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(54) Title: OPEN CELL RIGID POLYURETHANE SPRAY FOAM HAVING IMPROVED FIRE RETARDANCY

(57) Abstract: An open cell rigid polyurethane foam, particularly suitable for spray applications, is prepared from a formulation including at least a Novolac-initiated polyol, a brominated polyol, a polyisocyanate and water as a blowing agent. The foam may be capable of obtaining a Class I flammability rating based on ASTM E-84.



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OPEN CELL RIGID POLYURETHANE SPRAY FOAM HAVING IMPROVED FIRE RETARDANCY

BACKGROUND OF THE INVENTION

1. Technical Field

[0001] The invention relates to the field of open cell rigid polyurethane spray foams. More particularly, the invention relates to the field of open cell rigid polyurethane spray foams exhibiting reduction in flammability.

2. Background of the Art

[0002] Rigid polyurethane foams have been used for some time in spray foam systems, particularly for roof and pipe insulation. In such applications flame retardancy is particularly desirable, in order to mitigate the effects of both residential and commercial fires. A number of polyurethane foam formulations have been developed that exhibit, to varying degrees, a reduction in flammability.

[0003] For example, U.S. Patent Nos. 3,297,597; 4,137,265; and 4,383,102 disclose use of nitrogen-containing polyols prepared by alkoxylation of the reaction product of a phenol, alkanolamines and formaldehyde, which are referred to as Mannich polyols. Such foams allegedly exhibit flame retardancy as well as good dimensional strength.

[0004] In another example, U.S. Published Application 2002/0040122 A1 discloses use of an ultra low viscosity Mannich polyol (less than about 3,500 centipoise (cP) (3.5 Pa*s) at 25°C, to obtain improved flame retardancy. In some embodiments a second polyol is included, which may be a Novolac-initiated polyol. Novolac resins are prepared via the acid catalyzed polymerization of phenol and formaldehyde, and these are then alkoxyated with one or more epoxides to form the polyols.

[0005] In general, spray foams for these applications are relatively low density and are water-blown. They are typically prepared from a combination of high and low molecular weight polyols, and cell opening of the foam is controlled by including of rigid and/or flexible surfactants. Unfortunately, the use of relatively high amounts of water, to reduce density, tend to result in incompatibility of the polyol blends, and also may increase the viscosity of the blends, which may make spraying more difficult. Shelf-life may be poor

because of the incompatibility, leading to phase separation. Processing dynamics may be narrow because of the combinations of polyols, catalysts, and surfactants that are combined, and the system may emit an objectionable, pungent odor, which may be attributable to certain catalysts. Foams that do exhibit some flame retardancy may still fail to meet the requirements of a Class 1 flammability rating.

[0006] In view of the above, there is a continuing need in the art to identify formulations that can achieve a desirable, open cell, rigid foam meeting required flammability ratings. There is also a need that such foams be able to offer relatively wide processing windows, elimination of objectionable odors during spraying, and good miscibility that enables extended storage life, desirably greater than or equal to about 6 months, without phase separation.

SUMMARY OF THE INVENTION

[0007] The present invention provides, in one aspect, a sprayable polyurethane foam formulation comprising an A-component, comprising a polyisocyanate, and a B-component, comprising a Novolac-initiated polyol, a brominated polyol, and water as a blowing agent, wherein the A-component and the B-component may be reacted under conditions suitable to form an open cell rigid polyurethane foam that achieves a Class I flammability rating, according to ASTM E-84*. (*The flammability test results are not intended to reflect hazards presented by the test materials or any other materials under actual fire conditions.)

[0008] In another aspect, the invention provides a method of preparing a reduced flammability construction comprising preparing a sprayable formulation comprising an A-component, comprising a polyisocyanate, and a B-component, comprising a Novolac-initiated polyol, a brominated polyol, and water as a blowing agent, and spraying the formulation onto at least one substrate under conditions such that an open cell rigid polyurethane foam having a Class I flammability rating, according to ASTM E-84, is formed on the at least one substrate.

[0009] In yet another aspect, the invention provides a reduced flammability construction comprising at least one substrate having contiguous thereto an open cell rigid polyurethane foam prepared according to a method comprising preparing a sprayable

formulation comprising an A-component, comprising a polyisocyanate, and a B-component, comprising a Novolac-initiated polyol, a brominated polyol, and water as a blowing agent, and spraying the formulation onto the at least one substrate under conditions such that an open cell rigid polyurethane foam having a Class I flammability rating, according to ASTM E-84, is formed on the at least one substrate.

DETAILED DESCRIPTION OF THE INVENTION

[0010] In certain non-limiting embodiments the invention may provide an open cell, rigid polyurethane foam exhibiting a desirable flammability rating, wherein the formulation therefor has a wide processing window, relatively low odor, and is relatively storage stable. This foam may also contribute good insulation, including as an air barrier and as a sound-dampener.

[0011] The formulation includes certain typical polyurethane components, and may optionally include a number of additives or other modifiers. The first is a polyisocyanate component. This is referred to in the United States as the “A-component” (in Europe, as the “B-component”). Selection of the A-component may be made from a wide variety of polyisocyanates, including but not limited to those that are well known to those skilled in the art. For example, organic polyisocyanates, modified polyisocyanates, isocyanate-based prepolymers, and mixtures thereof may be employed. These can further include aliphatic and cycloaliphatic isocyanates, and in particular aromatic and, more particularly, multifunctional aromatic isocyanates. Also particularly preferred are polyphenyl polymethylene polyisocyanates (PMDI).

[0012] Other polyisocyanates useful in the present invention also include 2,4- and 2,6-toluenediisocyanate and the corresponding isomeric mixtures; 4,4'-, 2,4'- and 2,2'-diphenyl-methanediisocyanate and the corresponding isomeric mixtures; mixtures of 4,4'-, 2,4'- and 2,2'-diphenyl-methanediisocyanates and polyphenyl polymethylene polyisocyanates (PMDI); and mixtures of PMDI and toluene diisocyanates. Also useful for preparing the rigid polyurethanes of the present invention are aliphatic and cycloaliphatic isocyanate compounds such as 1,6-hexamethylene-diisocyanate; 1-isocyanato-3,5,5-trimethyl-1,3-isocyanatomethyl-cyclohexane; and 2,4- and 2,6-hexahydro-toluen-diisocyanate, as well as the corresponding isomeric mixtures; 4,4'-, 2,2'- and 2,4'-

dicyclohexylmethanediisocyanate, and the isomeric mixtures corresponding thereto. 1,3-tetramethylene xylene diisocyanate may also be used with the present invention.

[0013] Also advantageously used for the A-component are the so-called modified multifunctional isocyanates, that is, products which are obtained through chemical reactions of the above diisocyanates and/or polyisocyanates. Exemplary are polyisocyanates containing esters, ureas, biurets, allophanates and preferably carbodiimides and/or uretonomines; isocyanurate and/or urethane group containing diisocyanates or polyisocyanates. Liquid polyisocyanates containing carbodiimide groups, uretonomine groups and/or isocyanurate rings, having isocyanate groups (NCO) contents of from 120 to 40 weight percent, more preferably from 20 to 35 weight percent, can also be used. These include, for example, polyisocyanates based on 4,4'-, 2,4'- and/or 2,2'-diphenylmethane diisocyanate and the corresponding isomeric mixtures; 2,4- and/or 2,6-toluenediisocyanate and the corresponding isomeric mixtures; mixtures of diphenylmethane diisocyanates and PMDI; and mixtures of toluenediisocyanates and PMDI and/or diphenylmethane diisocyanates.

[0014] Suitable prepolymers for use as the polyisocyanate component of the formulations of the present invention are prepolymers having NCO contents of from 2 to 40 weight percent, more preferably from 4 to 30 weight percent. These prepolymers are prepared by reaction of the di- and/or poly-isocyanates with materials including lower molecular weight diols and triols, but may alternatively be prepared with multivalent active hydrogen compounds such as di- and tri-amines and di- and tri-thiols. Individual examples are aromatic polyisocyanates containing urethane groups, preferably having NCO contents of from 5 to 40 weight percent, more preferably 20 to 35 weight percent, obtained by reaction of diisocyanates and/or polyisocyanates with, for example, lower molecular weight diols, triols, oxyalkylene glycols, dioxyalkylene glycols, or polyoxyalkylene glycols having molecular weights up to about 800. These polyols can be employed individually or in mixtures as di- and/or polyoxyalkylene glycols. For example, diethylene glycols, dipropylene glycols, polyoxyethylene glycols, ethylene glycols, propylene glycols, butylene glycols, polyoxypropylene glycols and polyoxypropylenepolyoxyethylene glycols may be used. Polyester polyols can also be used, as well as alkyl diols such as butane diol. Other diols that are also useful include

bishydroxyethyl- and bishydroxypropyl-bisphenol A, cyclohexane dimethanol, and bishydroxyethyl hydroquinone.

[0015] Useful as the polyisocyanate component of prepolymer formulations are: (i) polyisocyanates having an NCO content of from 8 to 40 weight percent containing carbodiimide groups and/or urethane groups, from 4,4'-diphenylmethane diisocyanate or a mixture of 4,4'- and 2,4'-diphenylmethane diisocyanates; (ii) prepolymers containing NCO groups, having an NCO content of from 2 to 35 weight percent, based on the weight of the prepolymer, prepared by the reaction of polyols, having a functionality of preferably from 1.75 to 4 and a molecular weight of from 800 to 15,000 with 4,4'-diphenylmethane diisocyanate or with a mixture of 4,4'- and 2,4'-diphenylmethane diisocyanate; mixtures of (i) and (ii); and (iii) 2,4' and 2,6-toluene-diisocyanate and the corresponding isomeric mixtures.

[0016] PMDI in any of its forms is the most preferred polyisocyanate for use with the present invention. When used, it preferably has an equivalent weight between 125 and 300, more preferably from 130 to 175, and an average functionality of greater than about 1.5. More preferred is an average functionality of from 1.75 to 3.5. The viscosity of the polyisocyanate component is preferably from 25 to 5,000 centipoise (cP) (0.025 to about 5 Pa*s), but values from 100 to 1,000 cP at 25°C (0.1 to 1 Pa*s) are preferred for ease of processing. Similar viscosities are preferred where alternative polyisocyanate components are selected. Notwithstanding the above, the polyisocyanate component is preferably selected from the group consisting of MDI, PMDI, an MDI prepolymer, a PMDI prepolymer, a modified MDI, and combinations thereof.

[0017] The B-component of the formulation is the isocyanate-reactive portion, i.e., it includes a combination of a Novolac-initiated polyol and a brominated polyol in a relatively low viscosity polyol blend. As is well-known to those skilled in the art, Novolac-initiated polyols are the alkoxylation products of a phenol formaldehyde resin, which is formed by the elimination reaction of phenol with formaldehyde in the presence of an acid catalyst, such as glacial acetic acid, followed by concentrated hydrochloric acid. Usually a small amount of the acid catalyst or catalysts is/are added to a miscible phenol, such as p-toluenesulfonic acid, followed by formaldehyde. The formaldehyde will react between two phenols to form a methylene bridge, creating a dimer by electrophilic

aromatic substitution between the ortho and para positions of phenol and the protonated formaldehyde. This dimer is bisphenol F. As concentration of dimers increase, trimers, tetramers and higher oligomers may also form. However, because the molar ratio of formaldehyde to phenol is controlled at somewhat less than 1, polymerization is not completed. Thus, the Novolac may then be alkoxylated to build equivalent weight to a desired level, desirably from about 100 to about 500; in certain non-limiting embodiments, from about 200 to about 400; and in certain other non-limiting embodiments, from about 250 to about 350.

[0018] Phenols which may be used to prepare the Novolac initiator include: o-, m-, or p-cresols, ethylphenol, nonylphenol, p-phenylphenol, 2,2-bis(4-hydroxyphenol) propane, beta-naphthol, beta-hydroxyanthracene, p-chlorophenol, o-bromophenol, 2,6-dichlorophenol, p-nitrophenol, 4-nitro-6-phenylphenol, 2-nitro-4-methylphenol, 3,5-dimethylphenol, p-isopropylphenol, 2-bromo-4-cyclohexylphenol, 4-t-butylphenol, 2-methyl-4-bromophenol, 2-(2-hydroxypropyl)phenol, 2-(4-hydroxyphenol) ethanol, 2-carboethoxyphenol, 4-chloro-methylphenol, and combinations thereof. It is especially preferred that the phenols used to prepare the Novolacs useful in the present invention be unsubstituted phenols.

[0019] Alkoxylation of the Novolac initiator, to prepare the final Novolac-initiated polyol or a prepolymer from which the final Novolac-initiated polyol may be made, may, in certain embodiment,s be carried out using any alkylene oxide typically used by those skilled in the art. For example, ethylene oxide, propylene oxide, butylene oxide, and combinations thereof may be selected.

[0020] A second required polyol of the present invention's formulation is a brominated polyol. In general, the brominated flame retardants contribute to flame retardancy by inhibiting the ignition of combustible organic materials. They may also hinder the spread of fire, that is, the time to flashover, thereby providing valuable extra time in the early stages of a fire, during which escape may be possible. The brominated polyol may have a functionality of from about 1 to about 3, and a hydroxyl number from about 150 to about 260. It desirably has a viscosity ranging from about 20,000 centipoise (cP) to about 200,000 cP, and in certain more desirable but non-limiting embodiments, from about 100,000 cP to about 180,000 cP. In some non-limiting embodiments, the two polyols

together may have a viscosity ranging from about 20,000 cP to about 60,000 cP, and preferably from about 20,000 cP to about 40,000 cP.

[0021] While any brominated polyol may be selected herein, useful and easily obtained polyols of this type may include decabromodiphenyl ether (decaBDE) and other polybrominated diphenyl ethers (PBDEs), including, for example, pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE), tetrabromobisphenol A (TBBPA or TBBP-A), hexabromocyclododecane (HBCD), and combinations thereof. Also included are the brominated organophosphates, such as tris(2,3-dibromopropyl) phosphate (TRIS), bis(2,3-dibromopropyl) phosphate, combinations thereof, and the like.

[0022] In addition to the A-component and B-components described hereinabove, the formulation of the present invention may optionally include further additives or modifiers such as are well-known in the art. For example, surfactants, catalysts, other flame retardants, and/or fillers may be employed. Exemplary thereof are amine catalysts, including any organic compound which contains at least one tertiary nitrogen atom and is capable of catalyzing the hydroxyl/isocyanate reaction between the A-component(s) and B-component(s). Typical classes of amines include the N-alkylmorpholines, N-alkylalkanolamines, N,N-dialkylcyclohexylamines, alkylamines where the alkyl groups are methyl, ethyl, propyl, butyl and isomeric forms thereof, and heterocyclic amines. Typical but non-limiting specific examples thereof are triethylenediamine, tetramethylethylenediamine, bis(2-dimethylaminoethyl)ether, triethylamine, tripropylamine, tributylamine, triamylamine, pyridine, quinoline, dimethylpiperazine, piperazine, N,N-dimethylcyclohexylamine, N-ethylmorpholine, 2-methylpropanediamine, methyltriethylenediamine, 2,4,6-tri-dimethylaminomethylphenol, N,N',N''-tris(dimethylaminopropyl)-sym-hexahydrotriazine, and combinations thereof. A preferred group of tertiary amines comprises bis(2-dimethyl-aminoethyl)ether, dimethylcyclohexylamine, N,N-dimethylethanolamine, triethylenediamine, triethylamine, 2,4,6-tri(dimethylaminomethyl)phenol, N,N',N-ethylmorpholine, and combinations thereof.

[0023] Non-amine catalyst may also be used in the present invention. Typical of such catalysts are organometallic compounds of bismuth, lead, tin, titanium, iron, antimony, uranium, cadmium, cobalt, thorium, aluminum, mercury, zinc, nickel, cerium, molybdenum, vanadium, copper, manganese, zirconium, and combinations thereof.

Included as illustrative examples only are bismuth nitrate, lead 2-ethylhexoate, lead benzoate, lead naphthenate, ferric chloride, antimony trichloride, and antimony glycolate. A preferred group of organo-tin catalysts is the stannous salts of carboxylic acids, such as stannous acetate, stannous octoate, stannous 2-ethylhexoate, 1-methylimidazole, and stannous laurate, as well as the dialkyl tin salts of carboxylic acids, such as dibutyl tin diacetate, dibutyl tin dilaurate, dibutyl tin dimaleate, dioctyl tin diacetate, combinations thereof, and the like.

[0024] One or more trimerization catalysts may be used with the present invention. The trimerization catalyst employed may be any known to those skilled in the art which will catalyze the trimerization of an organic isocyanate compound to form the isocyanurate moiety. For typical isocyanate trimerization catalysts, see *The Journal of Cellular Plastics*, November/December 1975, page 329; U.S. Patents 3,745,133; 3,896,052; 3,899,443; 3,903,018; 3,954,684 and 4,101,465; the disclosures of which are incorporated herein in their entireties by reference. Typical trimerization catalysts include the glycine salts and tertiary amine trimerization catalysts, as well as the alkali metal carboxylic acid salts and combinations thereof. Preferred species within the classes are sodium N-2-hydroxy-5-nonylphenyl methyl-N-methylglycinate, and N,N-dimethyl-cyclohexylamine, and mixtures thereof. Also included in the preferred catalyst components are the epoxides disclosed in U.S. Patent 3,745,133, the disclosure of which is incorporated herein in its entirety by reference.

[0025] Other additives useful with the present invention are one or more non-brominated flame retardants, such as triethylphosphate, tris(2-chloroethyl) phosphate, tris(2-chloropropyl)phosphate, tris(1,3-dichloropropyl)phosphate, diammonium phosphate, halogenated aromatic compounds, antimony oxide, alumina trihydrate, polyvinyl chloride, and combinations thereof. Dispersing agents, cell stabilizers, and surfactants may also be incorporated into the formulations. Surfactants, including organic surfactants and silicone based surfactants, may also be added to serve as cell stabilizers. Some representative materials are sold under the designations SF-1109, L-520, L-521 and DC-193, which are, generally, polysiloxane polyoxylalkylene block copolymers, such as those disclosed in U.S. Patents 2,834,748; 2,917,480; and 2,846,458, for example, the disclosures of which are incorporated herein in their entireties by reference. Also included

are organic surfactants containing polyoxyethylene-polyoxybutylene block copolymers as described in U.S. Patent 5,600,019, the disclosure of which is incorporated herein in its entirety by reference. Other additives such as carbon black and colorants may be added. Finally, fillers such as barium sulfate and other inert inorganic particulates, including both natural and synthetic minerals, clays, and the like, may also be included in the rigid spray foams of the present invention.

[0026] The last component of the formulation is the blowing agent. While it may be included in the B-component, prior to combination with the A-component, it may also be a separate component in itself, combining simultaneously with the A-component and B-component in, for example, conventional spray equipment. In the present invention water is preferred. While other known blowing agents may be used, water offers the advantages of low cost, ease of use, and effectiveness in preparing specifically open cell, rigid polyurethane foams. Water and minor amounts of other blowing agents may also be used. For example, some of these other blowing agents may include hydrocarbons, chlorinated hydrocarbons, fluorinated hydrocarbons, combinations thereof, and the like. Preferably, the blowing agent used with water is selected from HCFC-141b, HCFC-22, HFC-134a, n-pentane, isopentane, cyclopentane, HCFC-124, HFC-245f, HFC-365 mfc, combinations thereof, and the like. Some halocarbon blowing agents, in particular, may be effective in reducing viscosity to a desirable level to optimize sprayability.

[0027] In proportions it is generally desirable that the A-component and the B-component be admixed at any suitable volume or weight ratio as desired for the particular composition, formulation method or equipment. In certain non-limiting embodiments, the Novolac-initiated polyol may be included in the B-component in an amount ranging from about 1 to about 99 parts by weight, based on 100 parts of total polyol, i.e., all polyols combined in the formulation. The brominated polyol may be included in any amount ranging from about 1 to about 60 parts by weight, and in certain particular and non-limiting embodiments, ranging from about 10 to about 40 parts by weight, on the same basis. Additional polyols, if desired, may be included in any amount ranging from 0 to about 60 parts by weight, on the same basis. Non-brominated phosphate additives, if desired, such as tris-chloro-isopropyl phosphate (TCPP) and/or triethylphosphate (TEP), may be included in any amount ranging from 0 to about 20

parts by weight, on the same basis. Surfactants, such as TEGOSTAB* B-8404, may be included in any amount ranging from 0 to about 6 parts by weight, on the same basis. (TEGOSTAB* B-8404 is available from Evonik.) Catalysts, such as NIAX* A-1, POLYCAT* 9 and/or POLYCAT* 77, may be included in amounts from about 1 to about 15 parts by weight, on the same basis. (NIAX* A-1 is available from General Electric. POLYCAT* 9 and POLYCAT* 77 are available from Air Products.) Additional catalysts, such as TOYOCAT* DM 70 or other gelling catalysts, may be included in amounts ranging from 0 to about 2 parts by weight, on the same basis. (TOYOCAT* DM 70 is available from Tosoh Corporation.) Finally, water may be included in amounts ranging from about 5 to about 40 parts by weight, on the same basis.

[0028] As an example only, the Novolac-initiated polyol may, in some non-limiting embodiments, be present in the B-component in an amount ranging from about 1 to about 99 parts by weight, based on 100 parts of total polyol, and the brominated polyol is in a range of from about 1 to about 60 parts by weight, on the same basis. Preferably, the Novolac-initiated polyol is present in an amount from about 30 to about 90 parts by weight, with the brominated polyol representing from about 10 to about 40 parts by weight, on the same basis. In certain other non-limiting embodiments, the Novolac-initiated polyol is present in an amount from about 40 to about 80 parts by weight, based on 100 parts of total polyol, with the brominated polyol representing from about 20 to about 30 parts by weight, on the same basis. The amount of Novolac-initiated polyol, brominated polyol, and if selected, other polyols known in the art as useful for making rigid polyurethane foams equals 100 parts by weight. In calculating these amounts, additional materials, such as surfactants, catalysts, other flame retardants, and/or fillers, are excluded.

[0029] In the polyurethane foam formulations including water as the only blowing agent, the water is desirably present in an amount of from about 0.5 to about 40 parts by weight, based on 100 parts of total polyol. In more particular and non-limiting embodiments, water may be used in an amount of from about 10 to about 35 parts by weight, on the same basis, and in still more preferred but non-limiting embodiments, water may be employed in an amount of from about 20 to about 30 parts by weight, again, on the same basis.

[0030] In preparing the formulations and final products of the present invention any methods and means known or contemplated by those skilled in the art as useful for preparing open cell, rigid polyurethane spray foams may be employed. It is typical to include any additives or modifiers with the B-component, and then enable the A-component and the B-component to contact one another and appropriate mix within a dual-action spray gun, whereby the polymerization reaction proceeds to completion on the substrate to which the spray foam is applied, e.g., a ceiling, wall, or other substrate. The equipment frequently used is so-called “double acting” positive displacement pumps which have the advantage of supplying an accurate component ratio of A-component to B-component in a continuous stream. Such systems tend to function more reliably, i.e., experience less cavitation, when each component has a viscosity of less than about 1,000 cP at 25°C. Another parameter that should be taken into account by those skilled in the art is that the commercially adopted standard design for such equipment usually requires a 1:1 volume ratio of A-component to B-component.

[0031] Final foam density may, in certain non-limiting embodiments, range from about 0.2 to about 10 pounds per cubic foot (pcf), and in other non-limiting embodiments, from about 0.4 to about 1.0 pcf. Such density range may be particularly desirable in preparing a reduced flammability construction wherein the foam is contiguous to surfaces of a substrate, such as a ceiling or wall, such that the foam provides both good flammability performance as well as a desirable level of insulation.

[0032] The description hereinabove is intended to be general and is not intended to be inclusive of all possible embodiments of the invention. Similarly, the examples hereinbelow are provided to be illustrative only and are not intended to define or limit the invention in any way. Those skilled in the art will be fully aware that other embodiments, within the scope of the claims, will be apparent, from consideration of the specification and/or practice of the invention as disclosed herein. Such other embodiments may include selections of specific polyols and isocyanates; mixing and reaction conditions; vessels and deployment apparatuses; protocols; performance and selectivity; identification of products and by-products; subsequent processing and use thereof; and the like; and those skilled in the art will recognize that such may be varied within the scope of the claims appended hereto.

EXAMPLE

[0033] A spray formulation is prepared using the following materials.

A-component:

A 100 percent PMDI-based product, PAPI* 27, manufactured by The Dow Chemical Company.

B-component:

[0034] A blend of the following:

IP* 585, manufactured by The Dow Chemical Company. A primary Novolac-based polyol containing OH # of 196, and a functionality of about 3.4.

PHT* 4-Diol, manufactured by Great Lakes Chemical. A flame suppressant tetrabromophthalate-based diol, OH # of 215, functionality of 2.

Triethylphosphate, a flame suppressant.

TEGOSTAB* B-8404, manufactured by Degussa. A silicone surfactant.

NIAX* A-1, manufactured by General Electric. A blowing catalyst comprising bis(2-dimethylaminoethyl)ether in dipropylene glycol, OH # of 250.

POLYCAT* 9, manufactured by Air Products. A gelling catalyst.

TOYOCAT* DM 70, manufactured by Tosoh Corporation. A curing catalyst comprising 70 percent 1,2-dimethylimidazole by weight, in 30 percent ethylene glycol by weight.

Water, as a blowing agent.

[0035] The formulation is fed through a Gusmer H20/35 Series Proportioning Machine and a GX 7 spray gun. One (volume) part of PAPI* 27 is matched with one (volume) part of B-component, which results in an isocyanate index of 0.38. The formulation is shown in Table 1, expressed in weight.

TABLE 1

A-COMPONENT:	Parts by weight, per 100 parts of total polyol	Percent by weight (of the specified component)
PAPI* 27 isocyanate	166.2	100
B-COMPONENT:		
IP* 585 polyol	73.0	46.7
PHT* 4-Diol	27.0	17.3
TEP (triethylphosphate)	15.0	9.6
TEGOSTAB* B-8404	3.0	1.9
NIAX* A-1	6.0	3.8
POLYCAT* 9	6.0	3.8
TOYOCAT* DM 70	0.2	0.1
Water	26.0	16.9

B-component viscosity is at 320 cP at 25°C (0.32 Pa*s), and the specific gravity of the B-component is 1.16 at 25°C. Hand-mixing tests of a 50 g sample at 75°F show a cream time of 2 seconds, a gel time of 6 seconds, and a core density of the final foam of 0.50 pounds per cubic foot (pcf).

[0036] The final spray applied foam exhibits a density of 0.58 pcf, and a k-Factor of 0.235 Btu.in/ft².hr.°F. Flame test screening under American Society for Testing Materials (ASTM) E-84 showed a flame spread, at a 4-inch thickness, of 25, and smoke development of 250. This qualifies as a Class I flammability rating.

WHAT IS CLAIMED IS:

1. A sprayable polyurethane foam formulation comprising an A-component, comprising a polyisocyanate, and a B-component, comprising a Novolac-initiated polyol, a brominated polyol, and water as a blowing agent, wherein the A-component and the B-component may be reacted under conditions suitable to form an open cell rigid polyurethane foam that achieves a Class I flammability rating, according to ASTM E-84.
2. The formulation of Claim 1 wherein the polyisocyanate is selected from the group consisting of organic polyisocyanates, modified polyisocyanates, isocyanate- based prepolymers, and mixtures thereof.
3. The formulation of Claim 2 wherein the polyisocyanate is selected from the group consisting of aliphatic isocyanates, cycloaliphatic isocyanates, and polyphenyl polymethylene polyisocyanates, methanedi-phenyl diisocyanates, and mixtures thereof.
4. The formulation of Claim 1 wherein the Novolac-initiated polyol is prepared from a phenol selected from the group consisting of o-, m-, or p-cresols, ethylphenol, nonylphenol, p-phenylphenol, 2,2-bis(4-hydroxyphenyl) propane, beta-naphthol, beta-hydroxyanthracene, p-chlorophenol, o-bromophenol, 2,6-dichloro-phenol, p-nitrophenol, 4-nitro-6-phenylphenol, 2-nitro-4-methylphenol, 3,5-dimethylphenol, p-isopropylphenol, 2-bromo-4-cyclohexylphenol, 4-t-butylphenol, 2-methyl-4-bromophenol, 2-(2-hydroxypropyl)phenol, 2-(4-hydroxyphenyl) ethanol, 2-carbethoxyphenol, 4-chloro-methylphenol, and combinations thereof.
5. The formulation of Claim 1 wherein the brominated polyol is selected from the group consisting of decabromodiphenyl ether, pentabromodiphenyl ether, octabromodiphenyl ether, tetrabromobisphenol A, hexabromocyclododecane, tris(2,3-dibromopropyl) phosphate, bis(2,3-dibromopropyl) phosphate, and combinations thereof.

6. The formulation of Claim 1 further comprising a blowing agent selected from the group consisting of hydrocarbons, chlorinated hydrocarbons, fluorinated hydrocarbons, and combinations thereof.
7. The formulation of Claim 6 further comprising a blowing agent selected from the group consisting of HCFC-141b, HCFC-22, HFC-134a, n-pentane, isopentane, cyclopentane, HCFC-124, HFC-245f, HFC-365 mfc, and combinations thereof.
8. The formulation of Claim 1 further comprising at least one catalyst selected from the group consisting of N-alkylmorpholines, N-alkylalkanolamines, N,N-dialkylcyclo-hexylamines, and alkylamines where the alkyl groups are methyl, ethyl, propyl, butyl and isomeric forms thereof, and heterocyclic amines; organometallic compounds of bismuth, lead, tin, titanium, iron, antimony, uranium, cadmium, cobalt, thorium, aluminum, mercury, zinc, nickel cerium, molybdenum, vanadium, copper, manganese, zirconium, and combinations thereof; and trimerization catalysts selected from glycine salts, tertiary amines, and alkali metal carboxylic acid salts; and combinations thereof.
9. The formulation of Claim 1 further comprising a non-brominated flame retardants selected from the group consisting of triethylphosphate, tris(2-chloroethyl)phosphate, tris(2-chloropropyl)phosphate, tris(1,3-dichloropropyl)phosphate, diammonium phosphate, halogenated aromatic compounds, antimony oxide, alumina trihydrate, polyvinyl chloride, and combinations thereof.
10. The formulation of Claim 1 further comprising a surfactant, a filler, a dispersing agent, a cell stabilizer, or a combination thereof.
11. The formulation of Claim 1 wherein the formulation is suitable to be sprayed, using a spray apparatus, such that at least the polyisocyanate, polyols and water are mixed within the spray apparatus and reaction is completed on a substrate.

12. The formulation of Claim 1 wherein the open cell rigid polyurethane foam prepared therewith has a density of from about 0.4 pcf to about 1.0 pcf.

13. The formulation of Claim 1 wherein the Novolac-initiated polyol is used in an amount of from about 1 to about 99 parts by weight, and the brominated polyol is used in an amount of from about 1 to about 60 parts by weight, based on 100 parts of total polyol.

14. The formulation of Claim 13 wherein the Novolac-initiated polyol is used in an amount of from about 30 to about 90 parts by weight, and the brominated polyol is used in an amount of from about 10 to about 40 parts by weight, based on 100 parts of total polyol.

15. The formulation of Claim 1 wherein water is the only blowing agent and is used in an amount of from about 0.5 to about 40 parts by weight, based on 100 parts of total polyol.

16. A method of preparing a reduced flammability construction comprising preparing a sprayable formulation comprising an A-component, comprising a polyisocyanate, and a B-component, comprising a Novolac-initiated polyol, a brominated polyol, and water as a blowing agent, and spraying the formulation onto at least one substrate under conditions such that an open cell rigid polyurethane foam having a Class I flammability rating, according to ASTM E-84, is formed on the at least one substrate.

17. A reduced flammability construction comprising at least one substrate having contiguous thereto an open cell rigid polyurethane foam prepared according to a method comprising preparing a sprayable formulation comprising an A component, comprising a polyisocyanate, and a B-component, comprising a Novolac-initiated polyol, a brominated polyol, and water as a blowing agent, and spraying the formulation onto the at least one substrate under conditions such that an open cell rigid polyurethane foam having a Class I flammability rating, according to ASTM E-84, is formed on the at least one substrate.

18. The construction of Claim 17 wherein the open cell rigid polyurethane foam has a density ranging from about 0.2 pcf to about 10 pcf.
19. The construction of Claim 18 wherein the open cell rigid polyurethane foam has a density ranging from about 0.4 pcf to about 1.0 pcf.
20. The construction of Claim 17 wherein the substrate is a wall or ceiling.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/066976

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/54

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 943 077 A (BELL REUBEN H ET AL) 9 March 1976 (1976-03-09) column 1, lines 4-8, 21-23, 36-67 column 3, line 65 - column 4, line 10 examples I, II, III claims 1, 2, 3, 4	1-20
X	US 4 579 876 A (ILIOPULOS MILTIADIS I [US]) 1 April 1986 (1986-04-01) column 1, lines 12-13 example 6	1-20
A	DE 197 36 574 A1 (BASF AG [DE]) 25 February 1999 (1999-02-25) examples 1, 2	1-20
A	US 2002/040122 A1 (MIRASOL SOL M [US] ET AL) 4 April 2002 (2002-04-04) example 1	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search

11 May 2010

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20/05/2010

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2009/066976

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US 4579876	A	01-04-1986	NONE	
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