

**A METHOD FOR FORMING INTEGRAL SKIN FLEXIBLE FOAMS
FROM HIGH PURITY CYCLOPENTANE AND BLEND THEREOF**

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The present invention relates to a process for the preparation of polyurethane containing molded articles having a compressed peripheral zone and a cellular core. The novel integral skin flexible foams according to the present invention are formed using a very stable/homogeneous high purity cyclopentane or cyclopentane/iso- or n-pentane blend blowing agent component. The molded articles according to the present invention are particularly suited for use in making shoe soles and products for the automobile and recreational vehicle industry, e.g., bumper coverings, impact protection moldings and body parts such as, drip moldings, fenders, spoilers and wheel extensions, as well as engineering housing components and rollers. These integral skin foams may also be used for example, as arm rests, head rests, safety coverings in the interior of automobiles and as motorcycle and bicycle saddles and finally as coverings for composite foams.

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BACKGROUND OF THE INVENTION

The preparation of molded articles having a cellular core and a compressed peripheral zone has been known for some time and, for example, is disclosed in the following patents: DE-A-1694138, GB-A-1209243, DE-A-955891, GB-A-1321679, and US-A-3824199. Such products are generally prepared by reacting organic polyisocyanates, higher molecular weight compounds having at least two reactive hydrogen atoms and, optionally, chain extending agents in the presence of blowing agents, more preferably physically active blowing agents, catalysts, auxiliaries and/or additives in a closed, optionally heated, mold using compression.

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Also known is the preparation and use of urethane group-containing shoe

soles prepared by the polyisocyanate addition polymerization process in the shoe industry. Direct shoe soling and the preparation of polyurethane finished soles are primary areas of application for polyurethanes in the shoe industry. Such polyurethane shoe soles can be manufactured using low pressure or high pressure technology (RIM) (SchuhTechnik + abc, 10/1980, pages 822 ff).

A comprehensive overview of polyurethane integral skin foams has been published, for example, in Integral Skin Foams by H. Piechoto and H. Rohr, Carl-Hanser Publishers, Munich, Vienna, 1975 and in the Plastics Handbook, Volume 7, Polyurethanes, by G. Oertel, Carl-Hanser Publishers, Munich, Vienna, 2nd Ed., 1983, pages 333 ff. The latter reference describes (pages 362-366) using integral skin foams in the shoe industry.

Essentially two types of blowing agents are used in the preparation of cellular plastics employing the polyisocyanate addition polymerization process: low boiling point inert liquids which evaporate under the influence of the exothermic addition polymerization reaction; for example, alkanes, like butane, pentane, etc. or preferably halogenated hydrocarbons, like methylene chloride, dichloromonofluoromethane, trichlorofluoromethane, etc.; and chemical compounds which form propellants through a chemical reaction or by thermal decomposition. Examples of the latter are the reaction of water with isocyanates to form amines and carbon dioxide which occurs in synchronization with polyurethane formation, and the cleavage of thermally labile compounds, such as, for example, azoisobutyric acid nitrile which along with nitrogen as a cleavage product forms the toxic cetramethylsuccinic acid dinitrile, or azodicarbonamide whose use as a component in a blowing agent combination is disclosed in EP-A-0092740. While the latter method in which thermally labile compounds such as azo-compounds, hydrazides, semicarbazides, N-nitrose compounds, benzoxazines, etc. are generally incorporated into a prefabricated polymer, or rolled into plastic granules following which the compound is foamed by extrusion has remained of

little industrial importance, the physically active low boiling point liquid, particularly chlorofluoroalkanes (CFC), are used throughout the world on a large scale to produce polyurethane foams and polyisocyanurate foams.

5 A disadvantage of propellants is the problem of environmental pollution. When propellants are formed by thermal cleavage or a chemical reaction, cleavage products and/or reactive byproducts are formed and become incorporated into the addition polymerization product or are chemically bound and thus can lead to an unwanted change in the mechanical properties of the plastic. In the case of
10 formation of carbon dioxide from water and diisocyanate, urea groups are formed in the addition polymerization product and, depending on their quantity, can lead to either an improvement in compressive strength or to embrittlement of the polyurethane.

15 Although aliphatic hydrocarbons such as pentane, hexane and heptane are inexpensive and non-hazardous to health, in the prior art they are only used for foaming thermoplastics. Pentane and its isomers are, for example, used in the preparation of expanded polystyrene (Kunststoffe 62 (1972), pages 206-208) and also in phenolic resin foams (Kunststoffe, 60 (1970), pages 548-549).

20 DE-A-1155234 (GB-A-904003) discloses the preparation of polyurethane foams from an isocyanate group containing prepolymer while using a blowing agent mixture comprising water and a soluble insert gas which is liquid under pressure. Cited as typical inert gases are, for example, gaseous hydrocarbons,
25 halogenated hydrocarbons, ethylene oxide, nitric oxides, sulfur dioxide and more preferably, carbon dioxide. According to GB-A-876977, saturated or unsaturated hydrocarbons, saturated or unsaturated dialkylethers and fluorine containing halogenated hydrocarbons can be used, for example, as blowing agents in the preparation of polyurethane rigid foams.

30 The high flammability, and accordingly the expensive safety measures

required to use gaseous alkanes in production, is why alkanes have not been used in the prior art as blowing agents for foaming polyisocyanate addition polymerization products. Heretofore, there have been no teachings dealing with using alkanes for the preparation of integral skin foams.

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CA-A-2000019 (Volkert) discloses a blowing agent which replaced the conventional CFC's used as blowing agents in the preparation of polyurethane integral skin foams. This blowing agent comprised aliphatic or cycloaliphatic hydrocarbons. The preferred low boiling point cycloalkanes have 4 to 8 carbon
10 atoms, more preferably 5 to 6 carbon atoms in the molecule. The most preferred are linear or branched alkanes having 4 to 8 carbon atoms, more preferably 5 to 7 carbon atoms in the molecule. Typical cycloaliphatic hydrocarbons are, for examples, cyclobutane, cyclopentane, cycloheptane, cyclooctane, and more preferably cyclohexane. Most preferably used are aliphatic hydrocarbons such as,
15 for example, butane, n- and isopentane, n- and isohexane, n- and isoheptane, and n- and isooctane. The most preferred is isopentane, more particularly n-pentane and mixtures of pentanes.

However, the problem associated with using conventional alkanes and
20 cycloalkanes as blowing agents: (1) they are not very soluble in polyols which reduces shelf life due to instability; and (2) low purity cyclopentane is also not soluble in polyols.

The present inventors have discovered that the use of a novel high purity
25 cyclopentane enables formulators to obtain solubility with such blowing agents and polyols, such that the shelf life is substantially increased verses low purity cyclopentanes. Blends with n- or iso-pentane also formulator to adjust the cell size of the core to increase or decrease core softness.

SUMMARY OF THE INVENTION

The present invention relates to a method for forming a molded article that exhibits a compressed peripheral zone and a cellular core. The process comprises contacting a polyfunctional isocyanate, an isocyanate-reactive compound having at least two active hydrogens, a blowing agent comprising high purity cyclopentane and a catalyst, wherein contacting is carried out at a temperature, pressure and length of time sufficient to produce an article having a compressed peripheral zone and a cellular core. The isocyanate-reactive compound is selected from the group consisting of a high molecular weight compound, a low molecular weight compound and a mixture thereof and the low molecular weight compound is selected from the group consisting of a chain extender, a crosslinking agent and a mixture thereof.

The present invention also includes a method for forming molded articles that are integral skin flexible foams or cellular elastomers. The method comprises: (1) introducing into a mold a molding mixture, comprising: (a) an organic and/or modified organic polyisocyanate, (b) at least one higher molecular weight compound having at least two reactive hydrogen atoms, (c) optionally, a lower molecular weight chain extending agent and/or crosslinking agent, (d) a blowing agent comprising high purity cyclopentane, and (e) a catalyst capable of forming a molded article having a compressed peripheral zone and a cellular core, and (2) allowing the molding mixture to react at a temperature, pressure and for a length of time sufficient to produce the molded article having a compressed peripheral zone and a cellular core.

The present invention also includes molded articles including integral skin flexible foams and cellular elastomers that are prepared by the processes of the present invention.

The high purity cyclopentane product is a viable alternative to HCFC1b as a blowing agent in polyurethane foam. However, impurities especially hexanes decrease the effectiveness of the cyclopentane as a blowing agent. The present inventors have discovered that n-pentane and hexanes in certain concentrations will
5 effect the solubility of cyclopentane in polyols (i.e., polyethers and polyesters). Any decrease in solubility of the blowing agent in polyols is undesirable because less solubility causes shorter shelf life of the resultant foam.

The unique high purity cyclopentane blowing agent according to the
10 present invention is formed by a process, comprising: (I) diluting cyclopentadiene with an aliphatic hydrocarbon to produce a cyclopentadiene-rich stream, comprising 15-50 weight % cyclopentadiene, (II) hydrogenating the cyclopentadiene-rich stream in the presence of hydrogen and a palladium-on alumina catalyst in a first hydrogenation step to convert a substantial portion of the
15 cyclopentadiene to cyclopentane, thereafter (III) hydrogenating the cyclopentane-rich stream formed in step (II) in the presence of a massive nickel catalyst in a second hydrogenation step to form crude cyclopentane, (IV) separating hydrogen from crude cyclopentane; and (V) flash stripping the crude cyclopentane to form a high purity cyclopentane. The process can further comprise the steps of: (VI)
20 recycling the hydrogen obtained from step (IV) into step (II) and/or step (III); (VII) cracking dicyclopentadiene to cyclopentadiene; and (VIII) separating the cyclopentadiene from higher boiling liquids to produce a cyclopentadiene-rich stream for use in step (I).

25 The present invention also includes high purity cyclopentadiene prepared by the process of the present invention that is substantially free of C₆-C₈ hydrocarbon impurities.

The reaction preferably takes place in a closed, optionally, heated mold
30 under compression. The process is particularly suited for the preparation of

flexible elastic shoe soles, having a total density of from 0.4 to 1.0 g/cm, yet the starting components are efficaciously reacted using a one shot process with the help of high pressure technology (RIM).

- 5 Other and further objects, advantages and features of the present invention will be understood by reference to the following specification in conjunction with the annexed drawings, wherein like parts have been given like numbers.

10 **BRIEF DESCRIPTION OF THE DRAWINGS**

Fig. 1 is a schematic diagram of the cyclopentane process according to the present invention.

15 **DESCRIPTION OF THE PREFERRED EMBODIMENT**

- It was unexpectedly found that the high purity cyclopentanes or mixtures of high purity cyclopentanes with n- or iso-pentanes used as blowing agents provide polyurethane integral skin foams having long shelf life and adjustable softness which are comparable or greater than products prepared while using
20 trichlorofluoromethane.

The blowing agent may preferably comprise 100% of a high purity cyclopentane or mixture thereof with n- or iso-pentane.

- 25 The high purity cyclopentane comprises pure cyclopentane in an amount of at least 50 molar %. When used in a mixture with n- or iso-pentane, it is preferable to have a blend of high purity cyclopentane with either n- or iso-pentane. Preferably, the high purity cyclopentane comprises (a) cyclopentane and (b) n-pentane and/or isopentane in a molar ratio of (a) to (b) between about 50:50 to
30 99:1. More preferably, the high purity cyclopentane comprises (a) cyclopentane

and (b) n-pentane and/or isopentane in a molar ratio of (a) to (b) between about 50:50 to 80:20. One highly preferred blend is high purity cyclopentane and isopentane in a molar ratio of 70:30.

5 The present invention is directed to a method for forming molded articles that exhibit a compressed peripheral zone and a cellular core (i.e., integral skin flexible foams). These integral skin flexible foams are preferably formed by a process, comprising:

- preparing a mixture, comprising:
 - 10 (a) an organic and/or modified organic polyisocyanate;
 - (b) at least one higher molecular weight compound having at least two reactive hydrogen atoms;
 - (c) optionally, a lower molecular weight chain extending agent and/or crosslinking agent;
 - 15 (d) a blowing agent comprising high purity cyclopentane; and
 - (e) a catalyst capable of forming an integral skin flexible foam; and
- allowing the mixture to react at a temperature, pressure and for a length of time sufficient to produce an integral skin flexible foam.

20 The molded article can optionally contain auxiliaries and/or additives.

 The term "high purity cyclopentane" as used in the present invention refers to a cyclopentane that is about 50% or greater pure cyclopentane.

25 The high purity cyclopentane blowing agent of the present invention also is substantially free of C₆ to C₈ hydrocarbons and particularly, it is substantially free of hexanes, 2,2-dimethylhexane and isomers thereof.

 The present inventors have discovered that the purity of the cyclopentane is
30 critical for effective blowing action. They also have discovered that the nature of

the impurities and the relative amounts present are similarly critical. It has been found that high purity cyclopentane that is suitable for use can contain at least one linear or branched pentane isomer, however, it must be substantially free of C₆ to C₈ hydrocarbons. Particularly, the high purity cyclopentane must be substantially free of 2,2-dimethylhexane and isomers thereof and must also be substantially free of hexanes.

Similarly, a cellular elastomer can be prepared by a process, comprising:

- preparing a mixture, comprising:
 - (a) an organic and/or modified organic polyisocyanate;
 - (b) at least one higher molecular weight compound having at least two reactive hydrogen atoms;
 - (c) optionally, a lower molecular weight chain extending agent and/or crosslinking agent;
 - (d) a blowing agent comprising high purity cyclopentane; and
 - (e) a catalyst capable of forming a cellular elastomer; and
- allowing the mixture to react at a temperature, pressure and for a length of time sufficient to produce a cellular elastomer.

The following should be noted with respect to typical starting components (a) through (f) for the preparation of molded articles such as shoe soles, more preferably urethane, or urethane and urea group-containing cellular elastomer molded articles and most preferably integral skin foams.

The preferred polyfunctional isocyanate is an organic and/or modified organic polyisocyanate. The organic polyisocyanates suitable for use in the present invention include all essentially known monomeric and polymeric polyfunctional isocyanates including aliphatic, cycloaliphatic, araliphatic and aromatic polyfunctional isocyanates. Aromatic polyfunctional isocyanates are preferred.

Specific examples include: alkylene diisocyanates with 4 to 12 carbons in the alkylene radical such as 1,12-dodecane diisocyanate, 2-ethyl-1,4-tetramethylene diisocyanate, 2-methyl-1,5-pentamethylene diisocyanate, 1,4-tetramethylene diisocyanate, and preferably 1,6-hexamethylene diisocyanate;
5 cycloaliphatic diisocyanates such as 1,3- and 1,4-cyclohexane diisocyanate as well as any mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate), 2,4- and 2,6-hexahydrotoluene diisocyanate as well as the corresponding isomeric mixtures, 4,4', 2,2', and 2,4'-dicyclohexylmethane diisocyanate as well as the corresponding
10 isomeric mixtures; and preferably aromatic diisocyanates and polyisocyanates such as 2,4- and 2,6-toluene diisocyanate and the corresponding isomeric mixtures, mixtures of 4,4'- and 2,4'-diphenylmethane diisocyanates and polyphenylpolymethylene polyisocyanates (polymeric MDI) as well as mixtures of polymeric MDI and toluene diisocyanates. Also included are dimers, trimers and
15 prepolymers derived from any of the preceding polyisocyanates. The organic di- and polyisocyanates can be used individually or in the form of mixtures.

Frequently, so-called modified multivalent isocyanates, i.e., products obtained by chemical reaction of organic diisocyanates and/or polyisocyanates, are
20 used. Examples of such organic diisocyanates and/or polyisocyanates are set forth in Canadian Patent No. 2,000,019 (Volkert), issued on April 14, 1990, which is incorporated herein by reference.

Another ingredient used in the process of the present invention is an
25 isocyanate-reactive compound having at least two active hydrogens. The isocyanate-reactive compound is selected from the group consisting of a high molecular weight compound, a low molecular weight compound and a mixture thereof. The low molecular weight compound is selected from the group consisting of a chain extender, a crosslinking agent and a mixture thereof.

Preferred higher molecular weight compounds (b) having at least two reactive hydrogens include those with a functionality of 2 to 8, preferably 2 to 4, and a molecular weight of 400 to 8000, preferably 1200 to 6300. For example, polyether polyamines and/or preferably polyols selected from the group consisting of polyether polyols, polyester polyols, polythioether polyols, polyester amides, polyacetals containing hydroxyl groups, aliphatic polycarbonates containing hydroxyl groups, diols, triols, polyfunctional alcohols, diamine, triamine, polyfunctional amine, polyether polyamine and mixtures of at least two of the aforementioned compounds have proven suitable. Polyester polyols and/or polyether polyols are preferred.

Suitable polyester polyols can be produced, for example, from organic dicarboxylic acids with 2 to 12 carbons, preferably aliphatic dicarboxylic acids with 4 to 6 carbons, and multivalent alcohols, preferably diols, with 2 to 12 carbons, preferably 2 to 6 carbons. Examples of dicarboxylic acids include succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid and terephthalic acid. The dicarboxylic acids can be used individually or in mixtures. Instead of the free dicarboxylic acids, the corresponding dicarboxylic acid derivatives may also be used such as dicarboxylic acid esters of alcohols with 1 to 4 carbons or dicarboxylic acid anhydrides. Dicarboxylic acid mixtures of succinic acid, glutaric acid and adipic acid in quantity ratios of 20:35:35-50:20:32 parts by weight are preferred, especially adipic acid. Examples of divalent and multivalent alcohols, especially diols, include ethanediol, diethylene glycol, 1,2- and 1,3-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, glycerol and trimethylolpropane. Ethanediol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol or mixtures of at least two of these diols are preferred, especially mixtures of 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol. Other suitable polyols are set forth in Canadian Patent No. 2000019, which is incorporated herein by reference.

The molded articles having a compressed peripheral zone and a cellular core and preferably urethane or urethane and urea group-containing molded articles can be prepared with or without using chain extending agents and/or crosslinking agents. To modify the mechanical properties, e.g., hardness, however, it has proven advantageous to add (c) chain extenders, crosslinking agents or mixtures thereof. Suitable chain extenders and/or crosslinking agents include diols and/or triols with molecular weights of less than 400, preferably 60 to 300. Examples include aliphatic, cycloaliphatic and/or araliphatic diols with 2 to 14 carbons, preferably 4 to 10 carbons, such as ethylene glycol, 1,3-propanediol, 1,10-decanediol, 1,2-, 1,3- and 1,4-dihydroxycyclohexane, diethylene glycol, dipropylene glycol and preferably 1,4-butanediol, 1,6-hexanediol and bis(2-hydroxyethyl)hydroquinone; triols such as 1,2,4- and 1,3,5-trihydroxycyclohexane, glycerol, trimethylolethane and trimethylolpropane and low molecular weight hydroxyl group-containing polyalkylene oxides based on ethylene oxide and/or 1,2-propylene oxide and the aforementioned diols and/or triols as initiator molecules.

In addition to the aforementioned diols and/or triols, or in admixture with them as chain extenders or crosslinking agents to prepare the cellular elastomer molded articles and integral skin foams, most preferably shoe soles according to this invention, it is also possible to use secondary aromatic diamines, primary aromatic diamines, 3,3 di- and/or 3,3', 5,5'-tetraalkyl-substituted diaminodiphenylmethanes. Such amines are set forth in Canadian Patent No. 2000019, which is incorporated herein by reference.

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These chain extenders and/or crosslinking agents (c) may be used individually or as mixtures of the same or different types of compounds.

If chain extenders, crosslinking agents or mixtures thereof are used, they are preferably used in amounts of 2 to 60 weight percent preferably 8 to 50 weight

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percent and especially 10 to 40 weight percent, based on the weight of components (b) and (c).

In the preparation of the flexible elastic shoe soles, one preferably uses as
5 the higher molecular weight compounds (b), polyester polyols or polyether polyols having a functionality of from 2 to 4, more preferably 2 and a molecular weight of 1200 to 6000 and as the chain extending agent or cross linking agent (c), primary aromatic diamines which in the ortho position relative to each amino group have at least one alkyl radical having 1 to 3 carbon atoms in bonded form, or mixtures of
10 such aromatic alkyl substituted diamines, and diols and/or triols.

Blowing agents (d) that can be used according to this invention include high purity cyclopentane and mixtures thereof with n- and iso-pentane.

15 It has been surprising to discover that cyclopentane synthesized from dicyclopentadiene ("DCP"), $C_{10}H_{12}$, is miscible with polyester polyols, not requiring additional surfactants or emulsifiers to mix well. As one skilled in the art will now appreciate upon comprehending this discovery, the miscibility of this unique cyclopentane creates a foamable blend having a viscosity low enough to
20 utilize, whereas the EXTRCP does not create this advantage.

The present inventors have further discovered that the use of the novel high purity cyclopentane blowing agents of the present invention enables formulators to obtain better solubility with polyols, which in turn, advantageously increases the
25 shelf life of the blend.

High purity cyclopentane has a boiling point of 120°F, which is primarily responsible for producing a maximum integral skin thickness. This specific boiling point allows for slow foam rise and less crushing of cells at the skin/mold interface.
30 In contrast to the above, high purity iso- or n-pentane, which have lower boiling

points individually or as a mixture, produces higher vapor pressure during foam blowing in the mold than cyclopentane. This increases cell crushing and produces thinner skin and softer foam. The use of high purity cyclopentane blended with iso- and/or n-pentane enables formulators to adjust skin thickness and firmness by
5 simply varying the cyclopentane to isopentane and or normal pentane ratio to obtain foams with specific, desired properties.

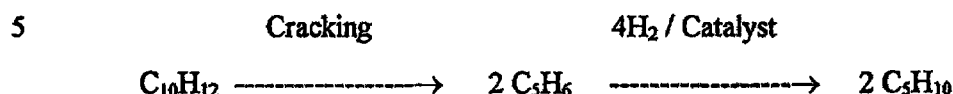
The unique, or special, synthesized cyclopentane (SYNCP) utilized in all embodiments of this invention is obtained from Exxon Chemical Americas as
10 imported "Exxsol™ Cyclopentane". In this regard, the cyclopentane utilized in embodiments of this invention is synthetically created by the "cracking" or depolymerization of DCP to CP. The synthetic cyclopentane used in the examples of this invention is in excess of 95% pure cyclopentane.

15 The unique high purity cyclopentane blowing agent according to the present invention is preferably formed by a process having the following steps: (a) cracking dicyclopentadiene to cyclopentadiene; (b) separating the cyclopentadiene-rich stream from the higher boiling liquids; (c) diluting the cyclopentadiene-rich stream with recycled saturates such that cyclopentadiene content is limited to 15-
20 50%; (d) conducting a first hydrogenation of the cyclopentadiene-rich stream in the presence of hydrogen and a palladium-on alumina catalyst, thereby converting a substantial portion of the cyclopentadiene to cyclopentane; (e) conducting a second hydrogenation of the cyclopentane-rich stream from step (d) in the presence of a massive nickel catalyst wherein any residual olefins are saturated to form a crude
25 cyclopentane product; (f) separating hydrogen from the crude cyclopentane product; (g) recycling the hydrogen from step (f) to step (a); and (h) flash stripping the crude cyclopentane product to form a substantially pure cyclopentane product (approximately 50% cyclopentane).

30 The simplified equation for synthesized cyclopentane (SYNCP) according

to the present invention is as shown as EQUATION 1 herebelow:

EQUATION 1



Examples of processes suitable for production of the synthesized cyclopentane (SYNCP) according to the present invention are described in GB-A-2271575 and GB-A-2273107, both of which are incorporated herein by reference. In GB-A-2271575, cyclopentane is used as a diluent, or carrier, during the depolymerization, e.g., "cracking", stage to reduce coking and the formation of trimers, tetramers, and higher polymers which are not readily decomposed to the monomer, as taught in GB-A-1302481, also incorporated herein by reference. In GB-A-2273107, catalyst powder is circulated through reaction zones in a slurry form until it is removed by filtration.

This processing method allows the hydrogenation of the unsaturated monomer to cyclopentane at temperatures below 175°C. The advantages of this process are outlined in GB-A-1115145 and GB-A-1264255, both of which are incorporated herein by reference.

As another example of an implementation of EQUATION 1, the C_5H_6 represents the unsaturated five-carbon hydrocarbons, either linear or cyclic. Some pentadiene (C_5H_8) may also be present during the conversion. In such process, the cyclopentadiene is hydrogenated to cyclopentane, and the pentadiene may undergo hydrogenation and cyclization to cyclopentane using a catalyst, e.g., a transition metal (or adducts thereof) catalyst. An example of a palladium metal adduct is PdCl_2 .

A process for manufacturing high-purity (i.e., 50% or greater) cyclopentane by splitting dicyclopentadiene and completely hydrogenating the cyclopentadiene monomer in a single unit as illustrated in attached Fig. 1.

5 The general process scheme involves diluting commercially available dicyclopentadiene with an aliphatic hydrocarbon fluid of specific volatility and solvency. This material is then introduced into a distillation apparatus in which the dicyclopentadiene decomposes (or depolymerizes) to cyclopentadiene monomers. Reflux to the distillation apparatus consists of a cyclopentane product recycle
10 stream. This reflux aids distillation and dilutes the cyclopentadiene monomer to prevent re-dimerization and cyclopentadiene yield reduction. The overhead stream from this step is a stream containing cyclopentane and cyclopentadiene.

 This stream is further diluted with cyclopentane-rich recycle liquid obtained
15 from the high-pressure separator drum. The purpose of the dilution is to minimize cyclopentadiene dimerization and to allow controlling of the exotherm in the subsequent hydrotreating reactors.

 The cyclopentadiene/cyclopentane stream is then pumped to a reactor and
20 combined with a stoichiometric excess of hydrogen contained in a treatgas stream. It is then passed over a palladium-on-alumina catalyst where the bulk of the hydrogenation reaction occurs converting most of the cyclopentadiene to cyclopentane. The first reactor effluent flows to a second reactor containing a massive nickel catalyst where any remaining olefins (i.e., cyclopentene) are
25 saturated.

 The fully hydrogenated nickel reactor effluent is cooled and enters a high-pressure flash drum. The vapor from this drum, which contains primarily hydrogen but also contains some cyclopentane vapor, is contacted with the
30 dicyclopentadiene feed stream in an absorber tower to minimize cyclopentane

losses.

A portion of the liquid product from the high-pressure separator drum is recycled as described earlier. The remainder flows to a product stripping tower in
5 which any remaining dissolved hydrogen and any compounds heavier than cyclopentane are removed. The stripper bottoms may be recycled to the dicyclopentadiene cracking tower.

The process according to the present invention can best be described by
10 referring to Fig. 1, wherein DCPD and an aliphatic hydrocarbon fluid of specific volatility and solvency are fed from tanks 1 and 3, respectively, via conduit 5 to distillation cracking tower 7 such that DCPD is cracked to form cyclopentadiene and cyclopentane. A cyclopentane product recycle stream from a high-pressure
flash drum 9 is recycled to tower 7 via conduit 11. The cyclopentane product
15 recycle stream aids distillation in tower 7 and dilutes the cyclopentadiene monomer to between 15-50% to prevent re-dimerization and cyclopentadiene yield reduction. The liquid cyclopentadiene and cyclopentane mixture is taken as
bottoms from tower 7 via conduit 13, and delivered to separator drum 15 where it is further diluted with cyclopentane-rich recycle liquid obtained from product
20 stripping tower 17 via conduits 19 and 21. The purpose of the dilution in separator drum 15 is to minimize cyclopentadiene dimerization and to allow controlling of the exotherm in the subsequent hydrotreating reactors. The
cyclopentadiene/cyclopentane stream having a cyclopentadiene content of between
about 15-50% is taken overhead from separator drum 15 via conduit 23 and mixed
25 with a stoichiometric excess of hydrogen from conduit 24. The hydrogen saturated cyclopentadiene/cyclopentane stream is then sent to first hydrogenation reactor 25
wherein it is passed over a palladium-on-alumina catalyst where the bulk of the hydrogenation reaction occurs converting most of the cyclopentadiene to
cyclopentane. The liquid effluent from first hydrogenation reactor 25 is taken via
30 conduit 27 and sent to the top of second hydrogenation reactor 29 containing a

massive nickel catalyst where any remaining olefins (i.e., cyclopentene) are saturated.

The fully hydrogenated product stream is taken as liquid bottoms from
5 reactor 29 via conduit 31 and cooled via heat exchanger 33 and thereafter sent to
high-pressure flash drum 9. The overhead (i.e., primarily hydrogen, but also
containing some cyclopentane vapor) from flash drum 9 is returned to tower 7 via
conduit 11, as discussed before, to minimize cyclopentane losses. The bottoms
from flash drum 9 are taken via conduit 35 and either recycled upstream of first
10 hydrogenation reactor 25 or sent via conduit 37 to product stripping tower 17
wherein any remaining dissolved hydrogen and any compounds heavier than
cyclopentane are removed overhead via conduit 39. The bottoms from stripping
tower 17 are removed via conduit 41 and, optionally, recycled to tower 7 or
purged from the system. Cyclopentane product is recovered from an intermediate
15 section of stripper tower 17 via conduit 19 and either sent to tankage, not shown,
or recycled via conduit 21 to separator drum 15, as discussed above. The
cyclopentane is preferably 95% pure cyclopentane at this point.

Some of the key advantages of high purity cyclopentane product, such as
20 Exxsol® Cyclopentane, over conventional blowing agents such as low purity
cyclopentanes, pentane isomers and hydrofluorocarbons are: (1) the high purity
cyclopentane product of the present invention is soluble or miscible in polyols,
whereas n-pentane and isopentane are not soluble in polyols; (2) insulating
efficiency of foams formed using high purity cyclopentane product of the present
25 invention is higher than with other pentane isomers for initial and aged R values;
(3) high purity cyclopentane product of the present invention has a much slower
diffusion rate out of polyurethane foams than other pentane isomers; and (4) high
purity cyclopentane product has no GWP, whereas hydrofluorocarbon blowing
agents have a high GWP.

The following is a comparison of various blowing agents' properties:

Blowing Agents	HCFC	HFC	HFC	95% CP	78% CP	Iso-Pen.	N-Pen.
	141b*	245FA**	365***				
5 Molecular Wt.	117	134	148	70	70	72	72
Vapor Thermal Conductivity BTU-in/hr-ft ² , 25°C	0.005	0.007	0.008	0.0065	0.0068	0.0076	0.0076
Soluble in Polyols	Yes	Yes	Yes	Yes	No	No	No
10 Boiling Point, °C	32.1	15.4	40	50	50	28	28
Flammability	Slight	None	Yes	Yes	Yes	Yes	Yes
Ozone Depletion	0.12	0	0	0	0	0	0
Global Warming	0.12	0.24	>0.20	None	None	None	None
VOC Status	No	No	No	Yes	Yes	Yes	Yes
15 *	<chem>CH3CCl2F</chem>						
**	<chem>CF3CH2CHF2</chem> manufactured by Allied Signal Inc.						
***	<chem>CF3CH2CF2CH3</chem> manufactured by Elf Atochem.						
	CP denotes cyclopentane having the general formula C ₅ H ₁₀ .						
	Iso Pen. denotes iso pentane having the general formula C ₅ H ₁₂ .						
20	N-Pen. denotes normal pentane having the general formula C ₅ H ₁₂ .						

The miscibility of the specially synthesized cyclopentane (SYNCP) of the invention is evidenced by TABLE I.

25 Furthermore, the addition of a potassium catalyst, a tertiary amine catalyst, and the normal silicone type surfactant to the above blends of synthesized cyclopentane (SYNCP) produces clear solutions in the useful ranges of from about 13% up to about 30% cyclopentane by weight. By contrast, these same additives do not make clear solutions of any ratio blend with the conventional blowing
30 agents.

TABLE I**(MISCIBILITY STUDIES OF THE PRESENT CYCLOPENTANE)**

	Weight Ratio of Polyol/Cyclopentane	Synthesized Cyclopentane
5	80/20	Stable Mixture
	75/25	Stable Mixture
	70/20	Stable Mixture
	50/50	Stable Mixture
	35/65	Stable Mixture
10	20/80	Stable Mixture

The mixtures of the high purity cyclopentane according to the present invention were all clear solutions and remained stable.

- 15 Suitable catalysts (e) for producing the molded articles having a compressed peripheral zone and a cellular core include especially compounds that greatly accelerate the reaction of the hydroxyl group containing compounds of component (b) and, optionally, (c) with the organic optionally modified polyisocyanates (a). Examples include organic metal compounds, preferably
- 20 organic tin compounds such as tin(II) salts of organic carboxylic acids, e.g., tin(II) acetate, tin(II) dioctoate, tin(II) ethylhexoate and tin(II) laurate, as well as the dialkyltin(IV) salts of organic carboxylic acids, e.g., dibutyltin diacetate and dibutyltin dilaurate. The organic metal compounds are used alone or preferably in combination with strong basic amines. Examples include amines such as 2,3-
- 25 dimethyl-3,4,5,6-tetrahydropyrimidine, tertiary amines such as triethylamine, tributylamine, dimethylbenzylamine, N-methylmorpholine, N-ethylmorpholine, N-cyclohexylmorpholine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylbutanediamine, pentamethyldiethylenetriamine, tetramethyldiaminoethyl ester, bis(dimethylaminopropyl) urea, dimethylpiperazine, 1,2-di-methylimidazole,
- 30 1-aza-bicyclo-[3.3.0]octane and preferably 1,4-diaza-bicyclo[2.2.2]octane and

alkanolamine compounds such as triethanolamine, triisopropanolamine, N-methyl- and N-ethyldiethanolamine and dimethylethanolamine.

Suitable catalysts when using a large polyisocyanate excess also include
5 tris(dialkylamino)-s-hexahydrotriazines, especially tris(N,N-dimethylaminopropyl)-s-hexahydrotriazine, tetraalkylammonium hydroxides such as tetramethylammonium hydroxide, alkali hydroxides such as sodium hydroxide and alkali alcoholates such as sodium methylate and potassium isopropylate as well as alkali salts of long-chain fatty acids with 10 to 20 carbons and optionally OH
10 pendent groups. 0.001 to 5 weight percent, especially 0.05 to 2 weight percent, of catalyst or catalyst combination based on the weight of component (b) is preferred.

Optionally, other additives and/or auxiliaries (f) may be incorporated into the reaction mixture to produce the molded articles. Examples include surface
15 active substances, foam stabilizers, cell regulators, fillers, dyes, pigments, flame retardants, hydrolysis preventing agents, fungistatic, bacteriostatic agents and a mixture thereof.

To produce the molded articles the organic polyisocyanates (a), higher
20 molecular weight compounds with at least two reactive hydrogens (b) and optional chain extenders and/or crosslinking agents (c) are reacted in amounts such that the equivalent ratio of NCO groups of polyisocyanates (a) to the total reactive hydrogens of component (b) and, optionally, (c) amounts to 1:0.85-1:1.25, preferably 1:0.95-1:1.15. If the molded articles contain at least some isocyanurate
25 groups in bonded form then conventionally a ratio of NCO groups or polyisocyanates (a) to the total reactive hydrogens of component (b) and optionally (c) will be from 1.5:1-60:1, preferably 0.5:1-8:1.

Molded articles, especially flexible elastic integral skin foams and cellular
30 elastomer molded articles are prepared employing a prepolymer process or

preferably a one shot process with the help of low pressure technology or more preferably high pressure reaction injection molding technology in closed, efficaciously heated molds, for example, metal molds made from aluminum, cast iron or steel, or molds made of fiber reinforced polyester compositions or epoxied
5 compositions.

It is proven to be most beneficial to work according to two component process and to incorporate starting components (b), (d), (e) and optionally (c) and (f) into component (A) and to use organic polyisocyanates, modified polyiso-
10 cyanates (a) or mixtures of the aforesaid polyisocyanates as the (B) component optionally including blowing agent (d).

The starting components are mixed together at a temperature of from 15 to 90°C, more preferably 20 to 35°C and injected into the closed mold optionally
15 under increased pressure. Mixing can be done mechanically using a stirrer or using a stirrer screw or even under an elevated pressure in so-called countercurrent injection process. The mold temperature is normally 20 to 90°C, more preferably 30 to 60°C, and most preferably 45 to 50°C.

20 The molded articles according to the present invention are particularly suited for use in making shoe soles and products for the automobile and recreational vehicle industry, e.g., bumper coverings, impact protection moldings and body parts such as, drip moldings, fenders, spoilers and wheel extensions, as well as engineering housing components and rollers. These integral skin foams
25 may also be used for example, as arm rests, head rests, safety coverings in the interior of automobiles and as motorcycle and bicycle saddles and finally as coverings for composite foams.

While we have shown and described several embodiments in accordance
30 with our invention, it is to be clearly understood that the same are susceptible to

numerous changes apparent to one skilled in the art. Therefore, we do not wish to be limited to the details shown and described but intend to show all changes and modifications that come within the scope of the appended claims.

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**WHAT IS CLAIMED IS:**

1. A method for preparing a molded article having a compressed peripheral zone and a cellular core, comprising:

5 introducing into a molding vessel a mixture comprising:

- (a) an organic and/or modified organic polyisocyanate;
- (b) at least one higher molecular weight compound having at least two reactive hydrogen atoms;
- (c) optionally, a lower molecular weight chain extending agent
- 10 and/or crosslinking agent;
- (d) a blowing agent comprising high purity cyclopentane; and
- (e) a catalyst capable of forming a molded article having a compressed peripheral zone and a cellular core; and

15 reacting said mixture at a temperature, pressure and for a length of time sufficient to produce said molded article having a compressed peripheral zone and a cellular core.

2. The method of claim 1, wherein said polyisocyanate is an aliphatic or aromatic polyisocyanate selected from the group consisting of: 1,12-dodecane

20 diisocyanate, 2-ethyl-1,4-tetramethylene diisocyanate, 2-methyl-1,5-pentamethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,3-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate), 2,4-hexahydrotoluene diisocyanate, 2,6-hexahydrotoluene

25 diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 2,2'-dicyclohexylmethane diisocyanate, 2,4'-dicyclohexylmethane diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, polyphenylpolymethylene polyisocyanates (polymeric MDI), dimers, trimers and prepolymers thereof, and a mixture thereof.

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3. The method of claim 1, wherein said higher molecular weight compound is selected from the group consisting of: polyether polyol, polyester polyol, polythioether polyol, polyester amide, hydroxyfunctional polyacetal,
5 hydroxyfunctional aliphatic polycarbonate, diol, triol, polyfunctional alcohol, polyether polyamine, diamine, triamine, polyfunctional amine and a mixture thereof.
4. The method of claim 1, wherein said lower molecular weight chain
10 extending or crosslinking agent is a polyfunctional amine or alcohol selected from the group consisting of polyethylene oxide, polypropylene oxide, hydroxy terminated polyester, ethylene glycol, 1,3-propanediol, 1,10-decanediol, 1,2-dihydroxycyclohexane, diethylene glycol, dipropylene glycol, 1,3-dihydroxycyclohexane, 1,4-dihydroxycyclohexane, 1,4-butanediol, 1,6-hexanediol,
15 bis(2-hydroxyethyl)hydroquinone, 1,2,4- trihydroxycyclohexane, 1,3,5-trihydroxycyclohexane, glycerol, trimethylolethane, trimethylolpropane and a mixture thereof.
5. The method of claim 1, wherein said high purity cyclopentane
20 comprises cyclopentane in an amount of at least 50 molar %.
6. The method of claim 5, wherein said high purity cyclopentane comprises (a) cyclopentane and (b) n-pentane and/or isopentane in a molar ratio of (a) to (b) between about 50:50 to 99:1.
- 25
7. The method of claim 6, wherein said high purity cyclopentane comprises (a) cyclopentane and (b) n-pentane and/or isopentane in a molar ratio of (a) to (b) between about 50:50 to 80:20.
- 30
8. The method of claim 5, wherein said high purity cyclopentane



comprises a mixture of cyclopentane and isopentane in a molar ratio of 70:30.

9. The method of claim 5, wherein said high purity cyclopentane is substantially free of C₆ to C₈ hydrocarbons.

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10. The method of claim 9, wherein said high purity cyclopentane is substantially free of hexanes.

11. The method of claim 10, wherein said high purity cyclopentane is substantially free of 2,2-dimethylhexane and isomers thereof.

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12. The method of claim 1 wherein said high purity cyclopentane is prepared from the following steps:

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(a) cracking dicyclopentadiene to cyclopentadiene;

(b) separating said cyclopentadiene-rich stream from the higher boiling liquids;

(c) diluting said cyclopentadiene-rich stream with recycled saturates such that cyclopentadiene content is limited to 15-50%;

20

(d) conducting a first hydrogenation of said cyclopentadiene-rich stream in the presence of hydrogen and a palladium-on alumina catalyst, thereby converting a substantial portion of the cyclopentadiene to cyclopentane, and thus forming a cyclopentane-rich stream;

25

(e) conducting a second hydrogenation of said cyclopentane-rich stream from step (d) in the presence of a massive nickel catalyst wherein any residual olefins are saturated to form a crude cyclopentane product;

(f) separating hydrogen from said crude cyclopentane product; and

(g) recycling the hydrogen from step (f) to step (d) and/or (e); and

(h) flash stripping said crude cyclopentane product to form a cyclopentane product having at least about 50% purity.

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13. The method of claim 1, wherein said catalyst comprises an organic metal compound and, optionally, a strong basic amine.

14. The method of claim 13, wherein said organic metal compound is
5 an organic tin compound selected from the group consisting of: a tin(II) salt of an organic carboxylic acid, dialkyltin(IV) salt of an organic carboxylic acid and a mixture thereof.

15. The method of claim 14, wherein said organic metal compound is
10 selected from the group consisting of: tin(II) acetate, tin(II) dioctoate, tin(II) ethylhexoate, tin(II) laurate, dibutyltin(IV) diacetate, dibutyltin(IV) dilaurate and a mixture thereof.

16. The method of claim 13, wherein said strong basic amine is selected
15 from the group consisting of: 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine, triethylamine, tributylamine, dimethylbenzylamine, N-methylmorpholine, N-ethylmorpholine, N-cyclohexylmorpholine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylbutanediamine, pentamethyldiethylenetriamine, tetramethyldiaminoethyl ester, bis(dimethylaminopropyl) urea, dimethylpiperazine,
20 1,2-di-methylimidazole, 1-aza-bicyclo-[3.3.0]octane, 1,4-diaza-bicyclo[2.2.2]octane, triethanolamine, triisopropanolamine, N-methyldiethanolamine, N-ethyldiethanolamine, dimethylethanolamine, tris(dialkylamino)-s-hexahydrotriazines, tris(N,N-dimethylaminopropyl)-s-hexahydrotriazine and a mixture thereof.

25

17. The method of claim 1, wherein the equivalent ratio of isocyanate groups in (a) to the total active hydrogen groups in (b) and (c) is from about 1:0.85 to 1:1.25.

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18. The method of claim 1, wherein said molded article is substantially



free of unreacted isocyanate.

19. The method of claim 1, further comprising an additive, said additive is selected from the group consisting of: a surface active substance, a foam
5 stabilizer, a cell regulator, a filler, a dye, a pigment, a flame retardant, a hydrolysis preventing agent, a fungistatic, a bacteriostatic agent and a mixture thereof.
20. A molded article prepared by the process of claim 1.
- 10 21. A process for preparation of integral skin flexible foam, comprising: preparing a mixture which comprises:
- (a) an organic and/or modified organic polyisocyanate;
 - (b) at least one higher molecular weight compound having at least two reactive hydrogen atoms;
 - 15 (c) optionally, a lower molecular weight chain extending agent and/or crosslinking agent;
 - (d) a blowing agent comprising high purity cyclopentane; and
 - (e) a catalyst capable of forming an integral skin flexible foam; and
 - 20 reacting said mixture at a temperature, pressure and for a length of time sufficient to produce an integral skin flexible foam.
22. An article in the form of integral skin flexible foam prepared by the process of claim 21.
- 25 23. A process for preparation of a cellular elastomer which comprises: preparing a mixture which comprises:
- (a) an organic and/or modified organic polyisocyanate;
 - (b) at least one higher molecular weight compound having at least two reactive hydrogen atoms;
 - 30 (c) optionally, a lower molecular weight chain extending agent and/or





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crosslinking agent;

(d) a blowing agent comprising high purity cyclopentane; and

(e) a catalyst capable of forming a cellular elastomer; and

reacting said mixture at a temperature, pressure and for a length of time

5 sufficient to produce a cellular elastomer.

24. An article in the form of a cellular elastomer prepared by the
process of claim 23.

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