Fire Rating	Class 1					

TABLE 7

Example	17	18	19
B-side			
DBAA	--	--	15.02
Saytex [®] RB-79	--	8.56	--
TCPP	14.96	--	--
DE	--	0.95	--
Stepanpol [®] PS-3152	62.67	36.72	--
Carpol [®] GSP-280	--	--	66.21
Voranol [®] 370	--	34.42	--
Dabco [®] DC 5598	1.25	1.27	1.23
Dabco [®] K-15	1.14	1.86	1.81
Pel-cat 9506	1.96	--	--
Pel-cat 9858-A	0.89	--	--
Jeffcat [®] Z-110	0.21	--	--
Jeffcat [®] ZF-20	0.37	--	--
Dabco [®] TMR-2	--	1.24	1.21
Dabco [®] T	--	0.65	0.62
Water	0.17	0.94	0.91
N-Pentane/isopentane (50/50)	16.38	13.40	13.00
A-side			
Papi [®] 27	100.00	100.00	100.00
Process			
A:B Volume Ratio	131.1:100	145.8:100	142.4:100
A:B Weight Ratio	153.4:100	169.1:100	164:100
Isocyanate Index	297.8	208.9	232.7

TABLE 8

Example	17	18	19
Foam Properties			
Density (lb/ft ³)	1.90	2.0	1.95
Density (kg/m ³)	30.4	32.0	31.2
Compressive Strength (kPa)	187	314	214
R-value (/inch)	6.2	6.8	5.25
R-value (m ² K/W)	1.092	1.198	0.925
Predicted Flame Spread Index	21	22	22.5
Predicted Smoke Density Index	25	48	439
Predicted Fire Rating	Class 1	Class 1	Class 1

[0069] Tables 7 and 8 show that using DBAA in panel foams achieves a Class 1 flame retardant rating for the foam.

TABLE 9A

Example 20 – Run	1	2	3	4	5	6	7	8	9	10
B side										
Viscosity (cPs; at 25°C)	255	410	250	170	200	245	1325	1440	1050	180
DBAA	0.69	0.69	5.45	7.32	7.32	7.32	7.63	7.63	7.95	9.41
Terate [®] HT 5349	51.61	51.61	51.61	47.36	47.36	47.36	51.61	51.61	48.04	42.88
Voranol [®] 370	0.14	0.14	1.09	1.46	1.46	1.46	0.80	0.80	1.58	1.88
Carpol [®] GSP-280	26.21	26.21	21.45	23.83	23.83	23.83	25.53	25.53	26.21	26.21
Dabco [®] DC193	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Dabco [®] K-15	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Dabco [®] T-120	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Polycat [®] 204	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Water	0.08	0.08	0.08	0.08	0.08	0.08	0.86	0.86	0.60	0.08
Genetron [®] 245fa	15.00	15.00	15.00	15.00	15.00	15.00	8.74	8.74	11.31	15.00
Process										
A:B vol. ratio	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1
Isocyanate Index	1.335	1.335	1.313	1.314	1.315	1.315	1.086	1.086	1.171	1.314

TABLE 9B

Example 20 - Run	11	12	13	14	15	16	17	18	19	20
B side										
Viscosity (cPs; at 25°C)	865	925	190	1290	930	65	920	965	1450	1540
DBAA	7.79	8.87	9.18	9.39	11.09	11.82	12.00	12.00	12.00	12.00
Terate [®] HT 5349	51.26	44.79	46.02	48.71	47.96	42.30	43.69	43.69	48.30	51.61
Voranol [®] 370	1.95	2.22	2.29	2.35	2.77	2.95	3.00	3.00	3.00	3.00
Carpol [®] GSP-280	21.45	26.21	21.45	25.36	21.45	21.45	24.28	24.28	26.21	22.90
Dabco [®] DC193	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Dabco [®] K-15	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Dabco [®] T-120	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Polycat [®] 204	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Water	0.62	0.57	0.00	1.08	0.72	0.08	0.67	0.67	1.59	1.59
Genetron [®] 245fa	11.06	11.41	14.57	7.71	10.24	15.00	10.54	10.54	4.00	4.00
Process										
A:B vol. ratio	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1
Isocyanate Index	1.148	1.167	1.307	1.048	1.111	1.292	1.124	1.124	0.947	0.941

TABLE 10A

Example 20 - Run	1	2	3	4	5	6	7	8	9	10
Density, lb/ft ³	2.12	2.22	2.12	2.13	2.28	2.05	1.96	1.95	2.04	2.1
Density, kg/m ³	34.0	35.6	34.0	34.1	36.5	32.8	31.4	31.2	32.7	33.6
Dimensional stability ¹ (vol. change)	7.29	5.55	3.75	5.58	7.49	4.44	2.27	-3.04	-4.00	5.69
Compressive Strength, psi	21.2	25.8	22.2	20.3	22.5	20.9	26.1	18.9	19.7	19.6
Compressive Strength, kPa	146.2	177.9	153.1	140.0	155.1	144.1	180.0	130.3	135.8	135.1
R-value, /in.	7.42	7.23	7.64	7.27	7.84	7.44	4.54	6.82	7.07	7.19
R-value, m ² K/W	1.307	1.273	1.345	1.280	1.381	1.310	0.800	1.201	1.245	1.266
Peak Heat Release Rate	288	276	238	234	224	235	235	245	242	226
Predicted Flame Spread Index	25.4	23.0	22.3	21.2	21.9	20.8	21.3	23.0	23.9	21.3
Predicted Smoke Index	153	89	47	19	28	52	28	24	30	35

¹ Dimensional stability was measured at 70°C for 14 days at 95% RH.

TABLE 10B

Example 20 - Run	11	12	13	14	15	16	17	18	19	20
Density, lb/ft ³	2.02	1.96	2.1	1.87	1.89	1.94	1.93	1.95	1.92	1.89
Density, kg/m ³	32.4	31.4	33.6	30.0	30.3	31.1	30.9	31.2	30.8	30.3
Dimensional stability ¹ (vol. change)	1.00	-1.10	6.37	-0.12	-2.47	7.20	-0.26	-2.74	0.41	2.33
Compressive Strength, psi	20.1	17.0	17.9	24.4	17.9	16.4	16.6	17.9	21.2	22.0
Compressive Strength, kPa	138.6	117.2	123.4	168.2	123.4	113.1	114.5	123.4	146.2	151.7
R-value, /in.	7.4	7.03	7.43	4.8	7.06	7.39	7.09	6.98	4.86	4.75
R-value, m ² K/W	1.303	1.238	1.308	0.845	1.243	1.301	1.249	1.229	0.856	0.837
Peak Heat Release Rate	247	231	211	226	226	229	203	200	222	231
Predicted Flame Spread Index	22.2	21.1	20.7	22.1	22.9	22.7	20.2	21.5	19.1	21.2
Predicted Smoke Index	48	18	22	27	18	29	17	21	28	37

¹ Dimensional stability was measured at 70°C for 14 days at 95% RH.

TABLE 11A

Example 21 – Run B side	1 ¹	2	3	4	5	6	7	8	9	10	11	12 ²	13
Viscosity (cPs; at 25°C)	1715	1350	1265	1275	1115	1125	965	1010	1610	1590	1165	1265	1395
DBAA	0	4.52	4.55	6.92	7.03	7.03	8.38	8.38	8.54	8.54	9.57	9.57	9.43
Terate® HT 5349	40.69	51.22	51.61	50.32	51.61	51.61	47.31	47.31	51.61	51.61	46.92	46.92	48.69
Voranol® 280	--	26.01	26.21	26.21	23.11	23.11	25.72	25.72	25.75	25.75	--	--	26.21
Voranol® 370	23.91	1.13	1.14	1.73	1.76	1.76	2.10	2.10	2.13	2.13	26.22	26.22	2.43
Dabco® DC193	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Dabco® T-120	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Dabco® K-15	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Polycat® 204	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Water	1.00	0.76	0.80	1.05	0.80	0.80	0.80	0.80	1.43	1.43	0.80	0.80	1.29
Solstice® LBA	10.00	10.00	10.00	8.32	10.00	10.00	10.00	10.00	5.48	5.48	10.00	10.00	6.45
Process													
A:B vol. ratio	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1
Isocyanate Index	1.078	1.139	1.164	1.098	1.144	1.144	1.147	1.147	1.015	1.015	1.049	1.052	1.04

¹ Comparative run.

² Contains 9% of a mixed ester of tetrabromophthalic anhydride with diethylene glycol and propylene glycol (Saytex® RB-79 flame retardant) and 6% tris(1-chloro-2-propyl)phosphate (TCPP).

TABLE 11B

Example 21 – Run	14	15	16	17	18	19	20	21	22	23	24	25	26
B side													
Viscosity (cPs; at 25°C)	1080	1655	1660	1085	1145	900	2070	1605	1590	1355	1075	820	1395
DBAA	10.51	10.72	10.77	11.07	11.07	11.24	12.00	12.00	12.00	12.00	12.00	12.00	10.92
Terate® HT 5349	47.61	50.33	48.28	49.75	49.75	45.02	51.61	51.61	51.61	47.17	45.22	42.30	48.96
Voranol® 280	24.11	26.21	25.23	21.45	21.45	26.21	26.21	23.25	23.25	25.69	23.29	26.21	--
Voranol® 370	2.63	2.68	2.69	2.77	2.77	2.81	3.00	3.00	3.00	3.00	3.00	3.00	--
Carpol® GSP-280	--	--	--	--	--	--	--	--	--	--	--	--	16.95
Carpol® GP-5015	--	--	--	--	--	--	--	--	--	--	--	--	10.00
Dabco® DC193	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Dabco® T-120	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Dabco® K-15	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Polycat® 204	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Water	0.96	1.70	1.40	0.98	0.97	1.02	2.10	1.65	1.65	1.38	0.76	0.77	1.36
Solstice® LBA	8.65	3.56	5.24	8.48	8.48	8.23	0.69	3.65	3.65	5.64	10.00	10.00	5.31
Process													
A:B vol. ratio	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1
Isocyanate Index	1.096	0.962	0.983	1.081	1.083	1.086	0.897	0.957	0.956	1.01	1.132	1.14	1.059

TABLE 12A

	1 ¹	2	3	4	5	6	7	8	9	10	11	12	13
Example 21 - Run	1.95	2.07	2.02	1.98	1.94	2.01	2.05	1.95	1.94	2.04	1.81	1.91	1.99
Density, lb/ft ³	31.2	33.2	32.4	31.7	31.1	32.2	32.8	31.2	31.1	32.7	29.0	30.6	31.9
Density, kg/m ³	-11.8	0.64	1.07	-3.67	-1.09	-1.11	-0.74	-2.93	-19.04	-16.27	-0.15	--	-14.24
Dimensional stability ² (vol. change)	26.0	20.1	18.63	18.13	17.50	18.27	19.40	19.63	17.93	19.63	24.7	--	18.10
Compressive Strength, psi	179.3	138.6	128.4	125.0	120.7	126.0	133.8	135.3	123.6	135.3	170.3	--	124.8
Compressive Strength, kPa	7.29	7.07	7.27	7.35	7.3	7.37	7.17	7.67	6.89	7.03	4.78	7.92	6.99
R-value, /in.	1.284	1.245	1.280	1.294	1.286	1.298	1.263	1.351	1.213	1.238	0.842	1.395	1.231
Peak Heat Release Rate	184	240	226	212	198	248	198	215	233	221	228	214	219
Predicted Flame Spread Index	19.8	21.4	22.1	21.9	21.1	23.3	20.9	19.6	24.0	21.0	19.9	18.6	22.9
Predicted Smoke Index	15	22	19	27	18	22	29	36	21	25	88	13	16

¹ Comparative run.

² Dimensional stability was measured at 70°C for 14 days at 95% RH.

TABLE 12B

Example 21 - Run	14	15	16	17	18	19	20	21	22	23	24	25	26
Density, lb/ft ³	1.98	1.86	1.89	1.75	1.94	1.93	1.92	1.89	2.02	1.99	1.86	1.96	1.90
Density, kg/m ³	31.7	29.8	30.3	28.0	31.1	30.9	30.8	30.3	32.4	31.9	29.8	31.4	30.4
Dimensional stability ¹ (vol. change)	-4.52	-43.42	1.62	3.36	0.33	-4.74	-69.19	-14.89	-24.33	2.12	0.07	-0.22	-39.22
Compressive Strength, psi	16.37	17.37	22.2	23.37	17.03	19.23	16.67	19.00	15.23	26.50	22.90	17.43	9.5
Compressive Strength, kPa	112.9	119.8	153.1	161.1	117.4	132.6	114.9	131.0	105.0	182.7	157.9	99.5	65.5
R-value, /in.	7.53	6.72	4.52	5.05	7.15	4.98	6.22	5.55	6.35	4.99	7.18	7.25	6.50
R-value, m ² K/W	1.326	1.183	0.796	0.889	1.259	0.877	1.095	0.977	1.118	0.879	1.264	1.277	1.145
Peak Heat Release Rate	214	210	238	197	210	192	197	197	204	201	193	187	453
Predicted Flame Spread Index	19.8	21.4	20.1	19.0	19.1	19.0	21.5	19.3	20.1	17.5	18.1	18.7	21.6
Predicted Smoke Index	17	48	109	38	42	43	58	32	50	56	76	49	1074

¹ Dimensional stability was measured at 70°C for 14 days at 95% RH.

TABLE 13A

Example 22 – Run	1*	2*	3	4	5	6	7	8	9	10	11	12	13	14	15	16
B side																
Viscosity (cPs; at 25°C)	4010	1560	1775	1635	2435	1645	2895	2750	2455	1620	1575	1585	1625	1425	955	1625
DBAA	0.00	0.00	1.23	2.80	5.37	6.60	8.00	8.00	8.00	8.61	8.61	8.61	8.61	9.83	9.85	9.85
Terate® HT 5349	64.74	52.75	64.74	64.35	62.72	48.93	60.00	60.00	40.01	54.66	54.66	54.66	54.66	57.98	47.87	47.87
Voranol® 280	--	--	--	--	--	--	--	--	--	--	--	--	--	--	10.00	15.00
Voranol® 370	--	--	0.31	0.70	1.34	1.65	2.00	2.00	2.00	2.15	2.15	2.15	2.15	2.46	2.46	2.46
Carpol® GSP-280	29.95	29.95	16.43	16.43	22.84	29.95	--	7.14	16.00	22.59	22.59	22.59	22.59	16.43	--	--
Carpol® GP-5015	--	--	--	--	--	--	16.05	8.92	20.00	--	--	--	--	--	--	--
Carpol® GP-700	--	--	--	--	--	--	--	--	--	--	--	--	--	--	14.52	--
Vorasurf® 504	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	9.52
Dabco® DC193	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Dabco® T-120	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Dabco® K-15	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Polycat® 204	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Water	2.26	0.89	0.86	1.04	1.94	1.36	1.45	1.44	1.49	1.43	1.43	1.43	1.43	1.26	1.25	1.25
Opteon™ 1100	0.01	12.00	12.00	10.43	2.43	7.56	6.00	6.00	6.00	6.69	6.69	6.69	6.69	8.00	8.00	8.00
Process																
A:B vol. ratio	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1
Isocyanate Index	0.899	1.156	1.128	1.082	0.917	1.026	1.083	1.031	1.149	0.991	0.991	0.991	0.991	1.007	1.058	1.119

* Comparative run.

TABLE 13B

Example 22 – Run	17	18	19	20	21	22	23	24	25	26	27	28	29	30
B side														
Viscosity (cPs; at 25°C)	695	470	--	890	1200	1955	1285	1395	2220	2420	2240	890	1010	1570
DBAA	9.85	12.31	12.42	12.43	12.47	12.86	12.90	13.44	13.44	13.54	15.28	16.11	17.23	20.57
Terate® HT 5349	47.87	47.87	48.72	41.01	56.81	59.66	58.38	58.84	61.34	64.74	49.47	36.64	49.21	55.50
Voranol® 280	--	10.00	2.46	2.48	2.49	2.49	2.57	2.58	2.69	2.69	2.71	3.06	3.22	3.45
Voranol® 370	12.46	--	--	--	--	--	--	--	--	--	--	--	--	--
Carpol® GSP-280	--	--	--	29.26	16.43	16.43	16.43	16.43	16.43	16.43	29.95	29.95	17.00	16.43
Carpol® GP-1500	14.52	14.52	24.74	--	--	--	--	--	--	--	--	--	--	--
Dabco® DC193	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Dabco® T-120	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Dabco® K-15	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Polycat® 204	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Water	1.25	1.25	1.50	0.85	1.15	1.52	1.38	1.48	1.78	2.17	2.19	0.81	0.87	1.88
Opteon™ 1100	8.00	8.00	6.00	12.00	9.00	5.77	7.00	6.00	3.50	0.00	0.00	12.00	11.26	2.21
Process														
A:B vol. ratio	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1
Isocyanate Index	1.075	1.111	1.097	1.122	1.028	0.957	0.982	0.963	0.913	0.856	0.868	1.12	1.074	0.877

TABLE 13C

Example 22 – Run	31	32	33	34	35	36	37
B side							
Viscosity (cPs; at 25°C)	600	1570	1630	1115	1035	575	650
DBAA	16.75	20.00	20.00	20.00	20.00	20.00	17.16
Terate® HT 5349	35.51	47.10	47.10	35.51	35.51	41.28	43.05
Voranol® 370	4.19	5.00	5.00	5.00	5.00	5.00	--
Carpol® GSP-280	26.25	22.60	22.60	29.95	29.95	16.43	21.47
Dabco® DC193	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Dabco® T-120	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Dabco® K-15	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Polycat® 204	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Water	0.78	2.12	2.13	1.66	1.65	0.74	0.73
Opteon™ 1100	12.00	0.00	0.00	4.24	4.24	12.00	12.00
Process							
A:B vol. ratio	1:1	1:1	1:1	1:1	1:1	1:1	1:1
Isocyanate Index	1.103	0.840	0.840	0.921	0.922	1.076	1.100

TABLE 14A

Example 22 - Run	1*	2*	3	4	5	6	7	8	9	10	11	12	13	14
Density, lb/ft ³	2.17	2.18	2.10	1.98	2.13	1.99	2.19	1.95	1.91	1.85	1.90	1.84	1.92	1.88
Density, kg/m ³	34.8	34.9	33.6	31.7	34.1	31.9	35.1	31.2	30.6	29.6	30.4	29.5	30.8	30.1
Dimensional stability ¹ (vol. change)	-66.50	0.14	-0.32	3.21	-56.61	1.21	1.37	1.99	-0.74	0.03	-1.30	-0.44	-0.20	1.25
Compressive Strength, psi	19.4	24.8	24.7	22.3	18.1	27.2	17.7	16.1	15.0	24.1	24.3	23.7	23.5	22.2
Compressive Strength, kPa	133.8	171.0	170.3	153.8	124.8	187.5	122.0	111.0	103.4	166.2	167.5	163.4	162.0	153.1
R-value, /in.	6.33	7.68	7.95	7.11	6.76	4.93	4.62	4.86	5.64	4.56	4.79	4.93	4.93	4.63
R-value, m ² K/W	1.115	1.353	1.400	1.252	1.191	0.868	8.41	0.856	0.993	0.803	0.844	0.868	0.868	0.815
Peak Heat Release Rate	280	275	241	233	227	235	656	507	435	215	199	225	219	208
Predicted Flame Spread Index	26.0	23.7	23.7	22.9	22.1	21.4	21.6	22.2	22.2	18.9	19.9	18.9	20.0	20.0
Predicted Smoke Index	43	109	35	13	19	64	1060	629	781	57	34	47	37	48

* Comparative run.

¹ Dimensional stability was measured at 70°C for 14 days at 95% RH.

TABLE 14B

Example 22 - Run	15	16	17	18	19	20	21	22	23	24	25	26	27
Density, lb/ft ³	1.93	1.97	1.94	1.93	1.87	1.81	1.97	1.95	1.93	1.91	1.93	2.19	2.08
Density, kg/m ³	30.9	31.6	31.1	30.9	30.0	29.0	31.6	31.2	30.9	30.6	30.9	35.1	33.3
Dimensional stability ¹ (vol. change)	9.36	-11.57	-27.1	-35.73	--	-4.72	2.01	-41.59	-0.68	1.32	-57.31	-62.93	-47.63
Compressive Strength, psi	21.9	11.1	11.2	11.4	7.5	18.3	26.3	15.4	23.4	23.0	12.6	13.6	12.9
Compressive Strength, kPa	151.0	76.5	77.2	78.6	51.7	126.2	181.3	106.2	161.3	158.6	86.9	93.8	88.9
R-value, /in.	6.37	6.70	6.92	7.06	6.40	7.73	4.76	7.04	4.81	4.81	7.01	6.24	6.58
R-value, m ² K/W	1.122	1.18	1.219	1.243	1.127	1.361	0.838	1.24	0.847	0.847	1.235	1.099	1.159
Peak Heat Release Rate	220	518	431	404	479	222	219	221	233	236	214	201	219
Predicted Flame Spread Index	21.3	21.9	19.9	21.6	22.5	19.9	20.6	20.2	21.0	20.3	21.6	22.4	21.5
Predicted Smoke Index	35	1003	1055	906	479	26	36	48	44	61	56	28	116

¹ Dimensional stability was measured at 70°C for 14 days at 95% RH.

TABLE 14C

Example 22 - Run	28	29	30	31	32	33	34	35	36	37
Density, lb/ft ³	1.82	1.96	1.90	1.83	1.93	2.17	1.99	1.88	1.67	1.85
Density, kg/m ³	29.1	31.4	30.4	29.3	30.9	34.8	31.9	30.1	26.8	29.6
Dimensional stability ¹ (vol. change)	1.18	-2.71	-1.04	-16.55	-47.57	-80.89	-39.23	-57.00	-23.00	-17.5
Compressive Strength, psi	16.5	16.7	22.2	15.6	10.0	14.5	11.5	12.6	13.3	14.6
Compressive Strength, kPa	113.8	115.1	153.1	107.6	68.9	100.0	79.3	86.9	91.7	100.7
R-value, /in.	7.67	7.24	4.97	7.66	5.69	6.89	6.97	7.01	7.85	7.21
R-value, m ² K/W	1.351	1.275	0.875	1.349	1.002	1.213	1.227	1.235	1.382	1.270
Peak Heat Release Rate	192	200	204	193	190	213	197	207	187	172
Predicted Flame Spread Index	20.3	19.0	16.9	18.1	17.7	18.3	17.6	18.2	16.8	18.1
Predicted Smoke Index	51	40	54	48	39	56	79	95	41	43

¹ Dimensional stability was measured at 70°C for 14 days at 95% RH.

[0070] 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.

[0071] 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.

THAT WHICH IS CLAIMED IS:

1. A polyurethane foam formed from ingredients comprising 2,3-dibromoallyl alcohol.
2. A polyurethane foam as in Claim 1 which is a flexible polyurethane foam.
3. A polyurethane foam as in Claim 1 which is a rigid polyurethane foam.
4. A polyurethane foam as in Claim 1 which also comprises a mixed ester of tetrabromophthalic anhydride with diethylene glycol and propylene glycol and/or tris(1-chloro-2-propyl)phosphate.
5. A formulation comprising 2,3-dibromoallyl alcohol, at least one polyol, at least one blowing agent, at least one catalyst, and at least one surfactant.
6. A formulation as in Claim 5 wherein the polyol is a polyether polyol and/or a polyester polyol.
7. A formulation as in Claim 5 wherein the blowing agent comprises water.
8. A formulation as in Claim 5 wherein the amount of 2,3-dibromoallyl alcohol is about 1 wt% to about 25 wt%, the amount of polyol is about 40 wt% to about 80 wt%, the amount of surfactant is about 0.1 wt% to about 5 wt%, the amount of blowing agent is 0.5 wt% to about 20 wt%, and/or the amount of catalyst is about 0.25 wt% to about 10 wt%, based on the total weight of the formulation.
9. A formulation as in Claim 5 wherein the polyol has a functionality of about 3 to about 7.
10. A formulation as in any of Claims 5-9 wherein water is the only blowing agent.
11. A polyurethane foam formed from components comprising at least one polyisocyanate and a formulation as in any of Claims 5-10.
12. A process for forming a polyurethane foam, which process comprises

contacting A) at least one isocyanate and/or polyisocyanate and B) a formulation formed from 2,3-dibromoallyl alcohol, at least one polyol, at least one blowing agent, at least one catalyst, and at least one surfactant, to form a mixture; and allowing the mixture to cure to form a polyurethane foam.

13. A process as in Claim 12 wherein A) and B) are in amounts such that the Isocyanate Index is about 80 to about 200, and wherein a flexible polyurethane foam is formed.

14. A process as in Claim 12 wherein A) and B) are in amounts such that the Isocyanate Index is about 85 to about 1000, and wherein a rigid polyurethane foam is formed.

15. A polyurethane foam formed as in any of Claims 12-14.

16. A polyurethane foam formed from ingredients comprising 2,3-dibromoallyl alcohol, at least one polyol, at least one blowing agent, at least one catalyst, at least one surfactant, and at least one polyisocyanate.

17. A polyurethane foam as in Claim 16 wherein the polyol is an aromatic polyester polyol and either a polyether polyol or at least one sucrose/glycerine polyol; wherein the blowing agent is water, *trans*-1-chloro-3,3,3-trifluoropropene, 1,2-bis(trifluoromethyl)ethene or a mixture of any two or more of these; wherein the catalyst is potassium octoate and/or dibutylbis(dodecylthio) stannane; wherein the surfactant is a silicone glycol; and/or wherein the polyisocyanate is diphenylmethane diisocyanate.

18. A polyurethane foam as in Claim 16 or 17 wherein the amount of 2,3-dibromoallyl alcohol is about 1.5 wt% to about 10 wt%; wherein the amount of polyol is about 25 wt% to about 35 wt%; wherein the amount of catalyst is about 0.5 wt% to about 4 wt%; and/or wherein the amount of surfactant is about 0.25 wt% to about 2.5 wt%, based on the total weight of the polyurethane foam.

19. A polyurethane foam as in Claim 17 wherein the aromatic polyester polyol has a functionality of about 1.75 to about 2.75 and a hydroxyl number in the range of about 200 to about 350.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/039578

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08G18/48 C08G18/54 C08G18/66 C08G18/76 C08G18/28
 C08G18/32 C08G18/42
 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)
 C08G

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.
A	US 4 002 580 A (RUSSO ROBERT VICTOR) 11 January 1977 (1977-01-11) cited in the application example 1 -----	1-19

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
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/039578

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