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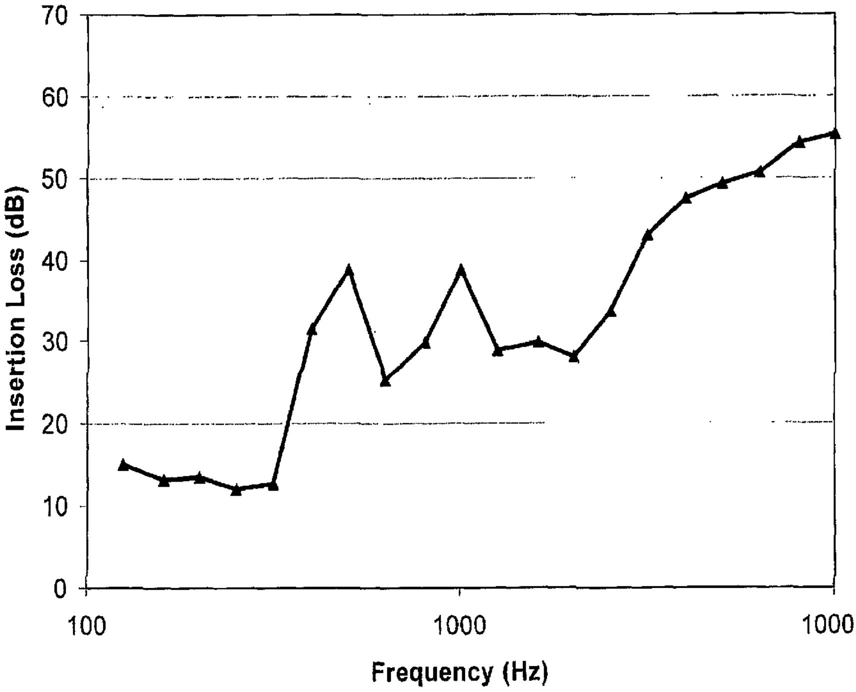
(54) Title: EXPANDABLE POLYOLEFIN COMPOSITIONS AND INSULATED VEHICLE PARTS CONTAINING EXPANDED POLYOLEFIN COMPOSITIONS



(57) Abstract: Polyolefin compositions that expand freely to form stable foams are disclosed. The compositions include at least one heat-activated expanding agent and typically include at least one heat-expanded crosslinker. The compositions are effective as sealers and noise/vibration insulation in automotive applications.

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EXPANDABLE POLYOLEFIN COMPOSITIONS AND INSULATED VEHICLE PARTS CONTAINING EXPANDED POLYOLEFIN COMPOSITIONS

This application claims benefit of United States Provisional Application No. 60/790,328, filed April 6, 2006.

The present invention relates to expandable polyolefin compositions and uses thereof as foam-in-place reinforcement and/or insulation materials.

Polymeric foams are finding increasing application in the automotive industry. These foams are used for structural reinforcement, preventing corrosion and damping sound and vibration. In many cases, manufacturing is simplest and least expensive if the foam can be formed in the place where it is needed, rather than assembling a previously-foamed part to the rest of the structure.

Foam-in-place formulations have gained favor because in many cases the foaming step can be integrated into other manufacturing processes. In many cases, the foaming step can be conducted at the same time as automotive coatings (such as cationic deposition primers such as the so-called "E-coat" materials). These foams can be formed in such cases by applying a reactive foam formulation to an automotive part or subassembly, before or after applying the E-coat, and then baking the coating. The foam formulation then expands and cures as the coating is baked.

Polyurethane foams are used in these applications, as they usually exhibit excellent adhesion to the substrate. However, polyurethane foams suffer from two significant problems. The first problem is that these foam formulations are usually two-part compositions. This means that starting materials must be metered, mixed and dispensed, which often requires equipment which not only can be expensive but also can take up a large amount of factory space. There are some one-part moisture curable polyurethane foam compositions that can be used in these applications, but moisture curing is slow and usually cannot result in low density foams.

The second problem with polyurethane foam is that of worker exposure to reactive chemicals like amines and isocyanates.

In addition to these problems, foamable polyurethane compositions often must be applied after coatings such as E-coats are baked and cured.

As a result of these problems, there have been attempts to substitute the polyurethane foams with expandable polyolefin compositions. The polyolefins have the advantage of being solid, one-component materials. As such, they can be extruded or otherwise formed into convenient shapes and sizes for insertion into specific cavities that require foam reinforcement or insulation. These compositions can be formulated so they expand under conditions of the E-coat baking step.

Heat resistance and adhesion to the substrate are concerns with the expandable polyolefin compositions, and for those reasons copolymers of ethylene with a polar, oxygen-containing monomer have been favored in these applications. Thus, for example, in U. S. Patent No. 5,385,951, an ethylene-methyl methacrylate copolymer is described as a polyolefin of choice due to its foaming characteristics, thermal stability and adhesive properties. In EP 452 527A1 and EP 457 928 A1, a copolymer of ethylene and a polar comonomer such as vinyl acetate is preferred due to the heat resistance of these copolymers. WO 01/30906 describes using a maleic anhydride-modified ethylene-vinyl acetate copolymer.

Expandable polyolefins have not performed optimally in these applications. Stable foam formation requires that the polyolefin becomes crosslinked during the expansion process. The timing of the crosslinking reaction in relation to the softening of the polyolefin and the activation of the expanding agent is very important. The timing of the crosslinking reaction is very important. If the crosslinking occurs too early, the resinous mass cannot expand fully. Late crosslinking also can result in incomplete expansion or even foam collapse. As a result of these problems, commercially available expandable polyolefin products usually expand to only 300 to 1600% of their initial volume. Higher expansion is desired, in order to more completely fill cavities using minimal amounts of material. A material that expands to 1800% or more, especially 2000% or more of its initial volume is highly desirable.

A further complication with compositions as described in U. S. Patent No. 5,385,951, EP 452 527A1, EP 457 928A1 and WO 01/30906 is that the polyolefin tends to soften too early during the expansion process The softened or melted resin tends to flow to the bottom of the cavity before it can crosslink and expand. If the cavity is not capable of retaining fluids, the polyolefin composition can even leak out before expansion and crosslinking can occur.

As a result, the expanded material tends to occupy the bottom of the cavity rather than uniformly filling the available space. If the cavity is small, this problem can be solved by simply using more of the expandable composition. This increases costs and does not solve the problem when larger or more complex cavities are to be filled. In some instances, the reinforcement or insulation is needed in only a portion of the cavity. It is very difficult to use an expandable polyolefin in those cases, unless that portion happens to be the bottom of the cavity, because of the tendency for the expandable polyolefins to run when heated.

As a result of these problems, it is common to form the expandable polyolefin composition onto a higher-melting support. The support helps to hold the polyolefin composition in position within the cavity until the expansion step is completed. Such supports tend only to retard, not prevent, the expandable polyolefin composition from running, unless the support is designed (and properly oriented) to retain fluids. Another problem with this approach is that it adds manufacturing steps and therefore increases costs. Furthermore, the supported expandable polyolefin often must be designed individually for each cavity in which it will be used. This adds even more to the cost, as specialized parts must be produced and inventoried. Despite this extra cost and complexity, very high failure rates are experienced with the expandable polyolefins. It would be highly desirable to produce an expandable polyolefin composition that could be produced inexpensively, preferably in a simple extrusion process, in a form that can be used easily to fill a variety of cavities, and which has low failure rates.

In one aspect, this invention is a method comprising

1) inserting a solid, thermally expandable polyolefin composition into a cavity,

2) heating the thermally expandable polyolefin composition in the cavity to a temperature sufficient to expand and crosslink the polyolefin composition and

3) permitting the polyolefin composition to expand freely to form a foam that fills at least a portion of the cavity, wherein the thermally expandable polyolefin composition comprises

a) from 35 to 99.5%, based on the weight of the composition, of (1) a crosslinkable ethylene hompolymer, (2) a crosslinkable interpolymer of ethylene and at least one C_{3-20} α-olefin or non-conjugated diene or triene comonomer, (3) a crosslinkable ethylene homopolymer or interpolymer of ethylene and at least one

C_{3-20} α-olefin containing hydrolyzable silane groups or (4) a mixture of two or more of the foregoing, the homopolymer,.interpolymer or mixture having a melt index of from 0.05 to 500 g/10 minutes when measured according to ASTM D 1238 under conditions of 190°C/2.16 kg load;

b) from 0 to 7% by weight, based on the weight of the composition, of a heat activated crosslinker for component a), said crosslinker being activated when heated to a temperature of at least 120°C but not more than 300°C;

c) from 1 to 25%, based on the weight of the composition, of a heat-activated expanding agent that is activated when heated to a temperature of at least 120°C but not more that 300°;

d) from 0 to 20%, based on the weight of the composition, of an accelerator for the expanding agent;

e) from 0 to 25%, based on the weight of the composition, of a copolymer of ethylene and at least one oxygen-containing comonomer; and

f) from 0 to 20%, based on the weight of the composition, of at least one antioxidant.

In another aspect, this invention is a thermally expandable polyolefin composition which is in the form of a solid at 22°C, comprising

a) from 35 to 80.75%, based on the weight of the composition, of a LDPE resin having a melt index of from 0.1 to 50 g/10 minutes when measured according to ASTM D 1238 under conditions of 190°C/2.16 kg load,

b) from 8 to 25%, based on the weight of the composition, of azodicarbonamide;

c) from 0.2 to 5% by weight, based on the weight of the composition, of an organic peroxide that decomposes at a temperature of from 120° to 300°C;

d) from 8 to 20%, based on the weight of the composition, by weight of zinc oxide or a mixture of zinc oxide and at least one zinc carboxylate;

e) from 2 to 7%, based on the weight of the composition, of a copolymer of ethylene and at least one oxygen-containing comonomer; and

f) from 0.25 to 3 parts, based on the weight of the composition, of at least one antioxidant.

The thermally expandable composition of the invention offers several advantages. It is typically capable of achieving high degrees of expansion under use conditions. Expansions of greater than 1000%, greater than 1500%, greater than 1800% and even greater than 2500% of the initial volume of the composition are often seen across a range of baking temperatures from 150 to over 200°C. In many cases, the thermally expandable composition is self-supporting during the expansion process. This can eliminate the need to attach the composition to a support to keep the composition from flowing to the bottom of the cavity during the expansion process. In addition, the expanded composition tends to be highly dimensionally stable when exposed repeatedly to high temperatures, as are often encountered in automotive assembly operations.

This invention is also a method comprising applying the thermally expandable polyolefin composition of the invention to a substrate and performing a heat-expansion step by heating the thermally expandable polyolefin composition to a temperature sufficient to expand the thermally expandable polyolefin composition while in contact with the substrate, such that the thermally expandable polyolefin composition expands freely to form a foam that is adhered to the substrate.

Figure 1 is a graph showing insertion loss exhibited by an embodiment of the invention over a range of sound frequencies.

Figure 2 is a graph showing insertion loss exhibited by an embodiment of the invention over a range of sound frequencies.

The composition of the invention contains as a main ingredient an ethylene homopolymer or certain ethylene interpolymers. The homopolymer or interpolymer is preferably not elastomeric, meaning for purposes of this invention that the homopolymer or interpolymer exhibits an elastic recovery of less than 40 percent when stretched to twice its original length at 20°C according to the procedures of ASTM 4649.

The ethylene polymer (component a)) has a melt index (ASTM D 1238 under conditions of 190°C/2.16 kg load) of 0.05 to 500 g/10 minutes. The melt index is preferably from 0.05 to 50 g/10 minutes, as higher melt index polymers tend to flow more, have lower melt strength and may not crosslink rapidly enough during the heat expansion step. A more preferred polymer has a melt index of 0.1 to 10 g/10 minutes, and an especially preferred polymer has a melt index of 0.3 to 5 g/10 minutes.

The ethylene polymer (component a)) preferably exhibits a melting temperature of at least 105°C, and more preferably at least 110°C.

A suitable type of interpolymer is one of ethylene and at least one C_{3-20} α-olefin. Another suitable type of interpolymer is one of ethylene and at least one non-conjugated diene or triene monomer. The interpolymer may be one of ethylene, at least one C_{3-20} α-olefin and at least one non-conjugated diene monomer. The interpolymer is preferably a random interpolymer, where the comonomer is distributed randomly within the interpolymer chains. Any of the foregoing homopolymers and copolymers may be modified to contain hydrolyzable silane groups. The homopolymers and interpolymers suitably contain less than 2 mole percent of repeating units formed by polymerizing an oxygen-containing monomer (other than a silane-containing monomer). The homopolymers and interpolymers suitably contain less than 1 mole percent of such repeating units and more preferably less than 0.25 mole percent of such repeating units. They are most preferably devoid of such repeating units.

Examples of such polymers include low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). Also useful are so-called "homogeneous" ethylene/α-olefin interpolymers that contain short-chain branching but essentially no long-chain branching (less than 0.01 long chain branch/1000 carbon atoms). In addition, substantially linear ethylene α-olefin interpolymers that contain both long-chain and short-chain branching are useful, as are substantially linear, long-chain branched ethylene homopolymers. "Long-chain branching" refers to branches that have a chain length longer than the short chain branches that result from the incorporation of the α-olefin or non-conjugated diene monomer into the interpolymer. Long chain branches are preferably greater than 10, more preferably greater than 20, carbon atoms in length. Long chain branches have, on average, the same comomoner distribution as the main polymer chain and can be as long as the main polymer chain to which it is attached. Short-chain branches refer to branches that result from the incorporation of the α-olefin or non-conjugated diene monomer into the interpolymer.

LDPE is a long-chain branched ethylene homopolymer that is prepared in a high-pressure polymerization process using a free radical initiator. LDPE preferably has a density of less than or equal to 0.935 g/cc (all resin densities are determined for purposes of this invention according to ASTM D792). It preferably has a density of from 0.905 to 0.930 g/cc and especially from 0.915 to 0.925 g/cc. LDPE is a preferred ethylene polymer due to its excellent processing characteristics and low cost. Suitable LDPE polymers include those described in U. S. Provisional Patent Application 60/624,434 and WO 2005/035566.

HDPE is a linear ethylene homopolymer or ethylene-α-olefin interpolymer that consists mainly of long linear polyethylene chains. HDPE typically contains less than 0.01 long chain branch/1000 carbon atoms. It suitably has a density of at least 0.94 g/cc. HDPE is suitably prepared in a low-pressure polymerization process using Zeigler polymerization catalysts, as described, for example, in U. S. Patent No. 4,076,698.

LLDPE is a short-chain branched ethylene-α-olefin interpolymer having a density of less than 0.940. It is usually prepared in a low pressure polymerization process using Zeigler catalysts in a manner similar to HDPE, but can be prepared using metallocene catalysts. The short-chain branches are formed when the α-olefin comonomers become incorporated into the polymer chain. LLDPE typically contains less than 0.01 long chain branch/1000 carbon atoms. The density of the LLDPE is preferably from about 0.905 to about 0.935 and especially from about 0.910 to 0.925. The α-olefin comonomer suitably contains from 3 to 20 carbon atoms, preferably from 3 to 12 carbon atoms. Propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 4-methyl-1-hexene, 5-methyl-1-hexene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene and vinylcyclohexane are suitable α-olefin comonomers. Those having from 4 to 8 carbon atoms are especially preferred.

"Homogeneous" ethylene/α-olefin interpolymers are conveniently made as described in U. S. Patent No. 3,645,992, or by using so-called single site catalysts as described in U. S. Patent Nos. 5,026,798 and 5,055,438. The comonomer is randomly distributed within a given interpolymer molecule, and the interpolymer molecules each tend to have similar ethylene/comonomer ratios. These interpolymers suitably have a density of less than 0.940, preferably from 0.905 to 0.930 and especially from 0.915 to 0.925. Comonomers are as described above with respect to LLDPE.

Substantially linear ethylene homopolymers and copolymers include those made as described in U. S. Patent Nos. 5,272,236 and 5,278,272. These polymers suitably have a density of less than or equal to 0.97 g/cc, preferably from 0.905 to 0.930 g/cc and especially from 0.915 to 0.925. The substantially linear homopolymers and copolymers suitably have an average of 0.01 to 3 long chain branch/1000 carbon atoms, and preferably from 0.05 to 1 long chain branch/1000 carbon atoms. These substantially linear polymers tend to be easily processible, similar to LDPE, and are also preferred types on this basis. Among these, the ethylene/α-olefin interpolymers are more preferred. Comonomers are as described above with respect to LLDPE.

In addition to the foregoing, interpolymers of ethylene and at least one nonconjugated diene or triene monomer can be used. These interpolymers can also contain repeating units derived from an α-olefin as described before. Suitable nonconjugated diene or triene monomers include, for example, 7-methyl-1,6-octadiene, 3,7-dimethyl-1,6-octadiene, 5,7-dimethyl-1,6-octadiene, 3,7,11-trimethyl-1,6,10-octatriene, 6-methyl-1,5-heptadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, bicyclo[2.2.1]hepta-2,5-diene (norbornadiene), tetracyclododecene, 1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene and 5-ethylidene-2-norborene.

The ethylene homopolymer or interpolymer, of any of the foregoing types, can contain hydrolyzable silane groups. These groups can be incorporated into the polymer by grafting or copolymerizing with a silane compound having at least one ethylenically unsaturated hydrocarbyl group attached to the silicon atom and at least one hydrolyzable group attached to the silicon atom. Methods of incorporating such groups are described, for example, in U. S. Patent No. 5,266,627 and 6,005,055 and WO 02/12354 and WO 02/12355. Examples of ethylenically unsaturated hydrocarbyl groups include vinyl, allyl, isopropenyl, butenyl, cyclohexenyl and γ-(meth)acryloxy allyl groups. Hydrolyzable groups include methoxy, ethoxy, formyloxy, acetoxy, propionyloxy, and alkyl- or arylamino groups. Vinyltrialkoxysilanes such as vinyltriethyoxysilane and vinyltrimethyoxysilane are preferred silane compounds; the modified ethylene polymers in such cases contain triethoxysilane and trimethoxysilane groups, respectively.

Ethylene homopolymers or interpolymers having long-chain branching are generally preferred, as these resins tend to have good melt strength and/or extensional viscosities which help them form stable foams. Mixtures of long-chain branched and short-chain branched or linear ethylene polymers are also useful, as the long-chain branched material in many cases can provide good melt strength and/or high extensional viscosity to the mixture. Thus, mixtures of LDPE with LLDPE or HDPE can be used, as can mixtures of substantially linear ethylene homopolymers and interpolymers with LLDPE or HDPE. Mixtures of LDPE with a substantially linear ethylene homopolymer or interpolymer (especially interpolymer) can also be used.

The ethylene homopolymer or copolymer constitutes from 40 to 99% of the weight of the composition. It preferably constitutes up to 80 and more preferably up to 70% of the weight of the composition. Preferred compositions of the invention contain from 45 to 80% by weight of the ethylene polymer or copolymer, or from 45 to 70% thereof. Especially preferred compositions contain from 50 to 65% by weight of the ethylene polymer or copolymer.

Mixtures of two or more of the foregoing ethylene homopolymers or copolymers can be used. In such a case, the mixture will have a melt index as described above.

The crosslinker is a material that, either by itself or through some degradation or decomposition product, forms bonds between molecules the ethylene homopolymer or interpolymer (component (a)). The crosslinker is heat-activated, meaning that below a temperature of 120°C, the crosslinker reacts very slowly or not at all with the ethylene polymer or interpolymer, such that a composition is formed which is storage stable at approximately room temperature (~22°C).

There are several possible mechanisms through which the heat-activation properties of the crosslinker can be achieved. A preferred type of crosslinker is relatively stable at lower temperatures, but decomposes at temperatures within the aforementioned ranges to generate reactive species which form the crosslinks. Examples of such crosslinkers are various organic peroxy compounds as described below. Alternatively, the crosslinker may be a solid and therefore relatively unreactive at lower temperatures, but melts at a temperature from 120 to 300°C to form an active crosslinking agent. Similarly, the crosslinker may be encapsulated in a substance that melts, degrades or ruptures within the aforementioned temperature ranges. The crosslinker may be blocked with a labile blocking agent that deblocks within those temperature ranges. The crosslinker may also require the presence of a catalyst or free-radical initiator to complete the crosslinking reaction. In such a case, heat activation may be accomplished by including in the composition a catalyst or free radical initiator that becomes active within the aforementioned temperature ranges.

Although optional in the broadest aspects of the invention, it is highly preferred to employ a crosslinker in the composition of the invention, especially when the melt index of component a) is 1 or greater. The amount of crosslinking agent that is used varies somewhat on the particular crosslinking agent that is used. In most cases, the crosslinking agent is suitably used in an amount from 0.5 to 7%, based on the weight of the entire composition, but some crosslinkers can be used in greater or lesser amounts. It is generally desirable to use enough of the crosslinking agent (together with suitable processing conditions) to produce an expanded, crosslinked composition having a gel content of at least 10% by weight and especially about 20% by weight. Gel content is measured for purposes of this invention in accordance with ASTM D-2765-84, Method A. .

A wide range of crosslinkers can be used with the invention, including peroxides, peroxyesters, peroxycarbonates, poly(sulfonyl azides), phenols, azides, aldehyde-amine reaction products, substituted ureas, substituted guanidines, substituted xanthates, substituted dithiocarbamates, sulfur-containing compounds such as thiazoles, imidazoles, sulfenamides, thiuramidisulfides, paraquinonedioxime, dibenzoparaquinonedioxime, sulfur and the like. Suitable crosslinkers of those types are described in U. S. Patent No. 5,869,591.

A preferred type of crosslinker is an organic peroxy compound, such as an organic peroxide, organic peroxyester or organic peroxycarbonate. Organic peroxy compounds can be characterized by their nominal 10-minute half-life decomposition temperatures. The nominal 10-minute half-life decomposition temperature is that temperature at which one half of the organic peroxy compound decomposes in 10 minutes under standard test conditions. Thus, if an organic peroxy compound has a nominal 10-minute half-life temperature of 110°C, 50% of the organic peroxy compound will decompose when exposed to that temperature for 10 minutes. Preferred organic peroxy compounds have nominal 10-minute half-lives in the range of 120 to 300°C, especially from 140 to 210°C, under the standard conditions. It is noted that the actual rate of decomposition of an organic peroxy compound may be somewhat higher or lower than the nominal rate, when it is formulated into the composition of the invention. Examples of suitable organic peroxy compounds include t-butyl peroxyisopropylcarbonate, t-butyl peroxylaurate, 2,5-dimethyl-2,5-di(benzoyloxy)hexane, t-butyl peroxyacetate, di-t-butyl diperoxyphthalate, t-butyl peroxymaleic acid, cyclohexanone peroxide, t-butyl diperoxybenzoate, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, t-butylcumyl peroxide, t-butyl hydroperoxide, di-t-butyl peroxide, 1,3-di(t-butylperoxyisopropyl) benzene, 2,5-dimethyl-2,5-di-t-butylperoxy)-hexyne-3, di-isopropylbenzene hydroperoxide, p-methane hydroperoxide and 2,5-dimethylhexane-2,5-dihydroperoxide. A preferred expanding agent is dicumyl peroxide. A preferred quantity of organic peroxy crosslinkers is from 0.5 to 5 percent of the weight of the composition.

Suitable poly(sulfonyl azide) crosslinkers are compounds having at least two sulfonyl azide ($-SO_2N_3$) groups per molecule. Such poly(sulfonyl azide) crosslinkers are described, for example, in WO 02/068530. Examples of suitable poly(sulfonyl azide) crosslinkers include 1,5-pentane bis(sulfonyl azide), 1,8-octane bis(sulfonyl azide),. 1,10-decane bis(sulfonyl azide), 1,18-octadecane bis(sulfonyl azide), 1-octyl-2,4,6-benzene tris(sulfonyl azide), 4,4'-diphenyl ether bis(sulfonyl azide), 1,6-bis (4'-sulfonazidophenyl)hexane, 2,7-naphthalene bis(sulfonyl azide), oxy-bis(4-sulfonylazido benzene), 4,4'-bis(sulfonyl azido)biphenyl, bis(4-sulfonylazidophenyl)methane and mixed sulfonyl azides of chlorinated aliphatic hydrocarbons that contain an average of from 1 to 8 chlorine atoms and from 2 to 5 sulfonyl azide groups per molecule.

When the ethylene polymer contains hydrolyzable silane groups, water is a suitable crosslinking agent. The water may diffuse in from a humid enviroment, such that ppm quantities are sufficient to complete the crosslinking reactions. Water also may be added to the composition. In this case, water suitably is used in an amount of from about 0.1 to 1.5 parts based on the weight of the composition. Higher levels of water will also serve to expand the polymer. Typically, a catalyst is used in conjunction with water in order to promote the curing reaction. Examples of such catalysts are organic bases, carboxylic acids, and organometallic compounds such as organic titanates and complexes or carboxylates of lead, cobalt, iron, nickel, tin or zinc. Specific examples of such catalysts are dibutyltin dilaurate, dioctyltinmaleate, dibutyltindiacetate, dibutyltindioctoate, stannous acetate, stannous octoate, lead naphthenate, zinc caprylate and cobalt naphthenate. Polysubstituted aromatic sulfonic acids as described in WO 2006/017391 are also useful. In order to prevent premature crosslinking, the water or catalyst, or both, may be encapsulated in a shell that releases the material only within the temperature ranges described before.

Another type of crosslinker is a polyfunctional monomer compound that has at least two, preferably at least three, reactive vinyl or allyl groups per molecule. These materials are commonly known as "co-agents" because they are used mainly in combination with another type of crosslinker (mainly a peroxy compounds) to provide some early-stage branching. Examples of such co-agents include triallyl cyanurate, triallyl isocyanurate and triallylmellitate.

Triallylsilane compounds are also useful. Another suitable class of co-agents are polynitroxyl compounds, particularly compounds having at least two 2,2,6,6-tetramethyl piperidinyloxy (TEMPO) groups or derivatives of such groups. Examples of such polynitroxyl compounds are bis(1-oxyl-2,2,6,6-tetramethylpiperadine-4-yl)sebacate, di-t-butyl N oxyl, dimethyl diphenylpyrrolidine-1-oxyl, 4-phosphonoxy TEMPO or a metal complex with TEMPO. Other suitable co-agents include α-methyl styrene, 1,1-diphenyl ethylene as well as those described in U. S. Patent No. 5,346,961. The co-agent preferably has a molecular weight below 1000.

The co-agent generally requires the presence of free radicals to engage in crosslinking reactions with the ethylene polymer or copolymer. For that reason, a free radical generating agent is generally used with a co-agent. The peroxy crosslinkers described before are all free radical generators, and if such crosslinkers are present, it is not usually necessary to provide an additional free radical initiator in the composition. Co-agents of this type are typically used in conjunction with such a peroxy crosslinker, as the co-agent can boost crosslinking. A co-agent is suitably used in very small quantities, such as from about 0.05 to 1% by weight of the composition, when a peroxy crosslinker is used. If no peroxy crosslinker is used, a co-agent is used in somewhat higher quantities.

Another type of suitable crosslinker is an epoxy- or anhydride-functional polyamide.

The expanding agent similarly is activated at the elevated temperatures described before, and, similar to before, the expanding agent can be activated at such elevated temperatures via a variety of mechanisms. Suitable types of expanding agents include compounds that react or decompose at the elevated temperature to form a gas; gasses or volatile liquids that are encapsulated in a material that melts, degrades, ruptures or expands at the elevated temperatures, expandable microspheres, substances with boiling temperatures ranging from 120°C to 300°C, and the like. The expanding agent is preferably a solid material at 22°C, and preferably is a solid material at temperatures below 50°C.

Expanding agents can also be classified as exothermic (releasing heat as they generate a gas) and endothermic (absorbing heat as they release a gas). Exothermic types are preferred.

A preferred type of expanding agent is one that decomposes at elevated temperatures to release nitrogen or, less desirably, ammonia gas. Among these are so-called "azo" expanding agents (which are exothermic types), as well as certain hydrazide, semi-carbazides and nitroso compounds (many of which are exothermic types). Examples of these include azobisisobutyronitrile, azodicarbonamide, p-toluenesulfonyl hydrazide, oxybissulfohydrazide, 5-phenyl tetrazol, benzoylsulfohydroazide, p-toluolsulfonylsemicarbazide, 4,4'-oxybis(benzensulfonyl hydrazide) and the like. These expanding agents are available commercially under trade names such as Celogen® and Tracel®. Commercially available expanding agents that are useful herein include Celogen® 754A, 765A, 780, AZ, AZ-130, AZ1901, AZ760A, AZ5100, AZ9370, AZRV, all of which are azodicarbonamide types. Celogen®OT and TSH-C are useful sulfonylhydrazide types. Azodicarbonamide expanding agents are especially preferred.

Blends of two or more of the foregoing blowing agents may be used. Blends of exothermic and endothermic types are of particular interest.

Nitrogen- or ammonia releasing expanding agents as just described, the azo types in particular, may be used in conjunction with an accelerator compound. The accelerator compound is especially preferred when the composition of the invention is to be expanded at temperatures below about 175°C, and especially below 160°C. Typical accelerator compounds include zinc benzosulphonate, and various transition metal compounds such as transition metal oxides and carboxylates. Zinc, tin and titanium compounds are preferred, such as zinc oxide; zinc carboxylates, particularly zinc salts of fatty acids such as zinc stearate; titanium dioxide; and the like. Zinc oxide and mixtures of zinc oxide and zinc fatty acid salts are preferred types. A useful zinc oxide/zinc stearate blend is commerically available as Zinstabe 2426 from Hoarsehead Corp, Monaca, PA.

The accelerator compound tends to reduce the peak decomposition temperature of the expanding agent to a predetermined range. Thus, for example, azodicarbonamide by itself tends to decompose at over 200°C, but in the presence of the accelerator compound its decomposition temperature can be reduced to 140-150°C or even lower. The accelerator compound may constitute from 0 to 20% or from 4 to 20% of the weight of the composition. Preferred amounts, when the composition is to be expanded at a temperature of below 175°C and preferably below 160°C, are from 6 to 18%. The accelerator may be added to the composition separately from the expanding agent. However, some commercial grades of expanding agent are sold as "preactivated" materials, and already contain some quantity of the accelerator compound. Those "preactivated" materials are also useful.

Another suitable type of expanding agent decomposes at elevated temperatures to release carbon dioxide. Among this type are sodium hydrogen carbonate, sodium carbonate, ammonium hydrogen carbonate and ammonium carbonate, as well as mixtures of one or more of these with citric acid. These are usually endothermic types which are less preferred unless used in conjunction with an exothermic type.

Still another suitable type of expanding agent is encapsulated within a polymeric shell. These are endothermic types of expanding agents and preferably are used in conjunction with an exothermic type. The shell melts, decomposes, ruptures or simply expands at temperatures within the aformentioned ranges. The shell material may be fabricated from polyolefins such as polyethylene or polypropylene, vinyl resins, ethylene vinyl acetate, nylon, acrylic and acrylate polymers and copolymers, and the like. The expanding agent may be a liquid or gaseous (at STP) type, including for example, hydrocarbons such as n-butane, n-pentane, isobutane or isopentane; a fluorocarbon such as R-134A and R152A; or a chemical expanding agent which releases nitrogen or carbon dioxide, as are described before. Encapsulated expanding agents of these types are commercially available as Expancel® 091WUF, 091WU, 009DU, 091DU, 092DU, 093DU and 950DU.

Compounds that boil at a temperature of from 120 to 300°C may also be used as the expanding agent. These compounds include C_{8-12} alkanes as well as other hydrocarbons, hydrofluorocarbons and fluorocarbons that boil within these ranges.

The composition may further contain a copolymer of ethylene with one or more oxygen-containing comonomers (which are not silanes). The comonomer is ethylenically polymerizable and capable of forming a copolymer with ethylene. Examples of such comononers include acrylic and methacrylic acids, alkyl and hydroxyalkyl esters of acrylic or methacrylic acid, vinyl acetate, glycidyl acrylate or methacrylate, vinyl alcohol, and the like. The copolymer can constitute from 0 to 25% of the weight of the composition, and preferably constitutes from 2 to 7% by weight thereof. The copolymer can improve the adhesion of the expanded composition to a variety of substrates. Specific examples of such copolymers include ethylene-vinyl acetate copolymers, ethylene-alkyl (meth)acrylate copolymer such as ethylene-methyl acrylate or ethylene butyl acrylate copolymers; ethylene-glycidyl (meth)acrylate copolymers, ethylene-glycidyl (meth)acrylate-alkyl acrylate terpolymers, ethylene-vinyl alcohol copolymers, ethylene hydroxyalkyl(meth)acrylate copolymers, ethylene-acrylic acid copolymers, and the like.

The composition of the invention may also contain one or more antioxidants. Antioxidants can help prevent charring or discoloration that can be caused by the temperatures used to expand and crosslink the composition. This has been found to be particularly important when the expansion temperature is about 170°C or greater, especially 190°C to 220°C. The presence of antioxidants, at least in certain quantities, does not significantly interfere with the crosslinking reactions. This is surprising, particularly in the preferred cases in which a peroxy expanding agent is used, as these are strong oxidants, the activity of which would be expected to be suppressed in the presence of antioxidants.

Suitable antioxidants include phenolic types, organic phosphites, phosphines and phosphonites, hindered amines, organic amines, organo sulfur compounds, lactones and hydroxylamine compounds. Examples of suitable phenolic types include tetrakis methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate) methane, octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate, 1,3,5-tris (3,5-di-t-butyl-4-hydroxybenzyl)-s-triazine-2,4,6-(1H, 3H, 5H) trione, 1,1,3-tris(2'-methyl-4'-hydroxy-5'-t-butylphenyl)butane, octadecyl -3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate, 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene propionic acid C13-15 alkyl esters, N,N-hexamethylene bis(3,5-di-t-butyl-4-hydroxyphenyl)propionamide, 2,6-di-t-butyl-4-methylphenol, bis [3,3-bis-(4'-hydroxy-3'-t-butylphenyl)butanoic acid] glycol ester (Hostanox O3 from Clariant) and the like. Tetrakis methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate) methane is a preferred phenolic antioxidant. Phenolic type antioxidants are preferably used in amount from 0.1 to 1.0% by weight of the composition.

Suitable phosphite stabilizers include bis (2,4-dicumylphenyl) pentaerythritol diphosphite, tris (2,4-di-tert-butylphenyl) phosphite, distearyl pentaerythritol diphosphite, bis-(2,4-di-t-butylphenyl)-pentaerythritol diphosphite and bis-(2,4-di-t-butyl-phenyl)-pentaerythritol-diphosphite. Liquid phosphite stabilizers include trisnonylphenol phosphite, triphenyl phosphite, diphenyl phosphite, phenyl diisodecyl phosphite, diphenyl isodecyl phosphite, diphenyl isooctyl phosphite, tetraphenyl dipropyleneglycol diphosphite, poly(dipropyleneglycol) phenyl phosphite, alkyl (C10-C15) bisphenol A phosphite, triisodecyl phosphite, tris (tridecyl) phosphite, trilauryl phosphite, tris (dipropylene glycol) phosphite and dioleyl hydrogen phosphite.

A preferred quantity of the phosphite stabilizer is from 0.1 to 1% of the weight of the composition.

A suitable organophosphine stabilizer is 1,3 bis-(diphenylphospino)-2,2-dimethylpropane. A suitable organophosphonite is tetrakis(2,4-di-t-butylphenyl-4,4'-biphenylene diphosphonite (Santostab P-EPQ from Clariant).

A suitable organosulfur compound is thiodiethylene bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)proprionate].

Preferred amine antioxidants include octylated diphenylamine, the polymer of 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-dispiro[5.1.11.2]-heneicosan-21-on (CAS No 64338-16-5, Hostavin N30 from Clariant), 1,6-hexaneamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-, polymers with morpholine-2,4,6-trichloro-1,3,5-triazine reaction products, methylated (CAS number 193098-40-7, commercial name Cyasorb 3529 from Cytec Industries), poly-[[6-(1,1,3,3-tetramethylbutyl)amino]-s-triazine-2,4-diyl][2,2,6,6-tetramethyl-4-piperidyl)imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino]](CAS No 070624-18-9 (Chimassorb 944 from Ciba Specialty Chemicals), 1,3,5-triazine-2,4,6-triamine-N,N'''-[1,2-ethanediylbis[[[4,6-bis[butyl-(1,2,2,6,6-pentamethyl-4 piperidinyl)amino]-1,3,5-triazine-2yl]imino]-3,1-propanediyl]]-bis-[N',N''-dibutyl-N',N'-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-106990-43-6 (Chimassorb 119 from Ciba Specialty Chemicals), and the like. The most preferred amine is 1,3,5-triazine-2,4,6-triamine-N,N'''-[1,2-ethanediylbis[[[4,6-bis[butyl-(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazine-2yl]imino]-3,1-propanediyl]]-bis-[N',N''-dibutyl-N',N'-bis(1,2,2,6,6-pentamethyl-4-piperidinyl. The composition of the invention preferably contains from 0.1 to 1.0% by weight of an amine antioxidant.

A suitable hydroxylamine is hydroxyl bis(hydrogenated tallow alkyl)amine, available as Fiberstab 042 from Ciba Specialty Chemicals.

A preferred antioxidant is a mixture of a hindered phenol and hindered amine and a more preferred antioxidant system is a mixture of hindered phenol, amine stabilizer, and a phosphite. This mixture is most preferably used in an amount from 0.25 to 2.0 weight percent of the composition.

In addition to the foregoing components, the composition may contain optional ingredients such as fillers, colorants, dies, preservatives, surfactants, cell openers, cell stabilizers, fungicides and the like. In particular, the composition may contain one or more polar derivatives of 2,2,6,6-tetramethyl piperidinyloxy (TEMPO) such a 4-hydroxy TEMPO, no only to retard scorch and/or boost crosslinking, but also to enhance adhesion to polar substrates. Some additional components may improve adhesion to various substrates during the expansion process. Examples of these include fillers that absorb oily materials. Bentonite clays are such a material, as are talc, calcium carbonate and wollastonite. In addition, various hydrolysable silanes or functional silane compounds can be used to improve adhesion. These should be thermally stable at the temperature of the expansion step. Tris(3-(trimethyoxysilyl)isocyanurate) and ß-(3,4-epoxycyclohexyl) ethyltriethoxysilane are examples of useful silane compounds.

The polyolefin composition is prepared by mixing the various components, taking care to maintain temperatures low enough that the expanding and crosslinking agents are not significantly activated. The mixing of the various components may be done all at once, or in various stages.

A preferred mixing method is a melt-processing method, in which the ethylene polymer (component (a)) is heated above its softening temperature and blended with one or more other components, usually under shear. A variety of melt-blending apparatus can be used, but an extruder is a particularly suitable device, as it allows for precise metering of components, good temperature control, and permits the blended composition to be formed into a variety of useful cross-sectional shapes. Temperatures during such a mixing step are desirably controlled low enough that any heat-activated materials as may be present (i.e, the expanding agent(s), crosslinkers, catalysts therefore and the like), do not become significantly activated. However, it is possible to exceed such temperatures if the residence time of the heat-activated materials at such temperatures is short. A small amount of activation of these materials can be tolerated. For example, a small amount of activation of a crosslinking agent can be tolerated, provided that the formation of gels during the mixing step is minimal. When the ethylene polymer (component (a)) is not long-chain branched, a certain amount of crosslinking during this step may be beneficial, as it may improve the melt rheology of the ethylene polymer. The gel content produced during the mixing step should be less than 10% by weight and is preferably less than 2% by weight of the composition. Greater gel formation causes the composition to become non-uniform, and to expand poorly during the expansion step. Similarly, some activation of the expanding agent can be tolerated, provided that enough unreacted expanding agent remains after the mixing step so that the composition can expand by at least 100%, preferably at least 500% and especially at least 1000% during the expansion step. If expanding agent loss is expected during this process, extra quantities may be provided to compensate for this loss.

The crosslinking and/or blowing agents may also be added during the mixing step, or may be soaked into the polymer (preferably when the polymer is in the form of pellets, powder or other high surface area form) prior to melt-mixing and fabrication of part.

It is of course possible to use somewhat higher temperatures to melt blend those components which are not heat-activated. Accordingly, the composition can be formed by performing a first melt-blend step at a higher temperature, cooling somewhat, and then adding the heat-activated component(s) at the lower temperatures. It is possible to use an extruder with multiple heating zones to first melt-blend components that can tolerate a higher temperature, and then cool the mixture somewhat to blend in the heat-activated materials.

It is also possible to form one or more concentrates or masterbatches of various components in the component a) and/or component e) material, and let the concentrate or masterbatch down to the desired concentrations by melt blending with more of the component a) or component e) material. Solid ingredients may be dry-blended together before the melt-blending step.

A useful method of producing the composition is an extrusion process using an apparatus which has multiple heating zones that can be heated (or cooled) independently to different temperatures. The apparatus also has at least two ports for introducing raw materials, one being downstream of the other, so that heat-activated materials can be introduced separately from the polyolefin polymer. In this method, the polyolefin is introduced into the apparatus and melted in one or more of the heating zones. Melt temperatures in these heating zones can be significantly higher than the activation temperatures of the blowing and crosslinking agents, if desired. Additives which are not heat-activated, such as the blowing agent accelerator, optional copolymer and antioxidant, can be added at this stage, if desired, either simultaneously with or separately from the polyolefin resin. The resulting molten polymer is then transferred to subsequent heating zones, which are maintained within a temperature range of 100 to 150°C, preferably 115 to 135°C, and the heat-activated components (blowing agent and crosslinker) are fed in. Cooling is generally needed because the polyolefin is typically heated to higher temperatures in the upsteam sections of the device in order to facilitate thorough melting, and because shear introduced by the mixing apparatus (typically the screw or screws of an extruder), introduces significant energy which tends to heat the composition. Cooling can be applied in many ways. A convenient cooling method is to supply a cooling fluid (such as water) to a jacket on the mixing apparatus. The addition of the heat-activated components also tends to have a certain amount of cooling effect. The mixing apparatus provides sufficient residence time downstream of the addition of the heat-activated materials that they are uniformly mixed into the composition, but this residence time is preferably minimized so that little activation of those materials occurs. The mixed composition is then brought to an extrusion temperature, which is preferably below 155°C and more preferably from 120 to 150°C, and passed through a die.

A melt-blended composition of the invention is then cooled below the softening temperature of the component a) material to form a solid, non-tacky product. The composition can be formed into a shape that is suitable for the particular reinforcing or insulation application. This is most conveniently done at the end of the melt-blending operation. As before, an extrusion process is particularly suitable for shaping the composition, in cases where pieces of uniform cross-section are acceptable. In many cases, the cross-sectional shape of the pieces is not critical to its operation, provided that they are small enough to fit within the cavity to be reinforced or insulated. Therefore, for many specific applications, an extrudate of uniform cross-section can be formed and simply cut into shorter lengths as needed to provide the quantity of material needed for the particular application.

Alternatively, the melt-blended composition can be extruded and cut into pellets, or otherwise formed into small particles which can be poured or placed into a cavity and expanded. Particles may also be packaged into a mesh or film container for insertion into a cavity. In such a case, the package must allow the particles to expand and so must either stretch, melt, degrade or rupture during the expansion process. A thermoplastic packaging material may melt under the expansion conditions. In such a case, the melting packaging material may function as an adhesive layer which helps to improve the adhesion of the expanded composition to the surrounding cavity.

If necessary for a specific application, the composition may be molded into a specialized shape using any suitable melt-processing operation, including extrusion, injection molding, compression molding, cast molding, injection stretch molding, and the like. As before, temperatures are controlled during such process to prevent premature gelling and expansion.

Solution blending methods can be used to blend the various components of the composition. Solution blends offers the possibility of using low mixing temperatures, and in that way helps to prevent premature gellation or expansion. Solution blending methods are therefore of particular use when the crosslinker and/or expansion agent become activated at temperatures close to those needed to melt-process the ethylene polymer (component a)). A solution-blended composition may be formed into desired shapes using methods described before, or by various casting methods. It is usually desirable to remove the solvent before the composition is used in the expanding step, to reduce VOC emissions when the product is expanded, and to produce a non-tacky composition. This can be done using a variety of well-known solvent removal processes.

The composition of the invention is expanded by heating to a temperature in the range of 120 to 300°C, preferably from 140 to 230°C and especially from 140 to 210°C. The particular temperature used will in general be high enough to soften the ethylene polymer (component a)) and activate both the heat-activated expansion agent and heat-activated crosslinker. For this reason, the expansion temperature will generally be selected in conjunction with the choice of resins, expansion agent and crosslinker. It is also preferred to avoid temperatures that are significantly higher than required to expand the composition, in order to prevent thermal degradation of the resin or other components. Expansion and cross-linking typically occurs within 1 to 60 minutes, especially from 5 to 40 minutes and most preferably from 5 to 20 minutes.

The expansion step is performed under conditions such that the composition rises freely to at least 100%, preferably at least 1000% of its initial volume. It more preferably expands to at least 1800% of its initial volume, and even more preferably expands to at least 2000% of its initial volume. The composition of the invention may expand to 3500% or more of its initial volume. More typically, it expands to 1800 to 3000% of its initial volume. The density of the expanded material is generally from 1 to 10 pounds/cubic foot (16-160 kg/m^3) and preferably from 1.5 to 5 pounds/cubic foot (24-80 kg/m^3).

In this invention, a composition is said to "expand freely", if the composition is not maintained under superatmospheric pressure or other physical constraint in at least one direction as it is brought to a temperature sufficient to initiate crosslinking and activate the expanding agent. As a result, the composition can begin to expand in at least one direction as soon as the necessary temperature is achieved, and can expand to at least 100%, to at least 500% and to at least 1000%, to at least 1500%, to at least 1800% or to at least 2000% of its initial volume without constraint. Most preferably, the composition can fully expand without constraint. In the free expansion process, crosslinking therefore occurs simultaneously with expansion, as the composition is free to expand at the time that the crosslinking reaction is taking place. This free expansion process differs from processes such as extrusion foaming or bun foam processes, in which the heated composition is maintained under pressure sufficient to keep it from expanding until the resin has become crosslinked and the crosslinked resin passes through the die of the extruder or the pressure is released to initiate "explosive foaming". The timing of the crosslinking and expansion steps is much more critical in a free expansion process than in a process like extrusion, in which expansion can be delayed through application of pressure until enough crosslinking has been produced in the polymer. The ability to produce highly-expanded foam from ethylene homopolymers or interpolymers of ethylene with another α-olefin or a non-conjugated diene or triene monomer in a free expansion process is surprising.

The expanded polyolefin composition may be mainly open-celled, mainly closed-celled, or have any combination of open and closed cells. For many applications, low water absorption is a desired attribute of the expanded composition. It preferably absorbs no more than 30% of its weight in water when immersed in water for 4 hours at 22°C, when tested according to General Motors Protocol GM9640P,Water Absorption Test for Adhesives and Sealants (January 1992).

The expanded polyolefin composition exhibits excellent ability to attenuate sound having frequencies in the normal human hearing range. A suitable method for evaluating sound attenuation properties of an expanded polymer is through an insertion loss test. The test provides a reverberation room and a semiechoic room, separated by a wall with a 3" X 3" X 10" (7.5 X 7.5 X 25 mm) channel connecting the rooms. .A foam sample is cut to fill the channel and inserted into it. A white noise signal is introduced into the reverberation room. Microphones measure the sound pressure in the reverberation room and in the semiechoic room. The difference in sound pressure in the rooms is used to calculate insertion loss. Using this test method, the expanded composition typically provides an insertion loss of 20 dB throughout the entire frequency range of 100 to 10,000 Hz. This performance over a wide frequency range is quite unusual and compares very favorably with polyurethane and other types of foam baffle materials.

The expandable composition of the invention is useful in a wide variety of applications, such as wire and cable insulation, protective packaging, construction materials such as flooring systems, sound and vibration management systems, toys, sporting goods, appliances, a variety of automotive applications, lawn and garden products, personal protective wear, apparel, footwear, traffic cones, housewares, sheets, barrier membranes, tubing and hoses, profile extrusions, seals and gaskets, upholstery, luggage, tapes and the like.

Applications of particular interest are sealing and insulation (sound, vibration and/or thermal) applications, especially in the ground transportation (especially automotive) industry. The composition of the invention is readily deposited into a cavity that needs sealing and/or insulating, and expanded in place to partially or entirely fill the cavity. "Cavity" in this context means only some space that is to be filled with a reinforcing or insulating material. No particular shape is implied or intended. However, the cavity should be such that the composition can expand freely in at least one direction as described before. Preferably, the cavity is open to the atmosphere such that pressure does not build up significantly in the cavity as the expansion proceeds.

Examples of vehicular structures that are conveniently sealed or insulated using the invention include reinforcement tubes and channels, rocker panels, pillar cavities, rear tail lamp cavities, upper C-pillars, lower C-pillars, front load beams or other hollow parts. The structure may be composed of various materials, including metals (such as cold-rolled steel, galvanized surfaces, galvanel surfaces, galvalum, galfan and the like), ceramics, glass, thermoplastics, thermoset resins, painted surfaces and the like. Structures of particular interest are electrocoated either prior to or after the composition of the invention is introduced into the cavity. In such cases, the expansion of the composition can be conducted simultaneously with the bake cure of the electrocoating.

Compositions used for these automotive applications advantageously are expandable within the entire temperature range of 150 to 210°C, so that multiple formulations are not required for different commonly-used bake temperatures. Especially preferred compositions achieve expansion under such conditions to at least 1500% of their initial volume within 10 to 40 minutes, especially within 10 to 30 minutes.

The composition of the invention is less prone to running off during the heat expansion step. As a result, the composition tends not to run to the bottom of the cavity during the expansion step. Because of this, the composition is readily adaptable to applications where only a portion of a cavity needs reinforcement or insulating. In such cases, the unexpanded composition is applied only to that portion of the cavity where needed, and subsequently expanded in place. If necessary, the unexpanded composition may be affixed in a specific location within the cavity through a variety of supports, fasteners and the like, which can be, for exmaple, mechanical or magnetic. Examples of such fasteners include blades, pins, push-pins, clips, hooks and compression fit fasteners. The unexpanded composition can easily be extruded or otherwise shaped such that it can be readily affixed to such a support or fastener. It may be cast molded over such a support or fastener. The unexpanded composition may instead be shaped in such a way that it is self-retaining within a specific location within the cavity. For example, the unexpanded composition may be extruded or shaped with protrusions or hooks that permit it to be affixed to a specific location within a cavity.

The following examples are provided to illustrate the invention, but is not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

Example 1

69 parts of a 0.918, 2.3 MI LDPE (LDPE 621i, from Dow Chemical) are heated in a Haake Blend 600 for 5 minutes 115°C, with stirring at 30 rpm. 20 parts of azodicarbonamide (Celogen AZ-130, from Cromptom Industries) and 8 parts of zinc oxide are added and mixed in for 30 minutes with continued stirring at 30 rpm. 3 parts of a 40% solution of dicumyl peroxide (Perkadox® 40-BPd, from Akzo Nobel), are then added and mixed in as before. The mixture is then removed

and allowed to cool to room temperature. After cooling, a solid composition is obtained. Samples of the composition are compression molded in.window frame molds at 110°C for 10 minutes with no measurable applied pressure. The thickness of the moldings is 0.5 inches (12.5 mm).

A sample of the molded composition is cut into an equilateral triangle having sides 4 inches (10 mm) in length. The triangle is inserted into the bottom of a triangularly-shaped metal column. The walls of the column are coated with an electrocoating composition. The triangular cross-section of the column closely matches the dimensions of the cut piece of expandable polyolefin composition, such that all expansion of the composition will be upward. The column is then placed into a 160°C oven for 30 minutes to expand the polyolefin composition, and subsequently cooled to room temperature. The electrocoat composition also cures during the heating step.

Expansion is determined by measuring the height of the expanded composition and comparing the height to the thickness of the unexpanded triangle. The material expands freely during the curing step to about 2800% of its initial thickness.

The column containing the expanded material is tested for adhesion after environmental cycling. The enviromental cycling consists of 5 cycles as follows: 16 hours exposure to 79°C, 24 hours at 38°C and 100% relative humidity, and 3 hours at 29°C. The column is then deconstructed and the walls pulled away from the expanded composition. The foam exhibits cohesive failure, which is desired in this test

VOC is measured on the expanded foam according to EPA 24B/ASTM 2369. No VOCs are detected.

A sample of the expanded foam is immersed in water for 4 hours at ~22°C, according to General Motors Protocol GM9640P,Water Absorption Test for Adhesives and Sealants (January 1992) The sample gains absorbs 29% of its weight in water..

A sample of the expanded foam is tested in the insertion loss test described above. The results of the test are shown graphically in Figure 1. The foam provides an insertion loss in the range of 10-15 decibels over the frequency range of about 100 to 400 hertz, and an insertion loss of about 24-50 db over the frequency range of about 400 to 10,000 hertz.

Examples 2 and 3

Expandable polyolefin compositions are prepared from the following components:

Component	Parts by Weight	
	Example 2	Example 3
LDPE[1]	55.7	60.7
Dicumyl peroxide[2]	2.5	2.5
Azodicarbonamide[3]	20	20
Zinc oxide	15	8
Zinc oxide/zinc stearate mixture[4]	0	7
Ethylene/butyl acrylate/glycidyl methacrylate interpolymer[5]	5	0
Antioxidant mixture[6]	1.8	1.8

[1] 621i from Dow Chemical. [2] Perkadox BC-40BP from Akzo Nobel. [3] AZ130 from Crompton Industries. [4] Zinstabe 2426 from Hoarsehead Corp., Monaca, PA. [5] Elvaloy 4170, from DuPont. [6] A mixture of a hindered phenol, phosphite and hindered amine antioxidants.

Examples 2 and 3 are separately prepared by heating LDPE and ethylene/butyl acrylate/glycidyl methacrylate interpolymer (LDPE 621i, from Dow Chemical) in a Haake Blend 600 for 5 minutes 115°C, with stirring at 30 rpm. The azodicarbonamide, zinc oxide and zinc oxide/zinc stearate mixture are added and mixed in for 30 minutes with continued stirring at 30 rpm. The dicumyl peroxide and antioxidant mixture are then added and mixed in as before. The mixture is then removed and allowed to cool to room temperature.

Portions of expandable composition Examples 2 and 3 are cut into triangles as described in Example 1, and separately expanded in the triangular column described in Example 1. Duplicate expansions are done for each of Examples 2 and 3, once at 150°C and once at 205°C. At 150°C, both of Examples 2 and 3 expand to 3000-3100% of their initial volume. At 205°C, Example 2 expands to 2800% of its initial volume and Example 3 expands to 3000%. These results indicate that these compositions are suitable for use over a wide range of curing temperatures. This is significant in the automotive industry, where various electrocoat bake temperatures are used. The ability of these compositions to expand over a range of temperatures permits eliminates the need to specially formulate the compositions for different electrocoat bake temperatures..

Insertion loss is measured for Example 2 using the method described before. Results are shown graphically in Figure 2. Insertion loss exceeds 20 decibels at all frequences below about 300 hertz, and exceeds 30 decibels at frequences between 300 and 10,000 hertz.

Examples 4-8

Examples 4-8 are prepared in the same manner as Example 1, except the levels of zinc oxide and dicumyl peroxide are varied as follows:

Example No.	Wt-% Zinc Oxide	Wt-% Dicumyl Peroxide
4	12.5	3
5	15	3.5
6	10	3.5
7	10	2.5
8	10	3

Samples of each composition are compression molds as described in Example 1, and cut into 1.5" X 1" X 0.5" (37 X 25 X 12.5 mm) sections. Duplicate sections from each of Examples 2 and 4-8 are baked in aluminum pans at 150°C, 160°C and 205°C to determine the expansion that is obtained at each temperature. The time required for expansion to begin at 150°C is also determined. Results are as set forth in the following table.

Ex. No.	Wt-% ZnO	Wt-% Dicumyl Peroxide	Expansion Time (min) at 150°C	% Expansion		
				150°C	160°C	205°C
2	15	2.5	20	2900	2900	1700
4	12.5	3	21	2700	3100	1800
5	15	3.5	19	3000	2900	1500
6	10	3.5	26	2100	3100	1600
7	10	2.5	24	2300	3100	2400
8	10	3	25	3500	3600	2000

WHAT IS CLAIMED IS:

1. A method comprising

1) inserting a solid, thermally expandable polyolefin composition into a cavity,

2) heating the thermally expandable polyolefin composition in the cavity to a temperature sufficient to expand and crosslink the polyolefin composition and

3) permitting the polyolefin composition to expand freely to form a foam that fills at least a portion of the cavity, wherein the thermally expandable polyolefin composition comprises

a) from 35 to 99.5%, based on the weight of the composition, of (1) a crosslinkable ethylene hompolymer, (2) a crosslinkable interpolymer of ethylene and at least one C_{3-20} α-olefin or non-conjugated diene or triene comonomer, (3) a crosslinkable ethylene homopolymer or interpolymer of ethylene and at least one $C_{3-2}0$ α-olefin containing hydrolyzable silane groups or (4) a mixture of two or more of the foregoing, the hompolymer, interpolymer or mixture having a melt index of from 0.05 to 500 g/10 minutes when measured according to ASTM D 1238 under conditions of 190°C/2.16 kg load;

b) from 0 to 7% by weight, based on the weight of the composition, of a heat activated crosslinker for component a), said crosslinker being activated when heated to a temperature of at least 120°C but not more than 300°C;

c) from 1 to 25%, based on the weight of the composition, of a heat-activated expanding agent that is activated when heated to a temperature of at least 120°C but not more that 300°C;

d) from 0 to 20%, based on the weight of the composition, of an accelerator for the expanding agent;

e) from 0 to 25%, based on the weight of the composition, of a copolymer of ethylene and at least one oxygen-containing comonomer; and

f) from 0 to 20%, based on the weight of the composition, of at least one antioxidant.

2. The method of claim 1 wherein the heat expansion step is performed by heating the polyolefin composition to a temperature from 140 to 220°C. .

3. The method of claim 2 wherein in step 2) the composition expands to at least 1000% of its initial volume.

4. The method of claim 3 wherein the composition contains from 0.5 to 7% of component b).

5. The method of claim 4, wherein in step 2) the composition expands to at least 1500% of its initial volume.

6. The method of claim 4, wherein the expanding agent decomposes when activated to release nitrogen, carbon dioxide or ammonia gas.

7. The method of claim 6, wherein component a) is LDPE.

8. The method of claim 7, wherein the melt index of component a) is 0.05 to 50 g/10 minutes when measured according to ASTM D 1238 under conditions of 190°C/2.16 kg load.

9. The method of claim 8, wherein the melt index of component a) is 0.2 to 50 g/10 minutes when measured according to ASTM D 1238 under conditions of 190°C/2.16 kg load.

10. The composition of claim 8, wherein the crosslinking agent is a peroxide, peroxyester or peroxycarbonate compound.

11. The composition of claim 10, wherein the crosslinking agent is dicumyl peroxide.

12. The composition of claim 11 wherein the expanding agent is azodicarbonamide.

13. The composition of claim 12 wherein the accelerator is zinc oxide or a mixture of zinc oxide and at least one zinc carboxylate.

14. The composition of claim 13 which contains from 2 to 7%, based on the weight of the composition, of component e), and the oxygen-containing comonomer is an alkyl acrylate, an alkyl methacrylate, a hydroxyalkyl acrylate, a hydroxyalkyl methacrylate, vinyl acetate, a glycidyl acrylate, or a glycidyl methacrylate.

15. The composition of claim 14, further containing at least one antioxidant.

16. The method of any of claims 1-15, wherein the cavity is contained in a part, assembly or sub-assembly of an automotive vehicle.

17. The method of claim 16, wherein the part, assembly or sub-assembly is coated with a bake-curable coating, and the heat-expansion step is conducted as the bake-curable coating is cured.

18. The method of claim 17, wherein the part, assembly or sub-assembly includes a reinforcement tube, a reinforcement channel, a rocker panel, a pillar cavity or a front load beam.

19. A solid, non-tacky thermally expandable polyolefin composition comprising

a) from 40 to 99.5%, based on the weight of the composition, of (1) a crosslinkable ethylene hompolymer, (2) a crosslinkable interpolymer of ethylene and at least one C_{3-20} α-olefin or non-conjugated diene or triene comonomer, (3) a crosslinkable ethylene homopolymer or interpolymer of ethylene and at least one $C_{3-2}0$ α-olefin containing hydrolyzable silane groups or (4) a mixture of two or more of the foregoing, the hompolymer, interpolymer or mixture having a melt index of from 0.1 to 500 g/10 minutes when measured according to ASTM D 1238 under conditions of 190°C/2.16 kg load;

b) from 0 to 7% by weight, based on the weight of the composition, of a heat activated crosslinker for .component a), said crosslinker being activated when heated to a temperature of at least 120°C but not more than 300°C;

c) from 1 to 25%, based on the weight of the composition, of a heat-activated expanding agent that is activated when heated to a temperature of at least 120°C but not more that 300°;

d) from 0 to 20%, based on the weight of the composition, of an accelerator for the expanding agent;

e) from 0 to 10%, based on the weight of the composition, of a copolymer of ethylene and at least one oxygen-containing comonomer; and

f) from 0 to 20%, based on the weight of the composition, of at least one antioxidant.

20. A thermally expandable polyolefin composition which is in the form of a solid at 22°C, comprising

a) from 40 to 80.75%, based on the weight of the composition, of a LDPE resin having a melt index of from 0.1 to 50 g/10 minutes when measured according to ASTM D 1238 Condition E, 190°C, 2.16 kg load,

b) from 8 to 25%, based on the weight of the composition, of azodicarbonamide;

c) from 0.2 to 5% by weight, based on the weight of the composition, of an organic peroxide that decomposes at a temperature of from 120° to 300°C;

d) from 8 to 20%, based on the weight of the composition, by weight of zinc oxide or a mixture of zinc oxide and at least one zinc carboxylate;

e) from 2 to 7%, based on the weight of the composition, of a copolymer of ethylene and at least one oxygen-containing comonomer; and

f) from 0.25 to 3 parts, based on the weight of the composition, of at least one antioxidant.

21. A method comprising

1) inserting the solid, thermally expandable polyolefin composition of claim 20 into a cavity and

2) performing a heat-expansion step by heating the thermally expandable polyolefin composition in the cavity to a temperature sufficient to

expand the polyolefin composition to form a foam that fills at least a portion of the cavity.

22. The method of claim 21, wherein the cavity is contained in a part, assembly or sub-assembly of an automotive vehicle.

23. The method of claim 22, wherein the part, assembly or sub-assembly is coated with a bake-curable coating, and the heat-expansion step is conducted as the bake-curable coating is cured.

24. The method of claim 23, wherein the part, assembly or sub-assembly includes a reinforcement tube, a reinforcement channel, a rocker panel, a pillar cavity or a front load beam.

25. A method comprising applying the thermally expandable polyolefin composition of claim 19 to a substrate and performing a heat-expansion step by heating the thermally expandable polyolefin composition to a temperature sufficient to expand the thermally expandable polyolefin composition while in contact with the substrate, such that the thermally expandable polyolefin composition expands freely to form a foam that is adhered to the substrate.

26. A method comprising applying the thermally expandable polyolefin composition of claim 20 to a substrate and performing a heat-expansion step by heating the thermally expandable polyolefin composition to a temperature sufficient to expand the thermally expandable polyolefin composition while in contact with the substrate, such that the thermally expandable polyolefin composition expands freely to form a foam that is adhered to the substrate.

FIGURE 1

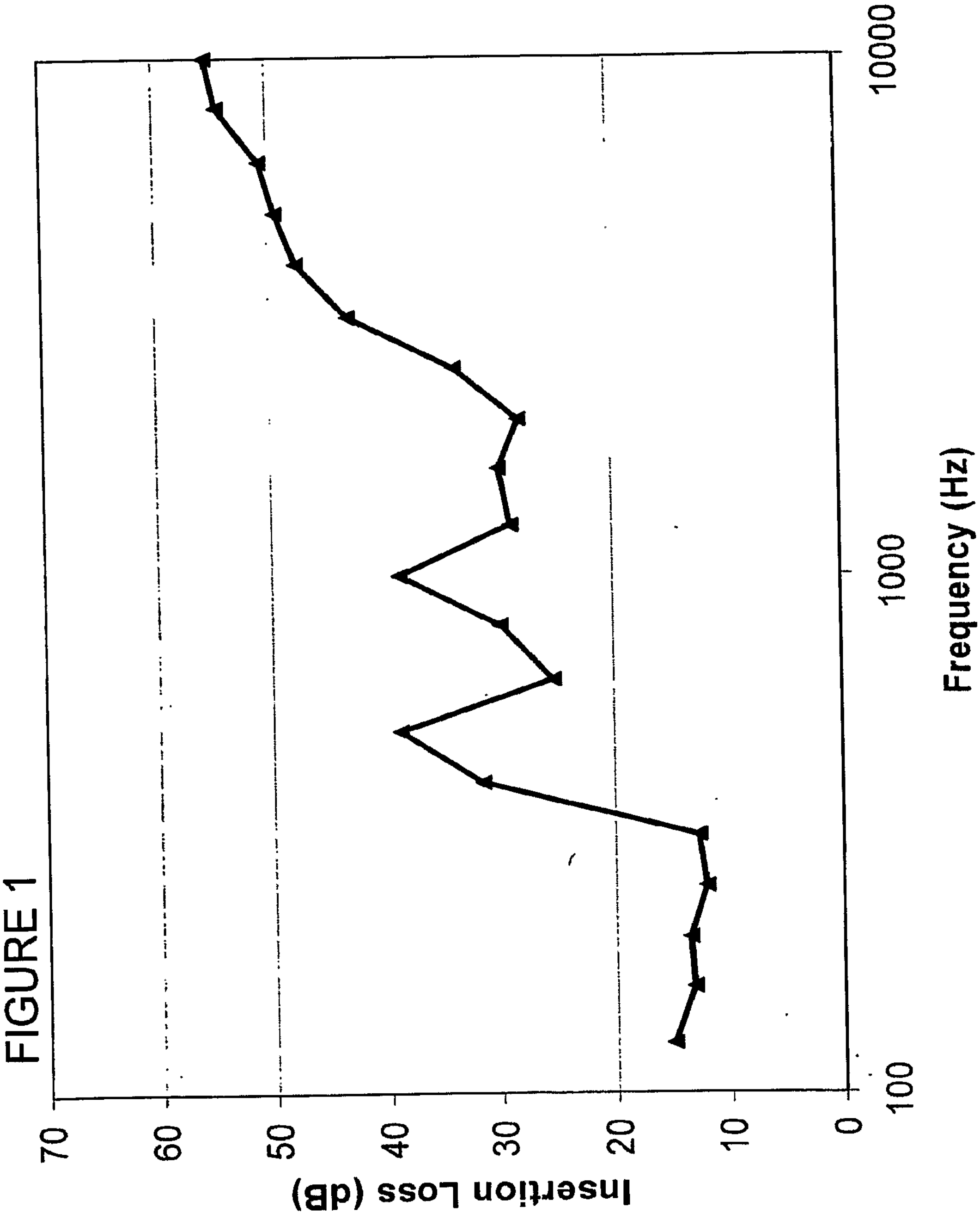
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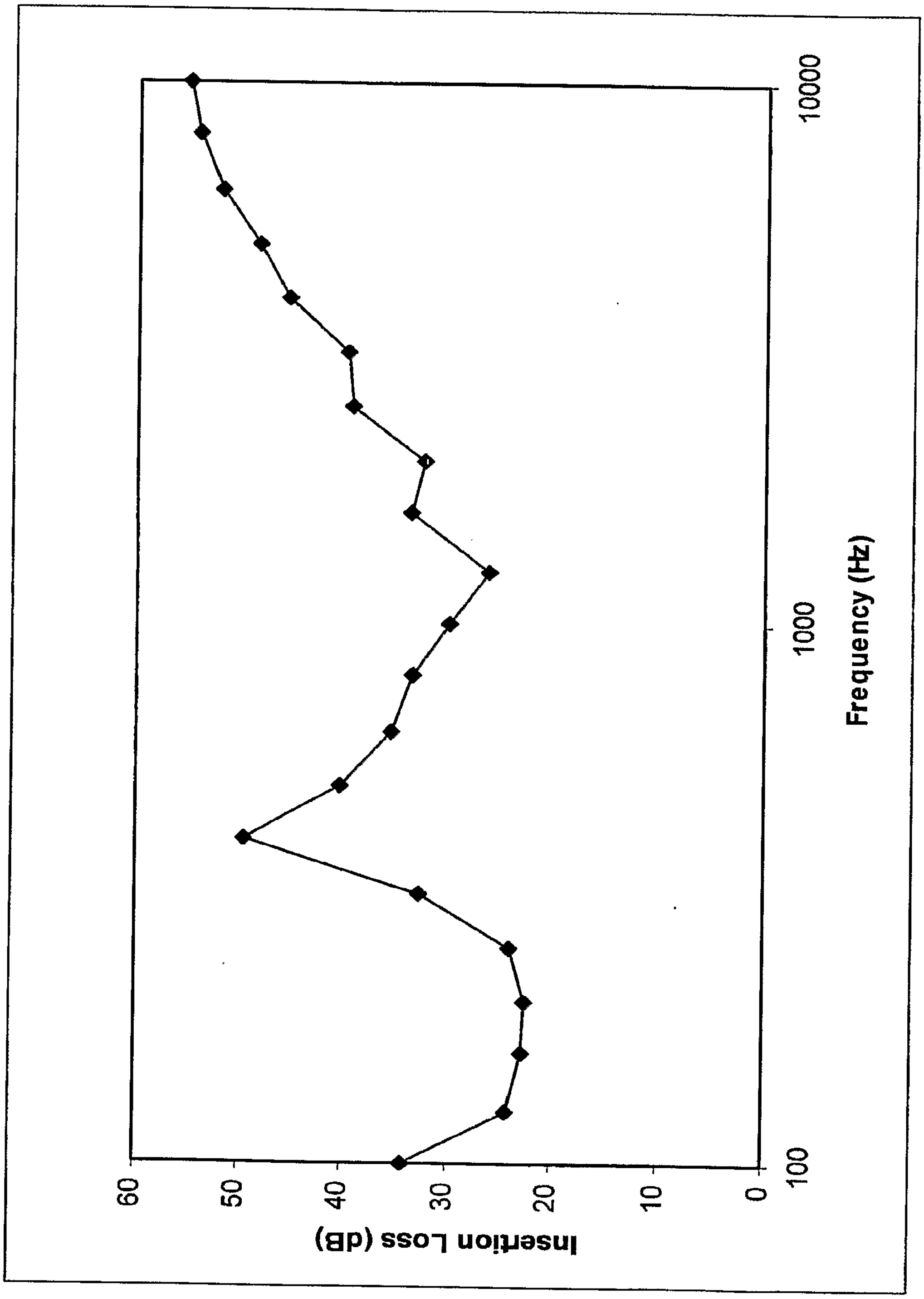
Figure 2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