

Flüssiges Kohlendioxid enthaltende Treibmittel

Beschreibung

Die Erfindung betrifft flüssiges Kohlendioxid enthaltende Treibmittel sowie deren Verwendung in Verfahren zur Herstellung geschäumter Kunststoffe.

Die Erfindung betrifft auch Treibmittelzusammensetzungen, welche zur Herstellung von Ein- oder Mehrkomponenten-Polyurethanschaumstoffen aus Druckbehältern geeignet sind.

Der Einsatz von Fluorchlorkohlenwasserstoffen (FCKWs) als Treibmittel bei der Herstellung geschäumter Kunststoffe ist aus ökologischen Gründen nicht mehr wünschenswert. Als Ersatzstoffe sind bisher auch gasförmige Substanzen, wie z. B. Kohlendioxid, vorgeschlagen worden. Kohlendioxid als gasförmiges physikalisches Treibmittel hat aber den Nachteil, daß es sich aufgrund seiner relativ niedrigen kritischen Temperatur bei der während der Produktion von Kunststoffschäumen herrschenden Bedingungen nur recht schwierig dosieren läßt. Weiterhin führt der Einsatz von Kohlendioxid nach bisher bekannten Verfahren zumeist zu offenzelligen Schaumstoffen mit einem unerwünscht hohen Wasseraufnahmevermögen und einer oft noch unbefriedigenden Wärmedämmung. Auch ist bisher die Herstellung geschäumter Kunststoffe mit vorwiegend geschlossenen Zellen bei der Verwendung von Kohlendioxid als alleinigem Treibmittel oder als Co-Treibmittel in Kombination mit anderen physikalischen Treibmitteln noch mit Schwierigkeiten verbunden.

Einkomponenten- bzw. Mehrkomponenten-Polyurethanschäume, die aus einem Druckbehälter, z. B. einer Sprühdose, abgegeben werden, werden hauptsächlich zur Aufschäumung von Hohl- oder Zwischenräumen im Bauwesen oder im Automobilbau eingesetzt. Beim sogenannten Einkomponenten-Polyurethanschaum (nachfolgend 1K-PUR-Schaum genannt) wird eine Polyolvormischung zusammen mit einem Überschuß an Di- und/oder Polyisocyanat in Gegenwart eines Katalysators und gegebenenfalls weiterer Hilfs- und Zusatzstoffe in einem Druckbehälter zu einem Isocyanatgruppen enthaltenden Prepolymer umgesetzt. Durch Betätigung des Sprühventils des Druckbehälters wird das Prepolymer durch ein Treibmittel aus der Dose herausgedrückt, wobei es zu einer spontanen Aufschäumung des Prepolymers kommt. Durch Reaktion der noch vorhandenen Isocyanatgruppen mit der Luftfeuchtigkeit entsteht ein weitgehend geschlossenzelliger Hartschaum.

Beim Zweikomponentenpolyurethanschaum (nachfolgend 2K-PUR-Schaum genannt) benötigt man zum Aushärten des Prepolymer-Schaumes eine weitere Hydroxygruppen tragende Komponente, z. B. ein Polyol, welches erst unmittelbar vor der Schaumbildung zugesetzt wird. Üblicherweise befindet sich dieses Polyol im Druckbehälter in einem von den übrigen Komponenten abgetrennten Füllraum und wird durch Betätigung des Sprühventils erst unmittelbar vor Austritt aus dem Druckbehälter der prepolymeren Komponente zugesetzt.

Die meisten für die Anwendung aus Druckbehältern eingesetzten Prepolymere für PUR-Schäume besitzen eine sehr hohe Viskosität, so daß die eingesetzten Treibmittel gute Lösungseigenschaften besitzen sollten, um die Komponenten problemlos aus dem Druckbehälter heraus verschäumen zu können. Der Einsatz von Fluorchlorkohlenwasserstoffen (FCKWs) als Treibmittel für derartige Anwendungen ist aus ökologischen Gründen nicht mehr wünschenswert. Viele der bisher vorge-

schlagenen Ersatzstoffe zeigen noch anwendungstechnische Nachteile wie z. B. eine noch unbefriedigende Wärmedämmung oder zu geringe Verdampfungsgeschwindigkeit.

Aufgabe der Erfindung war es daher, neue Verfahren zur Herstellung geschäumter Kunststoffe, und auch für die Erzeugung von PUR-Schäumen aus Druckbehältern, zur Verfügung zu stellen, welche die bisherigen Nachteile des Standes der Technik überwinden. Eine weitere Aufgabe bestand darin, für diese Verfahren neue Treibmittelzusammensetzungen zur Verfügung zu stellen.

Überraschend wurde nun gefunden, daß Zusammensetzungen, welche neben mindestens einer weiteren flüssigen Komponente Kohlendioxid in flüssiger Form enthalten, sich als Treibmittelzusammensetzungen in Verfahren zur Herstellung geschäumter Kunststoffe eignen. Treibmittelzusammensetzungen, welche verflüssigtes Kohlendioxid enthalten, eignen sich auch zur Erzeugung von PUR-Schäumen aus Druckbehältern.

Gegenstand der Erfindung sind Treibmittelzusammensetzungen, die 0,5 bis 50 Gew.-% flüssiges CO₂ enthalten. Bevorzugte Treibmittelzusammensetzungen enthalten 5 bis 50 Gew.-% flüssiges CO₂, insbesondere 10 Gew.-% bis 50 Gew.-%.

Zusätzlich zum flüssigen CO₂ ist mindestens eine weitere flüssige oder druckverflüssigte Komponente enthalten. Diese weitere flüssige Komponente oder die weiteren flüssigen Komponenten stellen vorzugsweise den Rest auf 100 Gew.-% der Treibmittelzusammensetzung dar. Bei der oder den weiteren flüssigen Komponenten kann es sich beispielsweise um flüssige oder druckverflüssigte physikalische Treibmittel und/oder um flüssige Flammenschutzmittel, beispielsweise aus der Gruppe der Phosphatester oder Phosphonsäureester, handeln. Außerdem können zusätzlich auch noch bekannte Zusatz- und Hilfsstoffe wie

Stabilisatoren oder Weichmacher enthalten sein.

Ein weiterer Gegenstand der Erfindung ist ein Verfahren zur Herstellung geschäumter Kunststoffe mit Hilfe von Treibmitteln, bei dem man eine flüssige Treibmittelzusammensetzung einsetzt, welche 0,5 bis 50 Gew.-%, vorzugsweise 5 bis 50 Gew.-%, insbesondere 10 bis 50 Gew.-%, ganz besonders 10 bis 20 Gew.-%, verflüssigtes Kohlendioxid enthält.

Verflüssigtes Kohlendioxid im Sinne der Erfindung kann nach allen an sich bekannten Verfahren zur Gasverflüssigung, vorzugsweise durch Druckverflüssigung erhalten werden.

Kohlendioxid ist bei Raumtemperatur unter Normaldruck ($1,01325 \cdot 10^5 \text{ Pa}$) ein farbloses Gas, welches sich durch Anwendung eines Druckes von 56,5 atm ($= 5,72486 \cdot 10^6 \text{ Pa}$) bei 20 °C zu einer farblosen, leicht beweglichen Flüssigkeit druckverflüssigen läßt. Verfahren zur Druckverflüssigung von Kohlendioxid sind allgemein bekannt.

Eine Ausführungsform der vorliegenden Erfindung bezieht sich auf die Herstellung von geschäumten Kunststoffen, beispielsweise durch das Gieß- oder Extrusionsverfahren. Eine andere Ausführungsform der Erfindung, die später erläutert wird, betrifft speziell die Herstellung von Ein- oder Zweikomponenten-Polyurethanschaumstoffen aus Druckbehältern (PUR = Polyurethan). Im folgenden wird zunächst die erstgenannte Ausführungsform näher erläutert.

Als weitere flüssige Komponenten neben dem druckverflüssigten Kohlendioxid sind bei der Herstellung geschäumter Kunststoffe alle üblichen flüssigen physikalischen Treibmittel, nämlich leichtflüchtige organische Verbindungen wie Ether, z. B. Diethylether, Ketone wie Aceton, Kohlenwasserstoffe wie Pentan, Hexan, Heptan, Benzingerichte, halogenhal-

tige Kohlenwasserstoffe oder halogenhaltige Ether verwendbar. Auch unter Druck verflüssigte Gase wie z. B. Propan oder Butan können neben dem verflüssigten Kohlendioxid eingesetzt werden. Weiterhin kommt als flüssige Treibmittelkomponente Wasser in Frage.

Bevorzugt setzt man zur Herstellung geschäumter Kunststoffe eine Treibmittelzusammensetzung ein, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 30 bis 90 Gewichtsteile mindestens eines flüssigen oder unter Druck verflüssigten physikalischen Treibmittels aus der Gruppe Alkohole mit 1 bis 5 Kohlenstoffatomen, aliphatische Kohlenwasserstoffe mit 2 bis 12 Kohlenstoffatomen, cyclische Kohlenwasserstoffe mit 3 bis 12 Kohlenstoffatomen, halogenhaltige Kohlenwasserstoffe mit 1 bis 5 Kohlenstoffatomen oder halogenhaltige Ether mit insgesamt 2 bis 6 Kohlenstoffatomen enthält oder daraus besteht, ein. Als Alkohole sind dabei insbesondere Ethanol und Isopropanol bevorzugt. Beispiele für aliphatische Kohlenwasserstoffe sind Pentan, Hexan, Heptan sowie Benzinfraktionen, insbesondere Leichtbenzine mit einem Siedepunkt im Bereich von 15 bis 80 °C. Ferner können auch als flüssige Treibmittelkomponente die niedersiedende Fraktionen, wie z. B. Propan und/oder Butan, druckverflüssigt eingesetzt werden. Beispiele für cyclische Kohlenwasserstoffe sind cycloaliphatische Kohlenwasserstoffe, vorzugsweise Cyclopropan, Cyclopentan und Cyclohexan. Unter halogenhaltigen Kohlenwasserstoffen werden Wasserstoff enthaltende Fluorchlor- oder Fluorkohlenwasserstoffe verstanden. Als Fluorchlorkohlenwasserstoffe sind z. B. Chlordifluormethan (R22), Trifluormethan (R23), 1,1-Dichlor-1-fluorethan (R141b), 1-Chlor-1,1-difluorethan (R142b) oder 1,3-Dichlor-1,1,2,2,3,3-Hexafluorpropan (R216a) einsetzbar. Beispiele für Fluorkohlenwasserstoffe sind Pentafluorethan (R125), 1,1,1,2-Tetrafluorethan (R134a), 1,1,1-Trifluorethan (R143a), 1,1,2-Trifluorethan (R143), 1,1-Difluorethan (R152a), 1,1,1,3,3-Pentafluor-

propan (R245fa) Octafluorpropan (R218), oder auch 1,1,1,3,3-Pentafluorbutan (R365mfc). Unter halogenhaltigen Ethern werden Wasserstoff enthaltende Fluorchlor- oder Fluorether, wie z. B. Difluormethoxy-2,2,2-trifluorethan (E245) verstanden.

Vorzugsweise wird eine Treibmittelzusammensetzung eingesetzt, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 30 bis 90 Gewichtsteile mindestens eines halogenhaltigen Kohlenwasserstoffes oder eines aliphatischen Kohlenwasserstoffes oder eines halogenhaltigen Ethers enthält oder aus dem genannten Gemisch besteht.

Besonders bevorzugt wird in dem erfindungsgemäßen Verfahren eine Treibmittelzusammensetzung eingesetzt, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 30 bis 90 Gewichtsteile 1,1-Difluorethan (R152a) und/oder 30 bis 90 Gewichtsteile 1,1-Dichlor-1-Fluorethan (R141b) enthält oder daraus besteht. Weitere besonders bevorzugt im erfindungsgemäßen Verfahren eingesetzte Treibmittelzusammensetzungen sind Treibmittelzusammensetzungen, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 80 bis 90 Gewichtsteile 1,1-Dichlor-1-Fluorethan (R141b) sowie gegebenenfalls zusätzlich noch 1 bis 3 Gewichtsteile Wasser enthalten oder aus dem genannten Gemisch bestehen. Ebenfalls besonders bevorzugt ist eine Treibmittelzusammensetzung, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid, 50 bis 70 Gewichtsteile 1,1-Difluorethan (R152a) und 20 bis 35 Gewichtsteile Ethanol enthält oder aus dem Gemisch besteht. Unter den halogenhaltige Ether enthaltenden erfindungsgemäßen Zusammensetzungen sind solche Treibmittelzusammensetzungen besonders bevorzugt, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 80 bis 90 Gewichtsteile Difluormethoxy-2,2,2-Trifluorethan (E245) enthalten oder aus solchen Gemischen bestehen. Von den aliphatischen Kohlenwasserstoffen ist besonders n-Pentan bevorzugt. Vorzugsweise sollte eine alipha-

tische Kohlenwasserstoffe enthaltende erfindungsgemäße Zusammensetzung 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 80 bis 90 Gewichtsteile n-Pentan sowie gegebenenfalls zusätzlich noch 1 bis 3 Gewichtsteile Wasser enthalten oder aus einem solchen Gemisch bestehen.

Bei all diesen Treibmittelgemischen kann durch Einsatz des flüssigen CO₂ die Einsatzmenge an den anderen Treibmitteln reduziert werden. CO₂ ist physiologisch unbedenklich und umweltverträglich.

Zweckmäßigerweise wird das erfindungsgemäße Verfahren zur Herstellung geschäumter Kunststoffe als Gießverfahren oder Extrusionsverfahren durchgeführt. Beim Extrusionsverfahren werden für die Herstellung von geschäumten Kunststoffen geeignete Mischungen direkt zu geschäumten Platten, Folien, Formkörpern, Profilen oder Partikeln extrudiert. Besonders bevorzugt werden erfindungsgemäß geschäumte thermoplastische Kunststoffe, insbesondere Polyethylen-, Polypropylen- oder Polystyrolschaumstoffe hergestellt. Erfindungsgemäß wird das Verfahren dabei so durchgeführt, daß man in eine Schmelze der zur Herstellung geschäumter Kunststoffe geeigneten Ausgangsprodukte die Treibmittelzusammensetzung aus verflüssigtem Kohlendioxid und einem weiteren flüssigen physikalischen Treibmittel zumischt und die Polymerisation der Ausgangsprodukte für den herzustellenden geschäumten Kunststoff gegebenenfalls unter Aufrechterhaltung eines schwachen Über- oder Unterdruckes während des Aufschäumvorganges durchführt. Für das erfindungsgemäße Verfahren können dabei an sich bekannte Verarbeitungsanlagen, z. B. Extruderanlagen eingesetzt werden. Besonders überraschend ist es dabei, daß es mit dem erfindungsgemäßen Verfahren möglich ist, Kohlendioxid in verflüssigtem Zustand auch bei erhöhter Temperatur, in den Extruder zum Zwecke der Aufschäumung thermoplastischer Polymer-schmelzen einzubringen. Im Gegensatz zu den bisher bekannten

Verfahren des Standes der Technik ist damit eine problemlose Dosierung des Kohlendioxids möglich. Nach dem erfindungsgemäßen Verfahren gelingt es damit unter Verwendung von Kohlendioxid vorwiegend geschlossenzellige Schaumstoffe von sehr gleichmäßiger feinzelliger Struktur herzustellen. Außerdem zeichnen sich die nach dem erfindungsgemäßen Verfahren erhaltenen geschäumten Kunststoffe durch ein hohes Wärmeisolierungsvermögen aus.

Das erfindungsgemäße Verfahren zur Herstellung geschäumter Kunststoffe kann dabei so durchgeführt werden, daß man eine in einem Druckbehälter vorkonfektionierte Treibmittelzusammensetzung einsetzt, welche hergestellt wurde, indem man in einem Druckbehälter das flüssige oder unter Druck verflüssigte physikalische Treibmittel in den gewünschten Gewichtsteilen vorlegt und auf an sich bekannte Weise druckverflüssigtes Kohlendioxid in der gewünschten Menge hineindrückt. Es kann nach dem erfindungsgemäßen Verfahren aber auch so vorgegangen werden, daß man die einzusetzende Treibmittelzusammensetzung erst unmittelbar vor dem Aufschäumvorgang der zu verschäumenden Polymere oder polymerisierbaren Komponenten herstellt. Hierbei wird in den entsprechenden Mengen in einem Druckgefäß außerhalb der eigentlichen Extruderanlage verflüssigtes Kohlendioxid in die weitere flüssige Treibmittelkomponente unter einem Druck, unter welchem Kohlendioxid im flüssigen Zustand vorliegt, eingeleitet, wobei sich die Komponenten weitgehend vermischen. Die so erhaltene homogene Mischung aus verflüssigtem Kohlendioxid und flüssiger Treibmittelkomponente wird dann über einen Einlaß für flüssige Treibmittel in die Extruderanlage eingeleitet.

Das erfindungsgemäße Verfahren eignet sich sowohl zur Herstellung offenzelliger wie geschlossenzelliger Hart- oder Weichschaumstoffe. Besonders geeignet ist das Verfahren zur Herstellung von geschäumten Polyurethan-Kunststoffen. Hierfür

können an sich bekannte PUR-Verarbeitungsanlagen, z. B. Hochdruck- bzw. Niederdruckvermischungsanlagen, welche mit dem nach dem Stand der Technik bekannten statischen Mischern ausgerüstet sind, eingesetzt werden.

In einer Variante zur Herstellung von geschäumten PUR-Kunststoffen können die erfindungsgemäßen Treibmittel neben druckverflüssigtem Kohlendioxid und einem oder mehreren flüssigen und/oder unter Druck verflüssigten physikalischen Treibmitteln noch weitere flüssige Zusatzmittel, z. B. Flamm- schutzmittel, als eine weitere Komponente enthalten. Übliche Flammenschutzmittel sind z. B. Phosphatester oder Phosphonate. Besonders gut geeignet sind entsprechende Phosphatester bzw. Phosphonester, die drei Niedrigalkylgruppen bzw. drei, durch ein oder mehrere Halogenatome substituierte Niedrigalkylgruppen aufweisen. Niedrigalkyl bedeutet vorzugsweise C₁- bis C₄- Gruppen. Geeignet sind z. B. Tris-chlorisopropylphosphat, Trichlorisopropylphosphat, Tris-chlorethylphosphat, Trichlor- ethylphosphat, Trichlorpropylphosphat, Tris-chlorpropylphosphat, Triethylphosphat, Dimethylethylphosphat, Tris-dichlor- isopropylphosphat oder Dimethylmethylethylphosphonat.

Wird das erfindungsgemäße Verfahren zur Herstellung geschäumter PUR-Kunststoffe eingesetzt, so können hierbei alle üblichen Schaumrohstoffe wie z. B. aliphatische, cycloaliphatische oder aromatische Di- oder Polyisocyanate eingesetzt werden. Beispiele für Schaumrohstoffe sind z. B. 2,4- und 2,6-Toluylendiisocyanat, Diphenylmethandiisocyanat, Polymethylenpolyphenylisocyanat und Mischungen davon. Es können auch Carbodiimidgruppen, Urethangruppen, Allophanatgruppen, Isocyanuratgruppen, Harnstoffgruppen oder Biuretgruppen enthaltene Polyisocyanate, die man als "modifizierte Polyisocyanate" oder "Isocyanat-Prepolymere" bezeichnet, verwendet werden. Bei der Herstellung von geschäumten PUR-Kunststoffen werden Polyisocyanate üblicherweise mit Verbindungen umge-

setzt, die mindestens zwei gegenüber Isocyanatgruppen reaktionsfähige Wasserstoffatome enthalten, beispielsweise Hydroxylgruppen aufweisende Verbindungen auf Polyester-, Polyether- und Aminbasis, sowie Amino- und/oder Carboxyl- und/oder Thiolgruppen aufweisende Verbindungen. Weiterhin können alle bei der Herstellung von geschäumten PUR-Kunststoffen eingesetzten Katalysatoren wie z. B. tertiäre Amine und/oder organische Metallverbindungen wie beispielsweise Zinnsalze von Carbonsäuren eingesetzt werden.

Wird das erfindungsgemäße Verfahren zur Herstellung von Polystyrol- oder Polyethylen-Schaumstoffen eingesetzt, können auch hierfür alle an sich bekannten Schaumrohstoffe verwendet werden.

Auf an sich bekannte Weise können dabei zusätzlich zu den Polymeren und/oder polymerisierbaren Bestandteilen alle an sich bekannte Zusatz- oder Hilfsstoffe, beispielsweise Nuklisierungsmittel, Porenreglersubstanzen, Flammenschutzmittel, Antistatika, Stabilisatoren, Weichmacher, Vernetzungsmittel, Füllstoffe oder Farbstoffe beigelegt sein.

Eine weitere Ausführungsform der Erfindung betrifft die Herstellung von Ein- oder Mehrkomponenten-PUR-Schaumstoffen aus Druckbehältern und wird im folgenden erläutert. Auch hier verwendet man eine Treibmittelzusammensetzung, die 0,5 bis 50 Gew.-% verflüssigtes CO₂ enthält.

Unter Treibmittelzusammensetzung wird der im Druckbehälter eingeschlossene flüssige Anteil der Treibmittelzusammensetzung, einschließlich der sich im Druckbehälter befindlichen Gasphase verstanden.

Die Treibmittelzusammensetzung enthält bei dieser Variante neben dem flüssigen CO₂ mindestens eine weitere

flüssige Komponente. Als weitere flüssige Komponente kann beispielsweise ein flüssiges oder druckverflüssigtes physikalisches Treibmittel enthalten sein. Halogenhaltige Treibmittel sind gut geeignet, halogenfreie Treibmittel sind oft umweltverträglich und vorzuziehen. Gemäß einer besonders vorteilhaften Variante ist flüssiges CO₂ als einziges Treibmittel enthalten, die flüssige weitere Komponente wird durch ein flüssiges Flammenschutzmittel aus der Gruppe der Ester der Phosphorsäure oder der Ester der Phosphonsäure gebildet.

Als weitere flüssige Komponenten neben dem druckverflüssigten Kohlendioxid sind alle üblichen flüssigen physikalischen Treibmittel, nämlich leichtflüchtige organische Verbindungen wie Ether, Aceton, Kohlenwasserstoffe wie Pentan, Heptan, Hexan, Benzingemische, halogenhaltige Kohlenwasserstoffe oder halogenhaltige Ether möglich. Auch unter Druck verflüssigte Gase wie z. B. Propan oder Butan können neben dem verflüssigten Kohlendioxid eingesetzt werden.

Vorzugsweise enthalten die erfindungsgemäßen Treibmittelzusammensetzungen mehr als 5 Gew-%, insbesondere 5 bis 50, z. B. 5 oder 10 bis 30 Gew-%, verflüssigtes Kohlendioxid.

Bevorzugt sind Treibmittelzusammensetzungen, welche 10 bis 50 Gewichtsteile verflüssigtes Kohlendioxid und 30 bis 90 Gewichtsteile mindestens eines flüssigen oder unter Druck verflüssigten Treibmittels aus der Gruppe der Ether mit insgesamt 2 bis 4 Kohlenstoffatomen, der Ketone mit 3 bis 5 Kohlenstoffatomen, der aliphatischen Kohlenwasserstoffe mit 2 bis 12 Kohlenstoffatomen, der halogenhaltigen Kohlenwasserstoffe mit 1 bis 5 Kohlenstoffatomen oder der halogenhaltigen Ether mit insgesamt 2 bis 6 Kohlenstoffatomen enthalten oder aus einem solchen Gemisch bestehen. Beispiele für aliphatische Kohlenwasserstoffe sind Pentan, Hexan, Heptan sowie Benzinfraktionen, insbesondere Leichtbenzine mit einem Siede-

punkt im Bereich von 15 bis 80 °C. Bevorzugt werden die niedersiedenden Fraktionen, wie z. B. Propan und/oder Butan, in druckverflüssigter Form eingesetzt. Beispiele für cyclische Kohlenwasserstoffe sind Cyclopropan, Cyclopentan und Cyclohexan. Unter halogenhaltige Kohlenwasserstoffen werden Wasserstoff enthaltende Fluorchlorkohlenwasserstoffe oder Fluorkohlenwasserstoffe verstanden. Als Fluorchlorkohlenwasserstoff sind z. B. Chlordifluormethan (R22), 1,1-Dichlor-1-fluorethan (R141b), 1-Chlor-1,1-difluorethan (R142b) oder 1,3-Dichlor-1,1,2,2,3,3-hexafluorpropan (R216a) möglich. Beispiele für Fluorkohlenwasserstoffe sind Trifluormethan (R23), Pentafluorethan (R125), 1,1,1,2-Tetrafluorethan (R134a), 1,1,1-Trifluorethan (R143a), 1,1,2-Trifluorethan (R143), 1,1-Difluorethan (R152a), 1,1,1,3,3-Pentafluorpropan (R245fa), Octafluorpropan (R218) oder 1,1,1,3,3-Pentafluorbutan (R365mfc). Unter halogenhaltigen Ethern werden Wasserstoff enthaltende Fluorchlor- oder Fluorether, wie z. B. Difluormethoxy-2,2,2-trifluorethan (E245) verstanden. Beispiele für mögliche Ether sind Dimethylether oder Diethylether. Von den Ketonen ist insbesondere Aceton bevorzugt.

Die erfindungsgemäßen Treibmittelzusammensetzungen können frei von halogenierten Treibmitteln sein und nur aus verflüssigtem Kohlendioxid als einziger Treibmittel-Komponente bestehen. Bevorzugt sind Abmischungen, die verflüssigtes Kohlendioxid in einer Menge von 20 bis 30 Gewichtsteilen und Butan oder ein Propan/Butan-Gemisch in einer Menge von 50 bis 60 Gewichtsteilen und/oder Aceton in einer Menge von 5 bis 15 Gewichtsteilen enthalten oder daraus bestehen. Als Propan/Butan-Gemisch kann ein an sich übliches Gemisch, beispielsweise ein Gemisch mit einem Dampfdruck von ca. 3,7 bar (abs.) verwendet werden.

Weiterhin bevorzugt sind erfindungsgemäße Treibmittelzusammensetzungen, welche 10 bis 50 Gewichtsteile verflüssig-

tes Kohlendioxid und 10 bis 90 Gewichtsteile eines halogenhaltigen Kohlenwasserstoffes oder eines halogenhaltigen Ethers, enthalten oder daraus bestehen. Besonders bevorzugt sind dabei Treibmittelzusammensetzungen, welche 10 bis 30 Gewichtsteile verflüssigtes Kohlendioxid und von den halogenhaltigen Kohlenwasserstoffen 10 bis 90 Gewichtsteile 1,1-Difluorethan (R152a) und/oder 1,1-Dichlor-1-fluorethan (R141b) enthalten oder daraus bestehen. Unter den halogenhaltige Ether enthaltenden erfindungsgemäßen Zusammensetzungen sind solche Treibmittelzusammensetzungen besonders bevorzugt, welche 15 bis 40 Gewichtsteile verflüssigtes Kohlendioxid und 10 bis 20 Gewichtsteile Difluormethoxy-2,2,2-trifluorethan (E245) enthalten oder daraus bestehen.

In einer anderen besonders bevorzugten Variante können die erfindungsgemäßen Treibmittel neben druckverflüssigtem Kohlendioxid als flüssige Komponente als Flammenschutzmittel gebräuchliche Phosphatester oder Phosphonate. Besonders gut geeignet sind Phosphat- bzw. Phosphonester, die drei C1- C4-Alkylgruppen, die gegebenenfalls doch ein oder mehrere Halogenatome substituiert sind, wie z. B. Trischlorisopropylphosphat, Trischlorethylphosphat, Trichlorethylphosphat, Trichlorpropylphosphat, Trischlorpropylphosphat, Triethylphosphat, Dimethylethylphosphat, Tris-dichlorisopropylphosphat oder Dimethylmethylethylphosphonate, enthalten. Zweckmäßigerweise liegen die Konzentrationen dabei bei 10 bis 50 Gewichtsteilen verflüssigtem Kohlendioxid und 80 bis 100 Gewichtsteilen Phosphatester oder Phosphonat. Bevorzugt setzt man Trischlorpropylphosphat ein. Diese besonders bevorzugten Treibmittelzusammensetzungen sind frei von anderen Treibmitteln als CO₂ und deshalb besonders umweltverträglich.

Die erfindungsgemäßen Treibmittelzusammensetzungen eignen sich zur Erzeugung von allen bisher bekannten PUR-Schäumen aus Druckbehältern, insbesondere zur Verschäumung 1K- und

2K-PUR-Schaumstoffen. Auch für die Herstellung von Mehrkomponenten-PUR-Schaumstoffen, bei denen die Schaumbildner mit mehr als einer reaktiven Komponente separat in einem Druckbehälter abgefüllt sind, können die erfindungsgemäßen Treibmittelzusammensetzungen eingesetzt werden. Auch zur Herstellung sogenannter 1,5 K-PUR-Schäume, bei denen im Gegensatz zu den 2K-Schäumen dem Prepolymer kurz vor dem Ausbringen eine zur Umsetzung der Isocyanatgruppen nicht ausreichende Menge einer Polyolkomponente zugesetzt wird, können die erfindungsgemäßen Treibmittelzusammensetzungen verwendet werden.

Als sehr vorteilhaft erweisen sich die erfindungsgemäßen Treibmittelzusammensetzungen zur Herstellung von 1K- oder 2K-PUR-Schaumstoffen.

In der zu verschäumenden 1K-PUR-Schaumstoffmischung können dabei auf an sich bekannte Weise eine Polyolkomponente, eine Polyisocyanatkomponente, ein Katalysator sowie gegebenenfalls noch als Hilfsstoff ein Flammenschutzmittel als weitere Bestandteile neben der erfindungsgemäßen Treibmittelzusammensetzung enthalten sein.

Als Polyolkomponente können z. B. Glycerin, Glykole oder Polyetherpolyole, die als Additionsprodukte von Propylenoxid oder Ethylenoxid an mehrwertige Alkohole, Wasser oder Ethylendiamin erhalten wurden, oder Polyesterpolyole, die als Polykondensationsprodukte aus Polyolen mit Dicarbonsäuren oder deren Anhydriden erhalten wurden, oder Gemische derselben in der 1K-PUR-Schaummischung enthalten sein. Eine typische Polyolkomponente kann z. B. ein Gemisch aus einem bromierten Polyetherpolyol (beispielsweise Diol oder Triol) mit einer Hydroxylzahl von 200 bis 350 und einem Polyetherpolyol (z. B. einem Diol) mit einer Hydroxylzahl von 110 sein. Weiterhin sind auch modifizierte Pflanzenöle mit einer OH-Zahl im Bereich von 100 bis 300, z. B. Rizinusöl, möglich.

Als Polyisocyanatkomponente können zum Beispiel Diphenylmethan-4,4'-diisocyanat, Diisocyanato-toluol, 1,5-Diisocyanato-naphthalin, Triisocyanato-triphenylmethan, 1,6-Diisocyanatohexan, vorzugsweise Diphenylmethan-4,4'-Diisocyanat, oder Gemische davon, eingesetzt werden.

Typische Katalysatoren in 1K-PUR-Schaummischungen, die im erfindungsgemäßen Verfahren mit einer erfindungsgemäßen Treibmittelzusammensetzung verschäumt werden können, sind organische Amine, Aminoalkohole oder Aminoether, z. B. 2-Dimethylaminoethyl-3-Dimethylaminopropylether, Diethanolamin, Dimethylcyclohexylamin, 2-Dimethylaminoethylether, oder Morphinverbindungen, wie z. B. 2,2-Dimorpholinodiethylether, N,N-Dimethylaminoethylmorpholin, N-Methylmorpholin. Bevorzugt sind die Morphinverbindungen, insbesondere 2,2-Dimorpholinodiethylether.

Als übliche Flammschutzmittel können Trischlorisopropylphosphat, Trichlorisopropylphosphat, Trischlorethylphosphat, Trichlorethylphosphat, Trischlorpropylphosphat, Trichlorpropylphosphat, Dimethylethylphosphat, Trisdichlorisopropylphosphat, Dimethylmethylphosphonat, Dimethylenethylphosphat vorzugsweise Trischlorpropylphosphat, eingesetzt werden.

Als Stabilisatoren sind z. B. Copolymere aus Siloxan geeignet.

Eine zu verschäumende 1K-PUR-Schaummischung enthält, bezogen auf die Schaummischung als 100 Gew.-%, beispielsweise 20 bis 30 Gew.-% einer Polyolkomponente, 40 bis 60 Gew.-% einer Polyisocyanatkomponente, 0,1 bis 3 Gew.-% Katalysator, gegebenenfalls 10 bis 15 Gew.-% eines Flammschutzmittels, gegebenenfalls 1 bis 2 Gew.-% Schaumstabilisator neben 15 bis 35 Gew.-% einer erfindungsgemäßen Treibmittelzusammensetzung. Eine typische 1K-PUR-Schaummischung, die sich vorteilhaft mit

Hilfe der erfindungsgemäßen Treibmittelzusammensetzung verschäumen läßt, besteht so beispielsweise aus ca. 22,5 Gew.-% einer Polyolkomponente, z. B. aus einem Gemisch eines bromierten Polyetherpolyols mit einer Hydroxylzahl von 200 bis 350 und einem Polyetherpolyol mit einer Hydroxylzahl von 110 im Mischungsverhältnis 1:1, ca. 42,5 Gew.-% einer Polyisocyanatkomponente, z. B. Diphenylmethan-4,4'-diisocyanat, ca. 0,5 Gew.-% einer Katalysatorsubstanz wie z. B. 2,2-Dimorpholinodiethylether, ca. 1,5 Gew.-% Silikonschaumstabilisator, ca. 13 Gew.-% eines Flammenschutzmittels wie z. B. Trischlorpropylphosphat, und einem Anteil von ca. 20 Gew.-% an einer erfindungsgemäßen Treibmittelzusammensetzung. Aus einer derartigen 1K-PUR-Schaummischung kann ein Einkomponentenschaumstoff mit einer gleichmäßigen feinzelligen Struktur und niedriger Rohdichte, z. B. mit einer Rohdichte von ca. 23 bis 25 kg/m³, hergestellt werden.

Von den Einkomponenten-Schaumstoffen unterscheiden sich die 1,5K- und 2K-PUR-Schaumstoffe dadurch, daß die zur Aushärtung des Schaumes benötigte Polyolkomponente im Druckbehälter getrennt von der Prepolymerzusammensetzung gehalten wird und erst unmittelbar vor der Verschäumung dem Prepolymer zugesetzt wird. Als zweite Komponente kommen dabei alle bereits genannten Polyolkomponenten in Frage. Zur schnelleren Aushärtung kann die zweite Komponente darüber hinaus einen üblichen Katalysator, beispielsweise die bereits genannten Amin- oder Morpholin-Verbindungen oder auch metallorganische Verbindungen, wie z. B. Zinndioctoat, Kobaltnaphtenat, Dibutylzinndilaurat oder Eisenacetylacetat, enthalten.

Die mit den erfindungsgemäßen Treibmittelzusammensetzungen hergestellten 1K- oder Mehrkomponenten-PUR-Schaumstoffe zeigen ein sehr gutes Wärmeisolierungsvermögen und sind daher gut für Dämmzwecke, z. B. im Bau- oder Wohnbereich, geeignet. Auch für die Herstellung von Sprühklebern auf Polyurethanba-

sis sind die erfindungsgemäßen Treibmittelzusammensetzungen geeignet.

Weiterhin umfaßt die Erfindung ein Verfahren zur Herstellung eines 1K- oder 2K-PUR-Schaumstoffes, bei dem man aus einem Druckbehälter, welcher eine PUR-Schaummischung aus einer Polyolkomponente, einem Isocyanatgruppen enthaltenen Prepolymer, einem Katalysator und gegebenenfalls weitere übliche Hilfsstoffe sowie eine der vorstehend beschriebenen Treibmittelzusammensetzungen enthält, einen PUR-Schaumstoff durch Entspannen des im Druckbehälter herrschenden Überdruckes auf Atmosphärendruck über ein Ventil erzeugt. Entsprechende Druckbehälter sowie für die Verschäumung geeignete Ventile sind allgemein bekannt.

Weiterhin betrifft die Erfindung 1K- oder Mehrkomponenten-PUR-Schaumstoffmischungen zur Erzeugung eines PUR-Schaumstoffes aus Druckbehältern, welche eine der vorstehend beschriebenen Treibmittelzusammensetzungen enthalten.

Ein weiterer Gegenstand der Erfindung ist ein Verfahren zur Herstellung einer Treibmittelzusammensetzung für die Erzeugung von PUR-Schaumstoffen aus Druckbehältern, bei dem man verflüssigtes Kohlendioxid als Treibmittelkomponente einsetzt. Bei dem erfindungsgemäßen Verfahren wird in einem Druckbehälter die flüssige oder unter Druck verflüssigte physikalische Treibmittelkomponente in den gewünschten Gewichtsteilen vorgelegt und auf an sich bekannte Weise verflüssigt, üblicherweise druckverflüssigt, Kohlendioxid in der gewünschten Menge hineingedrückt. In einen Druckbehälter (Aerosoldose), welcher bereits das Prepolymer und gegebenenfalls alle weiteren Komponenten enthält, kann anschließend diese erfindungsgemäßen hergestellte Treibmittelzusammensetzung in der gewünschten Menge injiziert werden. Die Menge an Kohlendioxid wird dabei nur durch den für Aerosoldosen er-

laubten Druck reglementiert (10 bis 18 bar).

Erfindungsgemäß ist es nunmehr möglich, PUR-Schaumstoff-Mischungen enthaltende Druckbehälter herzustellen, welche pro 1 kg-Dose ca. 20 bis 30 g Kohlendioxid enthalten können. Nach bisher verwendeten Verfahren, bei denen Kohlendioxid immer in gasförmiger Form eingesetzt wurde, war es bislang nur möglich, pro 1 kg-Dose nur ca. 3 bis 5 g Kohlendioxid einzubringen. In vorteilhafter Weise ist es erfindungsgemäß jetzt möglich, bei der Herstellung von PUR-Schaumstoffen aus Druckbehältern den Anteil an brennbarem physikalischen flüssigen oder unter Druck verflüssigtem Treibmitteln weiter zu reduzieren. Auch aus Kostengesichtspunkten ist eine Reduzierung der bisher üblichen flüssigen bzw. druckverflüssigten physikalischen Treibmittel äußerst vorteilhaft. Mit der erfindungsgemäßen Treibmittelzusammensetzung hergestellter 1K- oder Mehrkomponenten-PUR-Schaumstoffe besitzt eine vorwiegende geschlossenzellige sehr gleichmäßige feinzellige Struktur sowie ein sehr hohes Wärmeisolierungsvermögen. Dementsprechend eignen sich PUR-Schaumstoffe, welche mit einer erfindungsgemäßen Treibmittelzusammensetzung hergestellt wurden, besonders gut für Dämmzwecke im Bau- und Wohnbereich.

Die nachfolgenden Beispiele sollen die Erfindung näher erläutern, ohne sie jedoch in ihrem Umfang zu begrenzen.

Beispiele

1. Herstellung eines Polystyrol-Schaumstoffes

a) Verflüssigtes Kohlendioxid/R152a als Treibmittel:

Es wurden 200 kg Polystyrol (Schmelzindex 3,0-110) mit 2 kg Talkum als Nuklisierungsmittel vermischt und diese Mischung

in eine übliche Extruderanlage eindosiert und aufgeschmolzen. In die Schmelzzone des Extruders wurden über eine Einspritzdüse in die Polystyrolschmelze ca. 6 Gew.-% eines erfindungsgemäßen Treibmittels, bezogen auf Polystyrol, eindosiert. Die erfindungsgemäße Treibmittelzusammensetzung enthielt 14 Gewichtsteile verflüssigtes Kohlendioxid und 86 Gewichtsteile R152a. Der Dampfdruck dieser Treibmittelzusammensetzung betrug ca. 14 bar bei 20 °C.

In der Mischzone wurde die Polystyrolschmelze mit der erfindungsgemäßen Treibmittelzusammensetzung homogen vermischt und anschließend die erhaltene Mischung über eine Düse extrudiert. Man erhielt einen geschlossenzelligen Schaumstoff von gleichmäßiger, feinzelliger Struktur.

Es wurden sowohl Polystyrol-Schaumfolien als auch Polystyrol-Schaumplatten erfindungsgemäß hergestellt. Eine erfindungsgemäß hergestellte Polystyrol-Schaumfolie besaß eine Dichte von ca. 35 kg/m³, eine erfindungsgemäß hergestellte Polystyrol-Schaumplatte eine Dichte von ca. 33 kg/m³.

b) Verflüssigtes Kohlendioxid/R152a/Ethanol als Treibmittel:

Wie unter Beispiel 1 a) beschrieben, wurde in eine Polystyrolschmelze ca. 8,5 Gew.-% eines erfindungsgemäßen Treibmittels, bezogen auf Polystyrol, eindosiert. Die erfindungsgemäße Treibmittelzusammensetzung enthielt 14 Gewichtsteile verflüssigtes Kohlendioxid, 57 Gewichtsteile R152a und 29 Gewichtsteile Ethanol. Der Dampfdruck dieser Treibmittelzusammensetzungen betrug ca. 15 bar bei 20 °C.

Eine erfindungsgemäß hergestellte Polystyrol-Schaumfolie besaß eine Dichte von ca. 36 kg/m³, eine erfindungsgemäß hergestellte Polystyrol-Schaumplatte eine Dichte von ca. 34 kg/m³.

2. Herstellung eines Polyethylen-Schaumstoffes

a) Verflüssigtes Kohlendioxid/R152a/R141b als Treibmittel:

200 g Polyethylen (Schmelzindex 3,5-150) wurden unter identischen Bedingungen, wie in Beispiel 1 für Polystyrol-Schaumstoff beschrieben, extrudiert. Es wurden ca. 6 Gew.-% einer Treibmittelmischung, bezogen auf Polyethylen, eindosiert. Erfindungsgemäß wurde eine Treibmittelzusammensetzung aus 14 Gewichtsteilen verflüssigtem Kohlendioxid, 50 Gewichtsteilen R152a und 36 Gewichtsteilen R141b eingesetzt. Es wurde ein feinzelliger Polyethylen-Schaumstoff mit geringer Schrumpfung erhalten. Das erfindungsgemäß hergestellte Polyethylen-Schaumrohr wies eine Dichte von ca 40 kg/m³ auf.

3. Herstellung eines PUR-Schaumstoffes

Zur Herstellung des PUR-Schaumstoffes wurde als eine der Ausgangskomponenten eine Polyolmischung, bestehend aus 40 Gewichtsteilen eines Ethylendiamin/Propylenoxid-Polyethers (OH-Zahl 480), 60 Gewichtsteile eines Sorbitol/Glycerin/Propylenoxid-Polyethers (OH-Zahl 490), 1 Gewichtsteil Schaumstabilisator (Typ DC193 der Dow Corning Corporation) und 1,5 Gewichtsteile Dimethylcyclohylamin eingesetzt. Diphenylmethandiisocyanat wurde als Isocyanatkomponente in einer um 10 Gew.-% erhöhten stöchiometrischen Menge eingesetzt. Die PUR-Schaumstoffe wurden auf einer Niederdruckanlage mit einer Austragleistung von ca. 8 kg/min, mit der eine Dosierung von 3 Komponenten möglich ist, hergestellt. Als Mischaggregat diente ein statischer Mischer.

a) Verflüssigtes Kohlendioxid/R141b/Wasser als Treibmittel:

Erfindungsgemäß wurde eine Treibmittelzusammensetzung in ei-

ner Menge von 30 Gewichtsteilen eingesetzt. Die Treibmittelzusammensetzung bestand aus 13,9 Gewichtsteilen verflüssigtem Kohlendioxid, 85,1 Gewichtsteilen R141b und zusätzlich 1 Gewichtsteil Wasser. Mit dieser erfindungsgemäßen Treibmittelzusammensetzung wurde ein PUR-Hartschaumstoff mit einer feinzelligen Struktur und einer Dichte von ca. 24 kg/m³ hergestellt.

b) Verflüssigtes Kohlendioxid/n-Pentan/Wasser als Treibmittel:

Weiterhin wurde ein PUR-Schaumstoff mit 18 Gewichtsteilen einer Treibmittelzusammensetzung hergestellt. Diese Treibmittelzusammensetzung bestand erfindungsgemäß aus 13,9 Gewichtsteilen verflüssigtem Kohlendioxid und 85,1 Gewichtsteilen n-Pentan und zusätzlich 1 Gewichtsteil Wasser. Mit dieser Treibmittelzusammensetzung wurde ein PUR-Hartschaumstoff mit einer feinzelligen Struktur und einer Dichte von ca. 25,4 kg/m³ erhalten.

c) Verflüssigtes Kohlendioxid/E245 als Treibmittel:

Weiterhin wurde ein PUR-Schaumstoff mit 35 Gewichtsteilen einer Treibmittelzusammensetzung hergestellt. Diese Treibmittelzusammensetzung bestand erfindungsgemäß aus 14 Gewichtsteilen verflüssigten Kohlendioxid und 85 Gewichtsteilen E245. Mit dieser Treibmittelzusammensetzung wurde ein PUR-Hartschaum mit einer feinzelligen Struktur und einer Dichte von ca. 33,5 kg/m³ erhalten.

4. Verflüssigtes Kohlendioxid/Propan/Butan/Aceton als Treibmittel für 1K-PUR-Schaumstoffe:

a) 247 g einer Polyolvormischung, bestehend aus

73 g Polyetherpolyol (Diol), bromiert, Hydroxidzahl
ca. 240,

73 g Polyetherpolyol (Diol), Hydroxidzahl ca. 110,

89 g Trischlorpropylphosphat,

5 g Silikonschaumstabilisator,

7 g Dimorpholindiethylether,

wurden in eine Aerosoldose aus Aluminium mit einem Volumen von 1000 cm³ eingefüllt. Es wurden 356 g Diphenylmethan-4,4-Diisocyanat zugegeben und die Aerosoldose mit einem Schaumaerosolventil verschlossen. Eine erfindungsgemäße Treibmittelzusammensetzung wurde hergestellt, indem in einem Druckgefäß 62 g druckverflüssigtes Propan/Butan und 10 g Aceton vorgelegt und 28 g druckverflüssigtes Kohlendioxid unter Mischen zugegeben wurde. 99 g dieser erfindungsgemäßen Treibmittelzusammensetzung wurden dann über eine übliche Aerosolabfüllvorrichtung in die die Schaumkomponenten enthaltende Aerosoldose injiziert. Die Aerosoldose wurde kurzfristig geschüttelt und für ca. 24 Stunden zur Ausbildung des Prepolymers stehengelassen. Nach Ablauf dieser Zeit war die 1K-PUR-Schaumstoffmischung zur Anwendung gebrauchsfertig.

Die 1K-PUR-Schaummischung wurde mittels der erfindungsgemäßen Treibmittelzusammensetzung aus der Aerosoldose ausgetrieben. Man erhielt einen PUR-Schaumstoff mit einer Rohdichte von ca. 23 kg/m³ von gleichmäßiger, feinzelliger Struktur. Die Schrumpfung des PUR-Schaumstoffes nach einer Lagerung von 7 Tagen bei einer Luftfeuchtigkeit von ca. 90 % betrug im Mittel ca. 5 Längenprozent.

- b) Wie unter a) beschrieben, wurde eine Polyolabmischung und eine Polyisocyanat in eine Aerosoldose gleichen Volumens eingefüllt. Als erfindungsgemäße Treibmittelzusammensetzung wurde eine Zusammensetzung aus 50 g Propan/Butan,

7,5 g Aceton und 20 g verflüssigtem Kohlendioxid eingesetzt. Die Herstellung der Treibmittelzusammensetzung und die Abfüllung in die Aerosoldose erfolgte, wie unter a) beschrieben.

Der mit dieser erfindungsgemäßen Treibmittelzusammensetzung hergestellt PUR-Schaumstoff zeigte eine Rohdichte von ca. 25 kg/m³.

5. Verflüssigtes Kohlendioxid/Propan/Butan/R141b als Treibmittel für 1K-PUR-Schaumstoffe:

Eine Polyolabmischung und ein Polyisocyanat wurde, wie in Beispiel 4 beschrieben, in eine Aerosoldose mit einem Volumen von 1000 cm³ eingefüllt. Als erfindungsgemäße Treibmittelzusammensetzung wurde eine Zusammensetzung aus 62 g Propan/Butan, 10 g R141b und 28 g verflüssigtem Kohlendioxid eingesetzt. Die Herstellung der Treibmittelzusammensetzung und deren Abfüllung in die Aerosoldose erfolgte, wie in Beispiel 4 beschrieben.

Der mit dieser erfindungsgemäßen Treibmittelzusammensetzung hergestellte PUR-Schaumstoff zeigte eine Rohdichte von ca. 25 kg/m³.

6. Verflüssigtes Kohlendioxid/Trichlorpropylphosphat/R141b als Treibmittel für 1K-PUR-Schaumstoffe:

214 g einer Polyolabmischung und 356 g Polyisocyanat wurden, wie in Beispiel 4 beschrieben, in eine Aerosoldose mit einem Volumen von 1.000 cm³ eingefüllt. Eine erfindungsgemäße Zusammensetzung wurde hergestellt, indem 100 g Trischlorpropylphosphat und 10 g R141b in einem Druckgefäß vorgelegt und

28 g druckverflüssigtes Kohlendioxid unter Mischen zugegeben wurde. 99 g dieser Treibmittelzusammensetzung wurden, wie in Beispiel 4 beschrieben, in die Aerosoldose abgefüllt.



Patentansprüche

1. Treibmittelzusammensetzung zur Herstellung geschäumter Kunststoffe und zur Herstellung von Ein- oder Zweikomponenten-Polyurethanschaumstoffen aus Druckbehältern, dadurch gekennzeichnet, daß sie 0,5 bis 50 Gew.-% verflüssigtes Kohlendioxid enthält.

2. Treibmittelzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie 5 bis 50 Gew.-%, vorzugsweise 10 bis 50 Gew.-%, insbesondere 10 bis 20 Gew.-% verflüssigtes CO₂ enthält.

3. Treibmittelzusammensetzung nach Anspruch 1 oder 2 zur Herstellung geschäumter Kunststoffe, dadurch gekennzeichnet, daß sie 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 30 bis 90 Gewichtsteile mindestens eines flüssigen oder unter Druck verflüssigten physikalischen Treibmittels aus der Gruppe Alkohole mit 1 bis 5 Kohlenstoffatomen, der aliphatischen Kohlenwasserstoffe mit 2 bis 12 Kohlenstoffatomen, der cyclischen Kohlenwasserstoffe mit 3 bis 12 Kohlenstoffatomen, der halogenhaltigen Kohlenwasserstoffe mit 1 bis 5 Kohlenstoffatomen oder halogenhaltigem Ether mit insgesamt 2 bis 6 Kohlenstoffatomen enthält.

4. Treibmittelzusammensetzung nach Anspruch 1 oder 2 zur Herstellung von Ein- oder Zweikomponenten-Polyurethanschaumstoffen aus Druckbehältern, dadurch gekennzeichnet, daß sie 10 bis 50 Gewichtsteile verflüssigtes Kohlendioxid und 30 bis 90 Gewichtsteile mindestens eines flüssigen oder unter Druck verflüssigten Treibmittels aus der Gruppe der Ether mit insgesamt 2 bis 4 Kohlenstoffatomen, der Ketone mit 3 bis 5 Kohlenstoffatomen, der aliphatischen Kohlenwasserstoffe mit 2 bis 12 Kohlenstoffatomen, der cyclischen Kohlenwasserstoffe



mit 3 bis 12 Kohlenstoffatomen, der halogenhaltigen Kohlenwasserstoffe mit 1 bis 5 Kohlenstoffatomen oder der halogenhaltigen Ether mit insgesamt 2 bis 6 Kohlenstoffatomen enthält.

5. Treibmittelzusammensetzung nach Anspruch 1 oder 2 zur Herstellung von Ein- oder Zweikomponenten-Polyurethanschaumstoffen aus Druckbehältern, dadurch gekennzeichnet, daß sie 10 bis 50 Gewichtsteile verflüssigtes Kohlendioxid und 10 bis 100 Gewichtsteile mindestens eines Trialkylphosphates oder Trialkylphosphonates aus der Gruppe Triethylphosphat, Trichlorisopropylphosphat, Trischlorethylphosphat, Trischlorisopropylphosphat, Trischlorpropylphosphat, Trichlorethylphosphat, Trichlorpropylphosphat, Triethylphosphat, Dimethylethylphosphat, Trichlorisopropylphosphat, Dimethylmethylphosphonat Diethylmethylphosphonat oder Diethylethylphosphonat, vorzugsweise Trischlorpropylphosphat, enthält.

6. Halogenfreie Treibmittelzusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß sie 20 bis 30 Gewichtsteile verflüssigtes Kohlendioxid und 50 bis 60 Gewichtsteile Butan oder eines Propan/Butan-Gemisches und/oder 5 bis 15 Gewichtsteile Aceton enthält.

7. Treibmittelzusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß sie 20 bis 40 Gewichtsteile verflüssigtes Kohlendioxid und 10 bis 50 Gewichtsteile eines halogenhaltigen Kohlenwasserstoffes aus der Gruppe 1,1-Dichlor-1-fluorethan, Pentafluorethan oder 1,1-Difluorethan enthält.

8. Treibmittelzusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß sie 20 bis 40 Gewichtsteile verflüssigtes Kohlendioxid und 10 bis 50 Gewichtsteile Difluormethoxy-2,2,2-trifluorethan enthält.



9. Verfahren zur Herstellung geschäumter Kunststoffe mit Hilfe von Treibmitteln, dadurch gekennzeichnet, daß man eine flüssige Treibmittelzusammensetzung nach Anspruch 1, welche 0,5 bis 50 Gew.-% verflüssigtes Kohlendioxid enthält, einsetzt.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß man eine Treibmittelzusammensetzung, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 30 bis 90 Gewichtsteile mindestens eines flüssigen oder unter Druck verflüssigten Treibmittels aus der Gruppe Alkohole mit 1 bis 5 Kohlenstoffatomen, aliphatische Kohlenwasserstoffe mit 2 bis 12 Kohlenstoffatomen, cyclische Kohlenwasserstoffe mit 3 bis 12 Kohlenstoffatomen, halogenhaltige Kohlenwasserstoffe mit 1 bis 5 Kohlenstoffatomen oder halogenhaltige Ether mit insgesamt 2 bis 6 Kohlenstoffatomen enthält, einsetzt.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß man eine Treibmittelzusammensetzung, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 30 bis 90 Gewichtsteile mindestens eines aliphatischen oder halogenhaltigen Kohlenwasserstoffes oder halogenhaltigen Ethers enthält, einsetzt.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß man eine Treibmittelzusammensetzung, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 30 bis 90 Gewichtsteile 1,1-Difluorethan und/oder 30 bis 90 Gewichtsteile 1,1-Dichlor-1-fluorethan enthält, einsetzt.

13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß man eine Treibmittelzusammensetzung, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 80 bis 90 Gewichtsteile 1,1-Dichlor-1-fluorethan enthält, einsetzt.



14. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß man eine Treibmittelzusammensetzung, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid, 50 bis 70 Gewichtsteile 1,1-Difluorethan und 20 bis 35 Gewichtsteile Ethanol enthält, einsetzt.

15. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß man eine Treibmittelzusammensetzung, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 80 bis 90 Gewichtsteile Difluormethoxy-2,2,2-trifluorethan enthält, einsetzt.

16. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß man eine Treibmittelzusammensetzung, welche 10 bis 20 Gewichtsteile verflüssigtes Kohlendioxid und 80 bis 90 Gewichtsteile n-Pentan enthält, einsetzt.

17. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß man geschäumte Polyethylen-, Polystyrol- oder Poly-urethan-Kunststoffe herstellt.

18. Verfahren zur Herstellung eines Einkomponenten- oder Zweikomponenten-Polyurethanschaumstoffes, dadurch gekennzeichnet, daß man aus einem Druckbehälter, welcher ein Isocyanatgruppen enthaltendes Prepolymer, gegebenenfalls weitere übliche Hilfsstoffe sowie als Treibmittel eine Treibmittelzusammensetzung gemäß einem der Ansprüche 1 bis 2 oder 4 bis 8 enthält, einen Polyurethanschaumstoff durch Entspannen des im Druckbehälter herrschenden Überdruckes auf Atmosphärendruck über ein geeignetes Ventil erzeugt.

19. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß man eine Treibmittelzusammensetzung in einer Menge von 5 bis 40 Gew.-%, bezogen auf die Gesamtmischung aus Prepolymer und Treibmittelzusammensetzung, einsetzt.



20. Verfahren zur Herstellung einer Treibmittelzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß man in eine flüssige oder unter Druck verflüssigte weitere Komponente, vorzugsweise ein Treibmittel oder ein Flammenschutzmittel unter Druck verflüssigtes Kohlendioxid einleitet oder umgekehrt, sodaß die Treibmittelzusammensetzung 0,5 bis 50 Gew.-% flüssiges CO₂ enthält.

21. Zusammensetzung aus Prepolymer und Treibmittel zur Herstellung eines Einkomponenten- oder Zweikomponenten-Polyurethanschaumstoffes, dadurch gekennzeichnet, daß sie eine Treibmittelzusammensetzung gemäß einem der Ansprüche 1 bis 2 oder 4 bis 8 enthält.

22. Anordnung zur Herstellung eines Einkomponenten- oder Zweikomponenten-Polyurethanschaumstoffes, dadurch gekennzeichnet, daß sie ein Isocyanatgruppen enthaltendes Prepolymer und eine Treibmittelzusammensetzung gemäß einem der Ansprüche 1 bis 2 oder 4 bis 8 in einem mit einem Ventil versehenen Druckbehälter enthält.



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(54) Title: FOAMING AGENTS CONTAINING LIQUID CARBON DIOXIDE		
(54) Bezeichnung: FLÜSSIGES KOHLENDIOXID ENTHALTENDE TREIBMITTEL		
(57) Abstract		
The invention concerns a process for preparing foamed plastics, wherein a liquid foaming agent composition containing carbon dioxide liquefied under pressure is used. In addition to the carbon dioxide liquefied under pressure, all conventional liquid physical foaming agents such as alcohols, aliphatic or cyclical hydrocarbons, halogenous hydrocarbons or halogenous ethers can be used. The process is suitable in particular for preparing foamed polyethylene, polystyrene or polyurethane plastics. Foaming agent compositions containing carbon dioxide liquefied under pressure are also suitable for producing single or multi-component polyurethane foamed materials. In addition to the carbon dioxide liquefied under pressure all conventional liquid physical foaming agents such as ethers, ketones, aliphatic or cyclical hydrocarbons, halogenous hydrocarbons or halogenous ethers can be used. The invention further concerns a process for preparing these foaming agent compositions.		
(57) Zusammenfassung		
Beschrieben wird ein Verfahren zur Herstellung geschäumter Kunststoffe, bei dem man eine flüssige Treibmittelzusammensetzung einsetzt, welche unter Druck verflüssigtes Kohlendioxid enthält. Neben dem unter Druck verflüssigtem Kohlendioxid können dabei alle üblichen flüssigen physikalischen Treibmittel wie Alkohole, aliphatische oder cyclische Kohlenwasserstoffe, halogenhaltige Kohlenwasserstoffe oder halogenhaltige Ether verwendet werden. Das Verfahren eignet sich insbesondere für die Herstellung geschäumter Polyethylen-, Polystyrol- oder Polyurethan-Kunststoffe. Treibmittelzusammensetzungen, welche unter Druck verflüssigtes Kohlendioxid enthalten, eignen sich auch zur Erzeugung von Einkomponenten- oder Mehrkomponenten-Polyurethan-Schaumstoffen. Neben dem unter Druck verflüssigtem Kohlendioxid können auch hier alle üblichen flüssigen physikalischen Treibmittel wie Ether, Ketone, aliphatische oder cyclische Kohlenwasserstoffe, halogenhaltige Kohlenwasserstoffe oder halogenhaltige Ether eingesetzt werden. Weiterhin wird ein Verfahren zur Herstellung dieser Treibmittelzusammensetzungen beschrieben.		

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Foaming agents containing liquid carbon dioxide

Description

5 The invention relates to foaming agents containing liquid carbon dioxide and to the use thereof in methods for producing foamed plastics.

The invention also relates to foaming agent compositions which are suitable for the production of single-component or multi-component polyurethane foamed materials from pressurised vessels.

10 It is no longer desirable to use fluorochloro-hydrocarbons (FCHCs) as foaming agents in the production of foamed plastics for ecological reasons. Hitherto, substances which are also gaseous, such as carbon dioxide, have been proposed as substitutes.

15 However, carbon dioxide as gaseous physical foaming agent has the disadvantage that owing to its relatively low critical temperature under the conditions prevailing during the production of plastics foams it can be metered only with great difficulty.

20 Furthermore, the use of carbon dioxide using methods known hitherto for the most part results in open-celled foamed materials having an undesirably high water absorption capacity and heat insulation which is often still unsatisfactory. Also, hitherto the production of

25 foamed plastics with predominantly closed cells still involves difficulties when using carbon dioxide as the sole foaming agent or as co-foaming agent in combination with other physical foaming agents.

30 Single-component or multi-component polyurethane foams which are delivered from a pressurised vessel, e.g. an aerosol can, are mainly used for foaming cavities or

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interstices in the building or motor car industries. In so-called single-component polyurethane foam (hereafter referred to as 1C PU foam), an initial polyol mixture together with an excess of diisocyanate and/or polyisocyanate in the presence of a catalyst and optionally additional auxiliaries and additives is reacted in a pressurised vessel to form a prepolymer containing isocyanate groups. By actuating the spray valve of the pressurised vessel, the prepolymer is forced out of the can by a foaming agent, with spontaneous foaming of the prepolymer occurring. Reaction of the isocyanate groups still present with the atmospheric moisture produces a largely closed-celled rigid foam.

In the dual-component polyurethane foam (hereafter referred to as 2C PU foam), an additional component bearing hydroxy groups, e.g. a polyol, is required for hardening the prepolymer foam, and this is not added until immediately before foam formation. Usually, this polyol is located in the pressurised vessel in a charge space separated from the other components, and is not added to the prepolymeric component until immediately before emerging from the pressurised vessel by actuating the spray valve.

Most prepolymers for PU foams which are used for application from pressurised vessels have a very high viscosity, so that the foaming agents used should have good solvent properties, in order to be able to foam the components out of the pressurised vessel without difficulty. It is no longer desirable to use fluorochlorohydrocarbons (FCHCs) as foaming agents for such applications for ecological reasons. Many of the substitutes proposed hitherto still possess use-related disadvantages such as still unsatisfactory heat insulation or an excessively slow evaporation rate.



It was therefore an object of the invention to provide new methods for producing foamed plastics, and also for the production of PU foams from pressurised vessels, which overcome the former disadvantages of the prior art. A further object was to provide new foaming agent compositions for these methods.

Surprisingly, it has now been discovered that compositions which in addition to at least one additional liquid component contain carbon dioxide in liquid form are suitable as foaming agent compositions in methods for producing foamed plastics. Foaming agent compositions which contain liquefied carbon dioxide are also suitable for producing PU foams from pressurised vessels.

The subject of the invention is foaming agent compositions which contain 0.5 to 50% by weight liquid CO₂. Preferred foaming agent compositions contain 5 to 50% by weight liquid CO₂, in particular 10% by weight to 50% by weight.

In addition to the liquid CO₂, they contain at least one additional liquid or pressure-liquefied component. This additional liquid component or the additional liquid components preferably represent the remainder to make up to 100% by weight of the foaming agent composition. The additional liquid component or components may for example be liquid or pressure-liquefied physical foaming agents and/or liquid flame retardants, for example from the group of phosphate esters or phosphonic acid esters. Furthermore, the compositions may also additionally contain known additives and auxiliaries such as stabilisers or plasticisers.



A further subject of the invention is a method for producing foamed plastics with the aid of foaming agents, in which a liquid foaming agent composition is used which contains 0.5 to 50% by weight, preferably 5 to 50% by weight, in particular 10 to 50% by weight, very particularly 10 to 20% by weight, liquefied carbon dioxide.

Liquefied carbon dioxide in the spirit of the invention can be obtained according to all known methods of gas liquefaction, preferably by pressure liquefaction.

Carbon dioxide at room temperature and at normal pressure (1.01325×10^5 Pa) is a colourless gas which can be pressure-liquefied to give a colourless, readily mobile liquid by applying a pressure of 56.5 atm ($= 5.72486 \times 10^6$ Pa) at 20°C. Methods for pressure liquefaction of carbon dioxide are generally known.

One embodiment of the present invention relates to the production of foamed plastics, for example by means of the casting or extrusion process. Another embodiment of the invention which will be explained later relates specifically to the production of single-component or dual-component polyurethane foamed materials from pressurised vessels (PU = polyurethane). First of all, the first-mentioned embodiment will be explained in greater detail below.

In the production of foamed plastics, any conventional customary liquid physical foaming agents, namely readily volatile organic compounds such as ethers, e.g. diethyl ether, ketones such as acetone, hydrocarbons such as pentane, hexane, heptane, gasoline mixtures, halogenated hydrocarbons or halogenated ethers can be used as additional liquid components in addition to the pressure-liquefied carbon dioxide. Also gases



liquefied under pressure, such as propane or butane may be used in addition to the liquefied carbon dioxide. Furthermore, water can be used as liquid foaming agent component.

5 Preferably, for the production of foamed plastics a foaming agent composition is used which contains or consists of 10 to 20 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one
10 physical foaming agent which is liquid or has been liquefied under pressure, from the group consisting of alcohols with 1 to 5 carbon atoms, aliphatic hydrocarbons with 2 to 12 carbon atoms, cyclic hydrocarbons with 3 to 12 carbon atoms, halogenated hydrocarbons with 1 to 5 carbon atoms or halogenated
15 ethers with a total of 2 to 6 carbon atoms. Preferred alcohols in this case are in particular ethanol and isopropanol. Examples of aliphatic hydrocarbons are pentane, hexane, heptane and gasoline fractions, in particular light gasolines having a boiling point in
20 the range of 15 to 80°C. Furthermore, the low-boiling fractions, such as propane and/or butane, can also be used in the pressure-liquefied state as liquid foaming agent components. Examples of cyclic hydrocarbons are cycloaliphatic hydrocarbons, preferably cyclopropane, cyclopentane and cyclohexane. "Halogenated hydrocarbons" is understood to mean hydrogen-containing
25 fluorochlorohydrocarbons or fluorohydrocarbons. Examples of fluorochlorohydrocarbons which can be used are chlorodifluoromethane (R22), trifluoromethane (R23), 1,1-dichloro-1-fluoroethane (R141b), 1-chloro-1,1-difluoroethane (R142b) or 1,3-dichloro-1,1,2,2,3,3-hexafluoropropane (R216a). Examples of fluoro-
30 hydrocarbons are pentafluoroethane (R125), 1,1,1,2-tetrafluoroethane (R134a), 1,1,1-trifluoroethane (R143a), 1,1,2-trifluoroethane (R143),
35 1,1-difluoroethane (R152a), 1,1,1,3,3-pentafluoro-



propane (R245fa), octafluoropropane (R218), or alternatively 1,1,1,3,3-pentafluorobutane (R365mfc).

"Halogenated ethers" is understood to mean fluorochloroethers or fluoroethers containing hydrogen, such as difluoromethoxy-2,2,2-trifluoroethane (E245).

Preferably a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one halogenated hydrocarbon or an aliphatic hydrocarbon or a halogenated ether, or consists of the afore-mentioned mixture.

Particularly preferably, in the method according to the invention a foaming agent composition is used which contains or consists of 10 to 20 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight 1,1-difluoroethane (R152a) and/or 30 to 90 parts by weight 1,1-dichloro-1-fluoroethane (R141b). Further foaming agent compositions used particularly preferably in the method according to the invention are foaming agent compositions which contain 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight 1,1-dichloro-1-fluoroethane (R141b) and also optionally additionally 1 to 3 parts by weight water, or consist of the afore-mentioned mixture. Likewise preferably preferred is a foaming agent composition which contains 10 to 20 parts by weight liquefied carbon dioxide, 50 to 70 parts by weight 1,1-difluoroethane (R152a) and 20 to 35 parts by weight ethanol, or consists of this mixture. Among the compositions according to the invention containing halogenated ethers, those foaming agent compositions which contain 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight difluoromethoxy-2,2,2-trifluoroethane (E245) or consist of such mixtures are particularly preferred. Of the aliphatic hydrocarbons,



n-pentane is particularly preferred. Preferably, a composition according to the invention containing aliphatic hydrocarbons should contain 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight n-pentane and also optionally additionally 1 to 3 parts by weight water or consist of such a mixture.

With all these foaming agent mixtures, the amount of the other foaming agents used can be reduced by using the liquid CO₂. CO₂ is physiologically harmless and environmentally compatible.

Expediently, the method according to the invention for producing foamed plastics is carried out as a casting process or extrusion process. In the extrusion process, mixtures suitable for the production of foamed plastics are extruded directly into foamed sheets, films, moulded parts, profiles or particles. Particularly preferably, foamed thermoplastic materials, in particular polyethylene, polypropylene or polystyrene foamed materials, are produced according to the invention¹. According to the invention, the method is then carried out such that the foaming agent composition consisting of liquefied carbon dioxide and an additional liquid physical foaming agent is admixed to a melt of the starting products suitable for producing foamed plastics, and the polymerisation of the starting products for the foamed plastics material to be produced is carried out, optionally while maintaining a slight excess pressure or reduced pressure during the foaming operation. Known processing units, e.g. extruder units, may be used for the method according to the invention. It is particularly surprising here that using the method

¹ TRANSLATOR'S NOTE: This sentence could also be interpreted to mean "... thermoplastic materials, ... materials, foamed according to the invention, are produced."



according to the invention it is possible to introduce carbon dioxide in the liquefied state even at elevated temperature into the extruder for the foaming of thermoplastic polymer melts. In contrast to the methods of the prior art known hitherto, this makes metering of the carbon dioxide possible without difficulty. According to the method of the invention, it is thus possible, using carbon dioxide, to produce predominantly closed-celled foamed materials of very uniform fine-celled structure. Furthermore, the foamed plastics obtained according to the method of the invention are distinguished by very good heat insulation properties.

The method according to the invention for the production of foamed plastics can be carried out such that a foaming agent composition pre-formulated in a pressurised vessel is used, which composition was produced by placing the physical foaming agent which is liquid or has been liquefied under pressure in a pressurised vessel in the desired parts by weight and forcing in the desired quantity of pressure-liquefied carbon dioxide in known manner. However, it is also possible to proceed according to the method of the invention such that the foaming agent composition to be used is not produced until immediately before the foaming operation for the polymers or polymerisable components which are to be foamed. In this case, in a pressurised vessel outside the extruder unit proper liquefied carbon dioxide is introduced in the corresponding quantities into the additional liquid foaming agent component at a pressure at which carbon dioxide is in liquid state, when the components largely mix together. The homogenous mixture of liquefied carbon dioxide and liquid foaming agent component thus obtained is then introduced into the extruder unit via an inlet for liquid foaming agents.



The method according to the invention is suitable both for the production of open-celled and closed-celled rigid or flexible foams. The method is particularly suitable for producing polyurethane foamed plastics.

5 Known PU processing units, e.g. high-pressure or low-pressure mixing units which are equipped with the static mixers known from the prior art can be used for this.

10 In one variant for the production of foamed PU plastics, the foaming agents according to the invention may contain additional liquid additives, e.g. flame retardants, as an additional component in addition to pressure-liquefied carbon dioxide and one or more physical foaming agents which are liquid and/or have
15 been liquefied under pressure. Conventional flame retardants are e.g. phosphate esters or phosphonates. Corresponding phosphate esters or phosphonic esters which have three lower alkyl groups or three lower alkyl groups substituted by one or more halogen atoms
20 are particularly well suited. Lower alkyl preferably stands for C₁ to C₄ groups. Suitable examples are tris-chloroisopropyl phosphate, trichloroisopropyl phosphate, tris-chloroethyl phosphate, trichloroethyl phosphate, trichloropropyl phosphate, tris-chloropropyl
25 phosphate, triethyl phosphate, dimethylethyl phosphate, tris-dichloroisopropyl phosphate or dimethylmethyl phosphonate.

If the method according to the invention is used for the production of PU foamed plastics, all customary
30 foam raw materials, such as aliphatic, cycloaliphatic or aromatic diisocyanates or polyisocyanates may be used. Examples of foam raw materials are 2,4- and 2,6-toluylene diisocyanate, diphenylmethane diisocyanate, polymethylene polyphenyl isocyanate and
35 mixtures thereof. Polyisocyanates containing



carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups, which are referred to as "modified polyisocyanates" or "isocyanate prepolymers" may also be used. In the production of PU foamed plastics, polyisocyanates are usually reacted with compounds which contain at least two hydrogen atoms which are reactive to isocyanate groups, for example compounds containing hydroxyl groups on the basis of polyesters, polyethers and amines, and also compounds containing amino and/or carboxyl and/or thiol groups. Furthermore, all catalysts used in the production of PU foamed plastics, such as tertiary amines and/or organic metal compounds such as tin salts of carboxylic acids may be used.

If the method according to the invention is used for the production of polystyrene or polyethylene foamed materials, all foam raw materials known per se may also be used for this.

In known manner, in addition to the polymers and/or polymerisable constituents all known additives or auxiliaries, for example nucleation agents, pore regulator substances, flame retardants, antistatic agents, stabilisers, plasticisers, cross-linking agents, fillers or dyes may be added.

Another embodiment of the invention relates to the production of single-component or multi-component PU foamed materials from pressurised vessels, and will be explained below. In this case too, a foaming agent composition containing 0.5 to 50% by weight liquefied CO₂ is used.

"Foaming agent composition" is understood to mean the liquid content of the foaming agent composition



enclosed in the pressurised vessel, including the gas phase located in the pressurised vessel.

5 The foaming agent composition in this variant contains at least one additional liquid component in addition to the liquid CO₂. It may contain, for example, a liquid or pressure-liquefied physical foaming agent as additional liquid component. Halogenated foaming agents are highly suitable; halogen-free foaming agents are often environmentally compatible and to be preferred. According to a particularly advantageous variant, liquid CO₂ is contained as the sole foaming agent, and the liquid additional component is formed by a liquid flame retardant from the group of esters of phosphoric acid or the esters of phosphonic acid.

15 Any customary liquid physical foaming agents, namely readily volatile organic compounds such as ethers, acetone, hydrocarbons such as pentane, heptane, hexane, gasoline mixtures, halogenated hydrocarbons or halogenated ethers are possible as additional liquid components in addition to the pressure-liquefied carbon dioxide. Also gases liquefied under pressure, such as propane or butane, may be used in addition to the liquefied carbon dioxide.

25 Preferably the foaming agent compositions according to the invention contain more than 5% by weight, in particular 5 to 50, e.g. 5 or 10 to 30% by weight, liquefied carbon dioxide.

30 Foaming agent compositions which contain 10 to 50 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one foaming agent which is liquid or has been liquefied under pressure, from the group of ethers having a total of 2 to 4 carbon atoms, ketones having 3 to 5 carbon atoms, aliphatic hydrocarbons



having 2 to 12 carbon atoms, halogenated hydrocarbons having 1 to 5 carbon atoms or halogenated ethers having a total of 2 to 6 carbon atoms or consist of such a mixture are preferred. Examples of aliphatic hydrocarbons are pentane, hexane, heptane and gasoline fractions, in particular light gasolines having a boiling point in the range of 15 to 80°C. Preferably the low-boiling fractions, such as propane and/or butane, used in pressure-liquefied form. Examples of cyclic hydrocarbons are cyclopropane, cyclopentane and cyclohexane. "Halogenated hydrocarbons" are understood to mean hydrogen-containing fluorochlorohydrocarbons or fluorohydrocarbons. Possible fluorochlorohydrocarbons are e.g. chlorodifluoromethane (R22), 1,1-dichloro-1-fluoroethane (R141b), 1-chloro-1,1-difluoroethane (R142b) or 1,3-dichloro-1,1,2,2,3,3-hexafluoropropane (R216a). Examples of fluorohydrocarbons are trifluoromethane (R23), pentafluoroethane (R125), 1,1,1,2-tetrafluoroethane (R134a), 1,1,1-trifluoroethane (R143a), 1,1,2-trifluoroethane (R143), 1,1-difluoroethane (R152a), 1,1,1,3,3-pentafluoropropane (R245fa), octafluoropropane (R218) or 1,1,1,3,3,-pentafluorobutane (R365mfc). "Halogenated ethers" are understood to mean hydrogen-containing fluorochloroethers or fluoroethers, such as difluoromethoxy-2,2,2-trifluoroethane (E245). Examples of possible ethers are dimethyl ether or diethyl ether. Of the ketones, acetone is particularly preferred.

The foaming agent compositions according to the invention may be free of halogenated foaming agents and consist only of liquefied carbon dioxide as the sole foaming agent component. Blends which contain or consist of liquefied carbon dioxide in a quantity of 20 to 30 parts by weight and butane or a propane/butane mixture in a quantity of 50 to 60 parts by weight and/or acetone in a quantity of 5 to 15 parts by weight



are preferred. A customary mixture, for example a mixture having a vapour pressure of approximately 3.7 bar (absolute) can be used as the propane/butane mixture.

5 Also preferred are foaming agent compositions according to the invention which contain or consist of 10 to 50 parts by weight liquefied carbon dioxide and 10 to 90 parts by weight of a halogenated hydrocarbon or a halogenated ether. In this case, foaming agent
10 compositions which contain or consist of 10 to 30 parts by weight liquefied carbon dioxide and of the halogenated hydrocarbons 10 to 90 parts by weight 1,1-difluoroethane (R152a) and/or 1,1-dichloro-1-fluoroethane (R141b) are particularly preferred. Among
15 the compositions according to the invention containing halogenated ethers, those foaming agent compositions which contain or consist of 15 to 40 parts by weight liquefied carbon dioxide and 10 to 20 parts by weight difluoromethoxy-2,2,2-trifluoroethane (E245) are
20 particularly preferred.

In another particularly preferred variant, the foaming agents according to the invention may [contain] phosphate esters or phosphonates customary as flame
retardants in addition to pressure-liquefied carbon
25 dioxide as liquid component. Phosphate or phosphonic esters which contain three C1 - C4 alkyl groups, which are optionally substituted by one or more halogen atoms are particularly suitable, such as tris-chloroisopropyl phosphate, tris-chloroethyl phosphate, trichloroethyl
30 phosphate, trichloropropyl phosphate, tris-chloropropyl phosphate, triethyl phosphate, dimethylethyl phosphate, tris-dichloroisopropyl phosphate or dimethylmethyl phosphonate. Expediently, the concentrations are 10 to
50 parts by weight liquefied carbon dioxide and 80 to
35 100 parts by weight phosphate ester or phosphonate.



Preferably tris-chloropropyl phosphate is used. These particularly preferred foaming agent compositions are free of foaming agents other than CO₂ and are therefore particularly environmentally compatible.

- 5 The foaming agent compositions according to the invention are suitable for the production of all PU foams known hitherto from pressurised vessels, in particular for foaming 1C and 2C PU foamed materials. The foaming agent compositions according to the
10 invention can also be used for the production of multi-component PU foamed materials in which the foam-forming agents with more than one reactive component are poured separately into a pressurised vessel. The foaming agent compositions according to the invention can also
15 be used for the production of so-called 1.5C PU foams, in which, in contrast to the 2C foams, a quantity of a polyol component which is insufficient for reaction of the isocyanate groups is added to the prepolymer shortly before application.
- 20 The foaming agent compositions according to the invention have proved very advantageous for the production of 1C or 2C PU foamed materials.

- The 1C PU foamed material mixture to be foamed in known manner may in known manner contain a polyol component,
25 a polyisocyanate component, a catalyst and also optionally as auxiliary a flame retardant as additional constituents in addition to the foaming agent composition according to the invention.

- Glycerol, glycols or polyether polyols which were
30 obtained as addition products of propylene oxide or ethylene oxide to polyvalent alcohols, water or ethylene diamine, or polyester polyols which were obtained as polycondensation products from polyols with



dicarboxylic acids or their anhydrides, or mixtures thereof may for example be contained in the 1C PU foam mixture as the polyol component. A typical polyol component may for instance be a mixture of a brominated polyether polyol (for instance diol or triol) with a hydroxyl number of 200 to 350 and a polyether polyol (e.g. a diol) with a hydroxyl number of 110.

Furthermore, modified vegetable oils having an OH number in the range of 100 to 300, e.g. castor oil, are also possible.

Examples of polyisocyanate components which can be used are diphenylmethane-4,4'-diisocyanate, diisocyanato-toluene, 1,5-diisocyanato-naphthalene, triisocyanato-triphenylmethane, 1,6-diisocyanatohexane, preferably diphenylmethane-4,4'-diisocyanate, or mixtures thereof.

Typical catalysts in 1C PU foam mixtures which can be foamed in the method according to the invention with a foaming agent composition according to the invention are organic amines, aminoalcohols or aminoethers, e.g. 2-dimethylaminoethyl-3-dimethylaminopropyl ether, diethanolamine, dimethylcyclohexylamine, 2-dimethyl-aminoethyl ether, or morpholine compounds, such as 2,2-dimorpholinodiethyl ether, N,N-dimethylaminoethyl morpholine, N-methyl morpholine. The morpholine compounds, in particular 2,2-dimorpholinodiethyl ether, are preferred.

Tris-chloroisopropyl phosphate, trichloroisopropyl phosphate, tris-chloroethyl phosphate, trichloroethyl phosphate, tris-chloropropyl phosphate, trichloropropyl phosphate, dimethylethyl phosphate, tris-dichloro-isopropyl phosphate, dimethylmethyl phosphonate, dimethylene ethyl phosphate, preferably tris-chloro-propyl phosphate, may be used as customary flame retardants.



Copolymers of siloxane are for example suitable as stabilisers.

A 1C PU foam mixture which is to be foamed contains, relative to the foam mixture as 100% by weight, for example 20 to 30% by weight of a polyol component, 40 to 60% by weight of a polyisocyanate component, 0.1 to 3% by weight catalyst, optionally 10 to 15% by weight of a flame retardant, and optionally 1 to 2% by weight foam stabiliser in addition to 15 to 35% by weight of a foaming agent composition according to the invention. A typical 1C PU foam mixture, which can advantageously be foamed with the aid of the foaming agent composition according to the invention thus consists for example of approximately 22.5% by weight of a polyol component, e.g. of a mixture of a brominated polyether polyol with a hydroxyl number of 200 to 350 and a polyether polyol with a hydroxyl number of 110 in a mixture ratio of 1:1, approximately 42.5% by weight of a polyisocyanate component, e.g. diphenylmethane-4,4'-diisocyanate, approximately 0.5% by weight of a catalyst substance such as 2,2-dimorpholinodiethyl ether, approximately 1.5% by weight silicone foam stabiliser, approximately 13% by weight of a flame retardant such as tris-chloro-propyl phosphate, and a content of approximately 20% by weight of a foaming agent composition according to the invention. A single-component foamed material having a uniform, fine-celled structure and low bulk density, e.g. a bulk density of approximately 23 to 25 kg/m³, can be produced from such a 1C PU foam mixture.

The 1.5C and 2C PU foamed materials differ from the single-component foamed materials in that the polyol component required for hardening the foam is kept separate from the prepolymer composition in the pressurised vessel and is not added to the prepolymer until immediately before foaming. All the polyol



components already mentioned may be used as the second component. For more rapid hardening, the second component may furthermore contain a conventional catalyst, for example the afore-mentioned amine or morpholine compounds or alternatively organometallic compounds, such as tin dioctoate, cobalt naphthenate, dibutyl tin dilaurate or iron acetyl acetate.

The 1C or multi-component PU foamed materials produced with the foaming agent composition according to the invention possess very good heat insulation properties and are therefore well suited for insulation purposes, e.g. in the construction or housing field. The foaming agent compositions according to the invention are also suitable for the production of polyurethane-based spray adhesives.

Furthermore, the invention comprises a method for producing a 1C or 2C PU foamed material, in which a PU foamed material is produced from a pressurised vessel which contains a PU foam mixture consisting of a polyol component, a prepolymer containing isocyanate groups, a catalyst and optionally additional conventional auxiliaries and also one of the foaming agent compositions described above by relieving the excess pressure in the pressurised vessel to atmospheric pressure through a valve. Appropriate pressurised vessels and valves suitable for foaming are generally known.

Furthermore, the invention relates to 1C or multi-component PU foamed material mixture for producing a PU foamed material from pressurised vessels which contain one of the foaming agent compositions described above.

Another subject of the invention is a method for producing a foaming agent composition for the



production of PU foamed materials from pressurised vessels, in which liquefied carbon dioxide is used as a foaming agent component. In the method according to the invention, the physical foaming agent component which is liquid or has been liquefied under pressure is placed in a pressurised vessel in the desired parts by weight, and liquefied, usually pressure-liquefied, carbon dioxide is forced in in the desired amount in known manner. This foaming agent composition produced according to the invention can then be injected in the desired quantity into a pressurised vessel (aerosol can) which already contains the prepolymer and optionally all the other components. The quantity of carbon dioxide is then only regulated by the pressure permitted for aerosol cans (10 to 18 bar).

According to the invention, it is then possible to produce pressurised vessels containing PU foamed material mixtures which may contain approximately 20 to 30 g carbon dioxide per 1 kg can. According to methods used hitherto, in which carbon dioxide was always used in gaseous form, it was hitherto only possible to introduce only approximately 3 to 5 g carbon dioxide per 1 kg can. Advantageously, according to the invention it is now possible to reduce further the content of combustible physical foaming agents which are liquid or have been liquefied under pressure in the production of PU foamed materials from pressurised vessels. Also from the point of view of cost, reduction of the liquid or pressure-liquefied physical foaming agents customary hitherto is extremely advantageous. 1C or multi-component PU foamed materials produced with the foaming agent composition according to the invention have a predominantly closed-celled, very uniform, fine-celled structure and very high heat insulation properties. Accordingly, PU foamed materials which have been produced with a



foaming agent composition according to the invention are particularly suitable for insulation purposes in the field of construction and housing.

5 The following examples are intended to explain the invention in greater detail, but without restricting its scope.

Examples

1. Production of a polystyrene foamed material

a) Liquefied carbon dioxide/R152a as foaming agent:

10 200 kg polystyrene (melt index 3.0-110) were mixed with 2 kg talcum as nucleation agent and this mixture was metered into a conventional extruder and melted. Approximately 6% by weight of a foaming agent according to the invention, relative to polystyrene, were metered
15 into the melting zone of the extruder via an injection nozzle into the polystyrene melt. The foaming agent composition according to the invention contained 14 parts by weight liquefied carbon dioxide and 86 parts by weight R152a. The vapour pressure of this foaming
20 agent composition was approximately 14 bar at 20°C.

In the mixing zone, the polystyrene melt was mixed homogenously with the foaming agent composition according to the invention and then the resulting mixture was extruded via a nozzle. A closed-celled
25 foamed material of uniform, fine-celled structure was obtained.

Both polystyrene foam films and polystyrene foam sheets were produced according to the invention. A polystyrene foam film produced according to the



invention had a density of approximately 35 kg/m^3 , and a polystyrene foam sheet produced according to the invention had a density of approximately 33 kg/m^3 .

5 b) Liquefied carbon dioxide/R152a/ethanol as foaming agent:

As described under Example 1a), approximately 8.5% by weight of a foaming agent according to the invention, relative to polystyrene, was metered into a polystyrene melt. The foaming agent composition according to the invention contained 14 parts by weight liquefied carbon dioxide, 57 parts by weight R152a and 29 parts by weight ethanol. The vapour pressure of these foaming agent compositions was approximately 15 bar at 20°C .

15 A polystyrene foam film produced according to the invention had a density of approximately 36 kg/m^3 , and a polystyrene foam sheet produced according to the invention had a density of approximately 34 kg/m^3 .

2. Production of a polyethylene foam material

20 a) Liquefied carbon dioxide/R152a/R141b as foaming agent:

25 200 g polyethylene (melt index 3.5-150) were extruded under identical conditions as described in Example 1 for polystyrene foamed material. Approximately 6% by weight of a foaming agent mixture, relative to polyethylene, was metered in. According to the invention, a foaming agent composition consisting of 14 parts by weight liquefied carbon dioxide, 50 parts by weight R152a and 36 parts by weight R141b was used. A fine-celled polyethylene foamed material of low shrinkage was obtained. The polyethylene foam tube



produced according to the invention had a density of approximately 40 kg/m³.

3. Production of a PU foamed material

For production of the PU foamed material a polyol mixture, consisting of 40 parts by weight of an ethylene diamine/propylene oxide polyether (OH number 480), 60 parts by weight of a sorbitol/glycerol/propylene oxide polyether (OH number 490), 1 part by weight foam stabiliser (type DC193 by Dow Corning Corporation) and 1.5 parts by weight dimethyl-cyclohyllamine [sic] were used as one of the starting components. Diphenylmethane diisocyanate was used as the isocyanate component in a stoichiometric quantity increased by 10% by weight. The PU foamed materials were produced on a low-pressure installation having an output rate of approximately 8 kg/min, with which metering of 3 components is possible. A static mixer served as the mixing unit.

a) Liquefied carbon dioxide/R141b/water as foaming agent:

According to the invention, a foaming agent composition was used in a quantity of 30 parts by weight. The foaming agent composition consisted of 13.9 parts by weight liquefied carbon dioxide, 85.1 parts by weight R141b and additionally 1 part by weight water. With this foaming agent composition according to the invention, a PU rigid foam material having a fine-celled structure and a density of approximately 24 kg/m³ was produced.

b) Liquefied carbon dioxide/n-pentane/water as foaming agent:



Furthermore, a PU foamed material containing 18 parts by weight of a foaming agent composition was produced. This foaming agent composition consisted according to the invention of 13.9 parts by weight liquefied carbon dioxide and 85.1 parts by weight n-pentane and additionally 1 part by weight water. With this foaming agent composition, a PU rigid foam material having a fine-celled structure and a density of approximately 25.4 kg/m³ was obtained.

10 c) Liquefied carbon dioxide/E245 as foaming agent:

Furthermore, a PU foamed material was produced with 35 parts by weight of a foaming agent composition. This foaming agent composition consisted according to the invention of 14 parts by weight liquefied carbon dioxide and 85 parts by weight E245. With this foaming agent composition, a PU rigid foam having a fine-celled structure and a density of approximately 33.5 kg/m³ was obtained.

20 4. Liquefied carbon dioxide/propane/butane/acetone as foaming agent for 1C PU foamed materials:

a) 247 g of an initial polyol mixture, consisting of

73 g polyether polyol (diol), brominated, hydroxide number approximately 240,

25 73 g polyether polyol (diol), hydroxide number approximately 110,

89 g tris-chloropropyl phosphate,

5 g silicone foam stabiliser,

7 g dimorpholinodiethyl ether,

30 was poured into an aluminium aerosol can having a volume of 1000 cm³. 356 g diphenylmethane-4,4-



diisocyanate were added and the aerosol can was closed by a foam aerosol valve. A foaming agent composition according to the invention was produced by placing 62 g pressure-liquefied propane/butane and 10 g acetone in a pressurised vessel and adding 28 g pressure-liquefied carbon dioxide with mixing. 99 g of this foaming agent composition according to the invention was then injected via a conventional aerosol filling device into the aerosol can containing the foam components. The aerosol can was briefly shaken and allowed to stand for approximately 24 hours in order to form the prepolymer. Once this time had ended, the 1C PU foam mixture was ready for use.

The 1C PU foam mixture was expelled from the aerosol can by means of the foaming agent composition according to the invention. A PU foamed material having a bulk density of approximately 23 kg/m^3 of uniform, fine-celled structure was obtained. The shrinkage of the PU foamed material after 7 days' storage at an atmospheric humidity of approximately 90% was about 5 percent length on average.

b) As described under a), a polyol blend and a polyisocyanate were poured into an aerosol can of the same volume. A composition of 50 g propane/butane, 7.5 g acetone and 20 g liquefied carbon dioxide was used as foaming agent composition according to the invention. The foaming agent composition was produced and poured into the aerosol can as described under a).

The PU foamed material produced with this foaming agent composition according to the invention had a bulk density of approximately 25 kg/m^3 .



5. Liquefied carbon dioxide/propane/butane/R141b as foaming agent for 1C PU foamed materials:

5 A polyol blend and a polyisocyanate were poured into an aerosol can having a volume of 1000 cm³ as described in Example 4. A composition of 62 g propane/butane, 10 g R141b and 28 g liquefied carbon dioxide was used as the foaming agent composition according to the invention. The foaming agent composition was produced and poured into the aerosol can as described in Example 4.

10 The PU foamed material produced with this foaming agent composition had a bulk density of approximately 25 kg/m³.

6. Liquefied carbon dioxide/trichloropropyl phosphate/R141b as foaming agent for 1C PU foamed materials:

15 214 g of a polyol blend and 356 g polyisocyanate were poured into an aerosol can having a volume of 1000 cm³ as described in Example 4. A composition according to the invention was produced by placing 100 g tris-
20 chloropropyl phosphate and 10 g R141b in a pressurised vessel and adding 28 g pressure-liquefied carbon dioxide with mixing. 99 g of this foaming agent composition was poured into the aerosol can as described in Example 4.

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Claims

1. A foaming agent composition for the production of foamed plastics and for the production of single-component or dual-component polyurethane foamed materials from pressurised vessels, characterised in that it contains 0.5 to 50% by weight liquefied carbon dioxide.

2. A foaming agent composition according to Claim 1, characterised in that it contains 5 to 50% by weight, preferably 10 to 50% by weight, in particular 10 to 20% by weight, liquefied CO₂.

3. A foaming agent composition according to Claim 1 or 2 for the production of foamed plastics, characterised in that it contains 10 to 20 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one physical foaming agent which is liquid or has been liquefied under pressure, from the group consisting of alcohols with 1 to 5 carbon atoms, aliphatic hydrocarbons with 2 to 12 carbon atoms, cyclic hydrocarbons with 3 to 12 carbon atoms, halogenated hydrocarbons with 1 to 5 carbon atoms or halogenated ethers with a total of 2 to 6 carbon atoms.

4. A foaming agent composition according to Claim 1 or 2 for the production of single-component or dual-component polyurethane foamed materials from pressurised vessels, characterised in that they contain 10 to 50 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one foaming agent which is liquid or has been liquefied under pressure, from the group of ethers having a total of 2 to 4 carbon atoms, ketones having 3 to 5 carbon atoms, aliphatic hydrocarbons having 2 to 12 carbon atoms,





cyclic hydrocarbons with 3 to 12 carbon atoms, halogenated hydrocarbons having 1 to 5 carbon atoms or halogenated ethers having a total of 2 to 6 carbon atoms.

5 5. A foaming agent composition according to Claim 1
or 2 for the production of single-component or dual-
component polyurethane foamed materials from
pressurised vessels, characterised in that it contains
10 to 50 parts by weight liquefied carbon dioxide and
10 to 100 parts by weight of at least one trialkyl
phosphate or trialkyl phosphonate from the group
triethyl phosphate, trichloroisopropyl phosphate, tris-
chloroethyl phosphate, tris-chloroisopropyl phosphate,
tris-chloropropyl phosphate, trichloroethyl phosphate,
15 trichloropropyl phosphate, triethyl phosphate [sic],
dimethylethyl phosphate, trichloroisopropyl phosphate
[sic], dimethylmethyl phosphonate, diethylmethyl
phosphonate or diethylethyl phosphonate, preferably
tris-chloropropyl phosphate.

20 6. A halogen-free foaming agent composition according
to Claim 3, characterised in that it contains 20 to 30
parts by weight liquefied carbon dioxide and 50 to 60
parts by weight butane or a propane/butane mixture
and/or 5 to 15 parts by weight acetone.

25 7. A foaming agent composition according to Claim 3,
characterised in that it contains 20 to 40 parts by
weight liquefied carbon dioxide and 10 to 50 parts by
weight of a halogenated hydrocarbon from the group
1,1-dichloro-1-fluoroethane, pentafluoroethane or
30 1,1-difluoroethane.

8. A foaming agent composition according to Claim 3,
characterised in that it contains 20 to 40 parts by





weight liquefied carbon dioxide and 10 to 50 parts by weight difluoromethoxy-2,2,2-trifluoroethane.

5 9. A method for the production of foamed plastics with the aid of foaming agents, characterised in that a liquid foaming agent composition according to Claim 1 is used which contains 0.5 to 50% by weight liquefied carbon dioxide.

10 10. A method according to Claim 9, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one foaming agent which is liquid or has been liquefied under pressure, from the group consisting of alcohols with 1 to 5 carbon atoms, aliphatic hydrocarbons with 2 to 12
15 carbon atoms, cyclic hydrocarbons with 3 to 12 carbon atoms, halogenated hydrocarbons with 1 to 5 carbon atoms or halogenated ethers with a total of 2 to 6 carbon atoms.

20 11. A method according to Claim 10, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one aliphatic or halogenated hydrocarbon or halogenated ether.

25 12. A method according to Claim 11, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight 1,1-difluoroethane and/or 30 to 90 parts by weight 1,1-dichloro-1-fluoroethane.

30 13. A method according to Claim 12, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight 1,1-dichloro-1-fluoroethane.





14. A method according to Claim 9, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide, 50 to 70 parts by weight 1,1-difluoroethane and 20 to 35 parts by weight ethanol.

15. A method according to Claim 11, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight difluoromethoxy-2,2,2-trifluoroethane.

16. A method according to Claim 11, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight n-pentane.

17. A method according to Claim 9, characterised in that foamed polyethylene, polystyrene or polyurethane plastics are produced.

18. A method for producing a single-component or dual-component polyurethane foamed material, characterised in that a polyurethane foamed material is produced from a pressurised vessel which contains a prepolymer containing isocyanate groups, optionally additional conventional auxiliaries and a foaming agent composition according to one of Claims 1 to 2 or 4 to 8 as foaming agent by pressure-relieving the excess pressure prevailing in the pressurised vessel to atmospheric pressure via a suitable valve.

19. A method according to Claim 18, characterised in that a foaming agent composition is used in a quantity of 5 to 40% by weight, relative to the total mixture of prepolymer and foaming agent composition.





20. A method for producing a foaming agent composition according to Claim 1, characterised in that carbon dioxide which has been liquefied under pressure is introduced into an additional component which is liquid or has been liquefied under pressure, preferably a foaming agent or a flame retardant, or vice versa, so that the foaming agent composition contains 0.5 to 50% by weight liquid CO₂.

21. A composition consisting of prepolymer and foaming agent for the production of a single-component or dual-component polyurethane foamed material, characterised in that it contains a foaming agent composition according to one of Claims 1 to 2 or 4 to 8.

22. An arrangement for producing a single-component or dual-component polyurethane foamed material, characterised in that it contains a prepolymer containing isocyanate groups and a foaming agent composition according to one of Claims 1 to 2 or 4 to 8 in a pressurised vessel provided with a valve.



substitutes proposed hitherto still possess use-related disadvantages such as still unsatisfactory heat insulation or an excessively slow evaporation rate.

5 ~~It was therefore an object of the invention to provide new methods for producing foamed plastics, and also for the production of PU foams from pressurised vessels, which overcome the former disadvantages of the prior art. A further object was to provide new foaming agent~~
10 ~~compositions for these methods.~~

Surprisingly, it has now been discovered that
compositions which in addition to at least one
additional liquid component contain carbon dioxide in
liquid form are suitable as foaming agent compositions
15 in methods for producing foamed plastics. Foaming
agent compositions which contain liquefied carbon
dioxide are also suitable for producing PU foams from
pressurised vessels.

The subject of the invention is foaming agent
20 compositions which contain 0.5 to 50% by weight liquid
CO₂. Preferred foaming agent compositions contain 5 to
50% by weight liquid CO₂, in particular 10% by weight to
50% by weight.

In addition to the liquid CO₂, they contain at least one
25 additional liquid or pressure-liquefied component.
This additional liquid component or the additional
liquid components preferably represent the remainder to
make up to 100% by weight of the foaming agent
composition. The additional liquid component or
30 components may for example be liquid or pressure-
liquefied physical foaming agents and/or liquid flame
retardants, for example from the group of phosphate
esters or phosphonic acid esters. Furthermore, the

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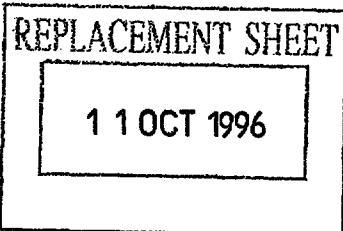
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International Patent Application WO 91/12287 discloses that liquid CO₂ can be used with co-foaming agents, for example water or higher-boiling solvents. In this manner, controlled pre- and post-expansion of the foam can be effected.

Japanese Patent Application JP-A 1/254 742 discloses that polyethylene resins can be foamed with a mixture of CO₂ and a readily-volatile organic foaming agent.

International Patent Application WO 91/08243 relates to the production of open-pored polyurethane foams. Preferably liquid CO₂ is used as foaming agent, and this may additionally contain water or other foaming agents in small quantities.



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~~substitutes proposed hitherto still possess use-related disadvantages such as still unsatisfactory heat insulation or an excessively slow evaporation rate.~~

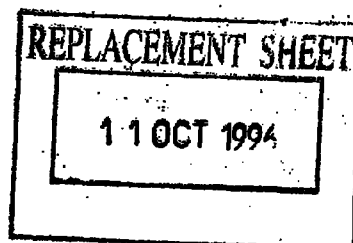
5 It was therefore an object of the invention to provide new methods for producing foamed plastics, and also for the production of PU foams from pressurised vessels, which overcome the former disadvantages of the prior art. A further object was to provide new foaming agent
10 compositions for these methods.

Surprisingly, it has now been discovered that compositions which in addition to at least one additional liquid component contain carbon dioxide in liquid form are suitable as foaming agent compositions
15 in methods for producing foamed plastics. Foaming agent compositions which contain liquefied carbon dioxide are also suitable for producing PU foams from pressurised vessels.

20 The subject of the invention is foaming agent compositions which contain 0.5 to 50% by weight liquid CO₂. Preferred foaming agent compositions contain 5 to 50% by weight liquid CO₂, in particular 10% by weight to 50% by weight.

25 In addition to the liquid CO₂, they contain at least one additional liquid or pressure-liquefied component. This additional liquid component or the additional liquid components preferably represent the remainder to make up to 100% by weight of the foaming agent composition. The additional liquid component or
30 components may for example be liquid or pressure-liquefied physical foaming agents and/or liquid flame retardants, for example from the group of phosphate esters or phosphonic acid esters. Furthermore, the compositions may also additionally contain known
35 additives and auxiliaries such as stabilisers or plasticisers.

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Claims

1. A foaming agent composition for the production of foamed plastics and for the production of single-component or dual-component polyurethane foamed materials from pressurised vessels, characterised in that it contains 0.5 to 50% by weight liquefied carbon dioxide.

2. A foaming agent composition according to Claim 1, characterised in that it contains 5 to 50% by weight.

3. A foaming agent composition according to Claim 2, characterised in that it contains 10 to 50% by weight liquefied CO₂.

4. A foaming agent composition according to Claim 3, characterised in that it contains 10 to 20% by weight liquefied CO₂.

5. A foaming agent composition according to Claims 1 to 4 for the production of foamed plastics, characterised in that it contains 10 to 20 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one physical foaming agent which is liquid or has been liquefied under pressure, from the group consisting of alcohols with 1 to 5 carbon atoms, aliphatic hydrocarbons with 2 to 12 carbon atoms, cyclic hydrocarbons with 3 to 12 carbon atoms, halogenated hydrocarbons with 1 to 5 carbon atoms or halogenated ethers with a total of 2 to 6 carbon atoms.

6. A foaming agent composition according to Claims 1 to 4 for the production of single-component or dual-component polyurethane foamed materials from pressurised vessels, characterised in that they contain

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10 to 50 parts by weight liquefied carbon dioxide and
30 to 90 parts by weight of at least one foaming agent
which is liquid or has been liquefied under pressure,
from the group of ethers having a total of 2 to 4
carbon atoms, ketones having 3 to 5 carbon atoms,
aliphatic hydrocarbons having 2 to 12 carbon atoms,
cyclic hydrocarbons with 3 to 12 carbon atoms,
halogenated hydrocarbons having 1 to 5 carbon atoms or
halogenated ethers having a total of 2 to 6 carbon
atoms.

7. A foaming agent composition according to Claims 1
to 4 for the production of single-component or dual-
component polyurethane foamed materials from
pressurised vessels, characterised in that it contains
10 to 50 parts by weight liquefied carbon dioxide and
80 to 100 parts by weight of at least one trialkyl
phosphate or trialkyl phosphonate from the group
triethyl phosphate, trichloroisopropyl phosphate, tris-
chloroethyl phosphate, tris-chloroisopropyl phosphate,
tris-chloropropyl phosphate, trichloroethyl phosphate,
trichloropropyl phosphate, triethyl phosphate [sic],
dimethylethyl phosphate, trichloroisopropyl phosphate
[sic], dimethylmethyl phosphonate, diethylmethyl
phosphonate or diethylethyl phosphonate.

8. A halogen-free foaming agent composition according
to Claim 5, characterised in that it contains 20 to 30
parts by weight liquefied carbon dioxide and 50 to 60
parts by weight butane or a propane/butane mixture
and/or 5 to 15 parts by weight acetone.

9. A foaming agent composition according to Claim 5,
characterised in that it contains 20 to 40 parts by
weight liquefied carbon dioxide and 10 to 50 parts by
weight of a halogenated hydrocarbon from the group

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1,1-dichloro-1-fluoroethane, pentafluoroethane or
1,1-difluoroethane.

10. A foaming agent composition according to Claim 5,
characterised in that it contains 20 to 40 parts by
weight liquefied carbon dioxide and 10 to 50 parts by
weight difluoromethoxy-2,2,2-trifluoroethane.

11. A method for the production of foamed plastics
with the aid of foaming agents, characterised in that a
liquid foaming agent composition according to Claim 1
is used which contains 0.5 to 50% by weight liquefied
carbon dioxide.

12. A method according to Claim 11, characterised in
that a foaming agent composition is used which contains
10 to 20 parts by weight liquefied carbon dioxide and
30 to 90 parts by weight of at least one foaming agent
which is liquid or has been liquefied under pressure,
from the group consisting of alcohols with 1 to 5
carbon atoms, aliphatic hydrocarbons with 2 to 12
carbon atoms, cyclic hydrocarbons with 3 to 12 carbon
atoms, halogenated hydrocarbons with 1 to 5 carbon
atoms or halogenated ethers with a total of 2 to 6
carbon atoms.

13. A method according to Claim 12, characterised in
that a foaming agent composition is used which contains
10 to 20 parts by weight liquefied carbon dioxide and
30 to 90 parts by weight of at least one aliphatic or
halogenated hydrocarbon or halogenated ether.

14. A method according to Claim 13, characterised in
that a foaming agent composition is used which contains
10 to 20 parts by weight liquefied carbon dioxide and
30 to 90 parts by weight 1,1-difluoroethane and/or 30
to 90 parts by weight 1,1-dichloro-1-fluoroethane.

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15. A method according to Claim 14, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight 1,1-dichloro-1-fluoroethane.

5 16. A method according to Claim 11, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide, 50 to 70 parts by weight 1,1-difluoroethane and 20 to 35 parts by weight ethanol.

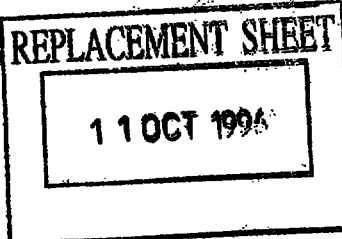
10 17. A method according to Claim 13, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight difluoromethoxy-2,2,2-trifluoroethane.

15 18. A method according to Claim 13, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight n-pentane.

20 19. A method according to Claim 11, characterised in that foamed polyethylene, polystyrene or polyurethane plastics are produced.

25 20. A method for producing a single-component or dual-component polyurethane foamed material, characterised in that a polyurethane foamed material is produced from a pressurised vessel which contains a prepolymer containing isocyanate groups, optionally additional conventional auxiliaries and a foaming agent composition according to one of Claims 1 to 4 or 6 to 10 as foaming agent by pressure-relieving the excess pressure prevailing in the pressurised vessel to
30 atmospheric pressure via a suitable valve.

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21. A method according to Claim 20, characterised in that a foaming agent composition is used in a quantity of 5 to 40% by weight, relative to the total mixture of prepolymer and foaming agent composition.

5 22. A method for producing a foaming agent composition according to Claim 1, characterised in that carbon dioxide which has been liquefied under pressure is introduced into an additional component which is liquid or has been liquefied under pressure, preferably a
10 foaming agent or a flame retardant, or vice versa, so that the foaming agent composition contains 0.5 to 50% by weight liquid CO₂.

15 23. A composition consisting of prepolymer and foaming agent for the production of a single-component or dual-component polyurethane foamed material, characterised in that it contains a foaming agent composition according to one of Claims 1 to 4 or 6 to 10.

20 24. An arrangement for producing a single-component or dual-component polyurethane foamed material, characterised in that it contains a prepolymer containing isocyanate groups and a foaming agent composition according to one of Claims 1 to 4 or 6 to 10 in a pressurised vessel provided with a valve.

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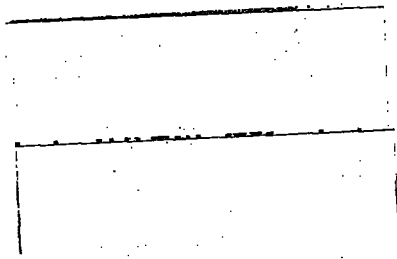


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Foaming agents containing liquid carbon dioxide

The invention relates to foaming agents containing liquid carbon dioxide and to the use thereof in methods for producing foamed plastics.

5 The invention also relates to foaming agent compositions which are suitable for the production of single-component or multi-component polyurethane foamed materials from pressurised vessels.

10 It is no longer desirable to use fluorochloro-hydrocarbons (FCHCs) as foaming agents in the production of foamed plastics for ecological reasons. Hitherto, substances which are also gaseous, such as carbon dioxide, have been proposed as substitutes. However, carbon dioxide as gaseous physical foaming agent has the disadvantage that, owing to its relatively low critical temperature under the conditions prevailing during the production of plastics foams, it can be metered only with great difficulty. Furthermore, the use of carbon dioxide using methods known hitherto for the most part results in open-celled foamed materials having an undesirably high water absorption capacity and heat insulation which is often still unsatisfactory. Also, hitherto the production of foamed plastics with predominantly closed cells still involves difficulties when using carbon dioxide as the sole foaming agent or as co-foaming agent in combination with other physical foaming agents.

25 Single-component or multi-component polyurethane foams which are delivered from a pressurised vessel, e.g. an aerosol can, are mainly used for filling cavities or

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interstices with foam in the building or motor car industries. In so-called single-component polyurethane foam (hereafter referred to as 1C PU foam), an initial polyol mixture together with an excess of diisocyanate and/or polyisocyanate in the presence of a catalyst and optionally additional auxiliaries and additives is reacted in a pressurised vessel to form a prepolymer containing isocyanate groups. By actuating the spray valve of the pressurised vessel, the prepolymer is forced out of the can by a foaming agent, with spontaneous foaming of the prepolymer occurring. Reaction of the isocyanate groups still present with the atmospheric moisture produces a largely closed-celled rigid foam.

In dual-component polyurethane foam (hereafter referred to as 2C PU foam), an additional component bearing hydroxy groups, e.g. a polyol, is required for hardening the prepolymer foam, and this is not added until immediately before foam formation. Usually, this polyol is located in the pressurised vessel in a charge space separated from the other components, and is not added to the prepolymeric component until immediately before emerging from the pressurised vessel by actuating the spray valve.

Most prepolymers for PU foams which are used for application from pressurised vessels have a very high viscosity, so that the foaming agents used should have good solvent properties, in order to be able to foam the components out of the pressurised vessel without difficulty. It is no longer desirable to use fluorochlorohydrocarbons (FCHCs) as foaming agents for such applications for ecological reasons. Many of the substitutes proposed hitherto still possess use-related disadvantages such as still unsatisfactory heat insulation or an excessively slow evaporation rate.

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International Patent Application WO 91/12287 discloses that liquid CO₂ can be used with co-foaming agents, for example water or higher-boiling solvents. In this manner, controlled pre- and post-expansion of the foam can be effected.

Japanese Patent Application JP-A 1/254 742 discloses that polyethylene resins can be foamed with a mixture of CO₂ and a readily-volatile organic foaming agent.

International Patent Application WO 91/08243 relates to the production of open-pored polyurethane foams. Preferably liquid CO₂ is used as foaming agent, and this may additionally contain water or other foaming agents in small quantities.

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It was therefore an object of the invention to provide new methods for producing foamed plastics, and also for the production of PU foams from pressurised vessels, which overcome the former disadvantages of the prior art. A further object was to provide new foaming agent compositions for these methods.

Surprisingly, it has now been discovered that compositions which in addition to at least one additional liquid component contain carbon dioxide in liquid form are suitable as foaming agent compositions in methods for producing foamed plastics. Foaming agent compositions which contain liquefied carbon dioxide are also suitable for producing PU foams from pressurised vessels.

The subject of the invention is foaming agent compositions which contain 0.5 to 50% by weight liquid CO_2 . Preferred foaming agent compositions contain 5 to 50% by weight liquid CO_2 , in particular 10% by weight to 50% by weight.

In addition to the liquid CO_2 , they contain at least one additional liquid or pressure-liquefied component. This additional liquid component or the additional liquid components preferably represent the remainder to make up to 100% by weight of the foaming agent composition. The additional liquid component or components may for example be liquid or pressure-liquefied physical foaming agents and/or liquid flame retardants, for example selected from the group consisting of phosphate esters and phosphonic acid esters. Furthermore, the compositions may also additionally contain known additives and auxiliaries such as stabilisers or plasticisers.

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A further subject of the invention is a method for producing foamed plastics with the aid of foaming agents, in which a liquid foaming agent composition is used which contains 0.5 to 50% by weight, preferably 5 to 50% by weight, in particular 10 to 50% by weight, very particularly 10 to 20% by weight, liquefied carbon dioxide.

Liquefied carbon dioxide in the spirit of the invention can be obtained according to all known methods of gas liquefaction, preferably by pressure liquefaction.

Carbon dioxide at room temperature and at normal pressure (1.01325×10^5 Pa) is a colourless gas which can be pressure-liquefied to give a colourless, readily mobile liquid by applying a pressure of 56.5 atm ($= 5.72486 \times 10^6$ Pa) at 20°C. Methods for pressure liquefaction of carbon dioxide are generally known.

One embodiment of the present invention relates to the production of foamed plastics, for example by means of the casting or extrusion process. Another embodiment of the invention which will be explained later relates specifically to the production of single-component or dual-component polyurethane foamed materials from pressurised vessels (PU = polyurethane). First of all, the first-mentioned embodiment will be explained in greater detail below.

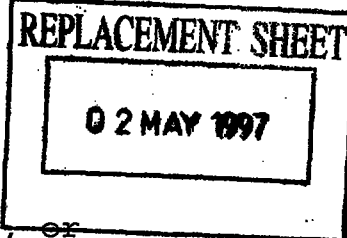
In the production of foamed plastics, any conventional customary liquid physical foaming agents, namely readily volatile organic compounds such as ethers, e.g. diethyl ether, ketones such as acetone, hydrocarbons such as pentane, hexane, heptane, gasoline mixtures, halogenated hydrocarbons or halogenated ethers can be used as additional liquid components in addition to the pressure-liquefied carbon dioxide. Also gases

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liquefied under pressure, such as propane or butane may be used in addition to the liquefied carbon dioxide. Furthermore, water can be used as a liquid foaming agent component.

5 Preferably, for the production of foamed plastics, a foaming agent composition is used which contains or consists of 10 to 20 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one physical foaming agent which is liquid or has been
10 liquefied under pressure, from the group consisting of alcohols with 1 to 5 carbon atoms, aliphatic hydrocarbons with 2 to 12 carbon atoms, cyclic hydrocarbons with 3 to 12 carbon atoms, halogenated hydrocarbons with 1 to 5 carbon atoms and halogenated
15 ethers with a total of 2 to 6 carbon atoms. Preferred alcohols in this case are in particular ethanol and isopropanol. Examples of aliphatic hydrocarbons are pentane, hexane, heptane and gasoline fractions, in particular light gasolines having a boiling point in
20 the range of 15 to 80°C. Furthermore, the low-boiling fractions, such as propane and/or butane, can also be used in the pressure-liquefied state as liquid foaming agent components. Examples of cyclic hydrocarbons are cycloaliphatic hydrocarbons, preferably cyclopropane, cyclopentane and cyclohexane. "Halogenated
25 hydrocarbons" is understood to mean hydrogen-containing fluoro-chloro-hydrocarbons or fluoro-hydrocarbons. Examples of fluoro-chloro-hydrocarbons which can be used are chlorodifluoromethane (R22), trifluoromethane
30 (R23), 1,1-dichloro-1-fluoroethane (R141b), 1-chloro-1,1-difluoroethane (R142b) and 1,3-dichloro-1,1,2,2,3,3-hexafluoropropane (R216a). Examples of fluoro-hydrocarbons are pentafluoroethane (R125), 1,1,1,2-tetrafluoroethane (R134a), 1,1,1-trifluoroethane (R143a), 1,1,2-trifluoroethane (R143),
35 1,1-difluoroethane (R152a), 1,1,1,3,3-pentafluoro-



propane (R245fa), octafluoropropane (R218), ~~or~~
alternatively, 1,1,1,3,3-pentafluorobutane (R365mfc).

"Halogenated ethers" is understood to mean
fluorochloroethers or fluoroethers containing hydrogen,
such as difluoromethoxy-2,2,2-trifluoroethane (E245).

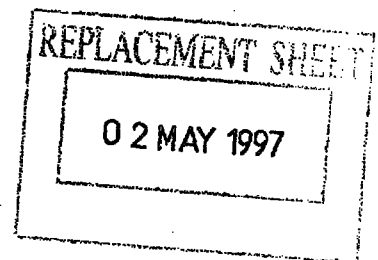
Preferably a foaming agent composition is used which
contains 10 to 20 parts by weight liquefied carbon
dioxide and 30 to 90 parts by weight of at least one
halogenated hydrocarbon or an aliphatic hydrocarbon or
a halogenated ether, or consists of the afore-mentioned
mixture.

Particularly preferably, in the method according to the
invention, a foaming agent composition is used which
contains or consists of 10 to 20 parts by weight
liquefied carbon dioxide and 30 to 90 parts by weight
1,1-difluoroethane (R152a) and/or 30 to 90 parts by
weight 1,1-dichloro-1-fluoroethane (R141b). Further
foaming agent compositions used particularly preferably
in the method according to the invention are foaming
agent compositions which contain 10 to 20 parts by
weight liquefied carbon dioxide and 80 to 90 parts by
weight 1,1-dichloro-1-fluoroethane (R141b) and also
optionally additionally 1 to 3 parts by weight water,
or consist of the afore-mentioned mixture. Likewise
preferably preferred is a foaming agent composition
which contains 10 to 20 parts by weight liquefied
carbon dioxide, 50 to 70 parts by weight 1,1-difluoro-
ethane (R152a) and 20 to 35 parts by weight ethanol, or
consists of this mixture. Among the compositions
according to the invention containing halogenated
ethers, those foaming agent compositions which contain
10 to 20 parts by weight liquefied carbon dioxide and
80 to 90 parts by weight difluoromethoxy-2,2,2-
trifluoroethane (E245) or consist of such mixtures are
particularly preferred. Of the aliphatic hydrocarbons,

n-pentane is particularly preferred. Preferably, a composition according to the invention containing aliphatic hydrocarbons should contain 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight n-pentane and also optionally additionally 1 to 3 parts by weight water or consist of such a mixture.

With all these foaming agent mixtures, the amount of the other foaming agents used can be reduced by using the liquid CO₂. CO₂ is physiologically harmless and environmentally compatible.

Expediently, the method according to the invention for producing foamed plastics is carried out as a casting process or extrusion process. In the extrusion process, mixtures suitable for the production of foamed plastics are extruded directly into foamed sheets, films, moulded parts, profiles or particles. Particularly preferably, foamed thermoplastic materials, in particular polyethylene, polypropylene or polystyrene foamed materials, are produced according to the invention. According to the invention, the method is then carried out such that the foaming agent composition consisting of liquefied carbon dioxide and an additional liquid physical foaming agent is admixed to a melt of the starting products suitable for producing foamed plastics, and the polymerisation of the starting products for the foamed plastics material to be produced is carried out, optionally while maintaining a slight excess pressure or reduced pressure during the foaming operation. Known processing units, e.g. extruder units, may be used for the method according to the invention. It is particularly surprising here that using the method



according to the invention it is possible to introduce carbon dioxide in the liquefied state even at elevated temperature into the extruder for the foaming of thermoplastic polymer melts. In contrast to the methods of the prior art known hitherto, this makes metering of the carbon dioxide possible without difficulty. According to the method of the invention, it is thus possible, using carbon dioxide, to produce predominantly closed-celled foamed materials of very uniform fine-celled structure. Furthermore, the foamed plastics obtained according to the method of the invention are distinguished by very good heat insulation properties.

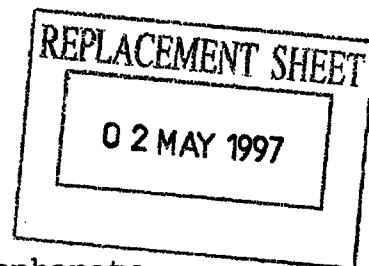
The method according to the invention for the production of foamed plastics can be carried out such that a foaming agent composition pre-formulated in a pressurised vessel is used, which composition was produced by placing the physical foaming agent which is liquid or has been liquefied under pressure in a pressurised vessel in the desired parts by weight and forcing in the desired quantity of pressure-liquefied carbon dioxide in known manner. However, it is also possible to proceed according to the method of the invention such that the foaming agent composition to be used is not produced until immediately before the foaming operation for the polymers or polymerisable components which are to be foamed. In this case, in a pressurised vessel outside the extruder unit proper liquefied carbon dioxide is introduced in corresponding quantities into the additional liquid foaming agent component at a pressure at which carbon dioxide is in liquid state, whereby the components largely mix together. The homogeneous mixture of liquefied carbon dioxide and liquid foaming agent component thus obtained is then introduced into the extruder unit via an inlet for liquid foaming agents.

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The method according to the invention is suitable both for the production of open-celled and closed-celled rigid or flexible foams. The method is particularly suitable for producing polyurethane foamed plastics. Known PU processing units, e.g. high-pressure or low-pressure mixing units which are equipped with the static mixers known from the prior art can be used for this.

In one variant for the production of foamed PU plastics, the foaming agents according to the invention may contain additional liquid additives, e.g. flame retardants, as an additional component in addition to pressure-liquefied carbon dioxide and one or more physical foaming agents which are liquid and/or have been liquefied under pressure. Conventional flame retardants are e.g. phosphate esters or phosphonates. Corresponding phosphate esters or phosphonic esters which have three lower alkyl groups or three lower alkyl groups substituted by one or more halogen atoms are particularly well suited. Lower alkyl preferably stands for C₁ to C₄ groups. Suitable examples are tris-chloroisopropyl phosphate, trichloroisopropyl phosphate, tris-chloroethyl phosphate, trichloroethyl phosphate, trichloropropyl phosphate, tris-chloropropyl phosphate, triethyl phosphate, dimethylethyl phosphate, tris-dichloroisopropyl phosphate and dimethylmethyl phosphonate.

If the method according to the invention is used for the production of PU foamed plastics, all customary foam raw materials, such as aliphatic, cycloaliphatic or aromatic diisocyanates or polyisocyanates may be used. Examples of foam raw materials are 2,4- and 2,6-toluylene diisocyanate, diphenylmethane diisocyanate, polymethylene polyphenyl isocyanate and mixtures thereof. Polyisocyanates containing



carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups, which are referred to as "modified polyisocyanates" or "isocyanate prepolymers" may also be used. In the production of PU foamed plastics, polyisocyanates are usually reacted with compounds which contain at least two hydrogen atoms which are reactive to isocyanate groups, for example compounds containing hydroxyl groups on the basis of polyesters, polyethers and amines, and also compounds containing amino and/or carboxyl and/or thiol groups. Furthermore, all catalysts used in the production of PU foamed plastics, such as tertiary amines and/or organometallic compounds such as tin salts of carboxylic acids may be used.

If the method according to the invention is used for the production of polystyrene or polyethylene foamed materials, all foam raw materials known per se may also be used for this.

In known manner, in addition to the polymers and/or polymerisable constituents, all known additives or auxiliaries, for example nucleation agents, pore regulator substances, flame retardants, antistatic agents, stabilisers, plasticisers, cross-linking agents, fillers or dyes may be added.

Another embodiment of the invention relates to the production of single-component or multi-component PU foamed materials from pressurised vessels, and will be explained below. In this case too, a foaming agent composition containing 0.5 to 50% by weight liquefied CO₂ is used.

"Foaming agent composition" is understood to mean the liquid content of the foaming agent composition

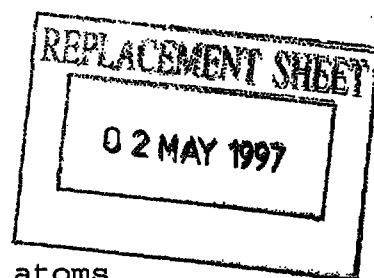
enclosed in the pressurised vessel, including the gas phase located in the pressurised vessel.

5 The foaming agent composition in this variant contains at least one additional liquid component in addition to the liquid CO₂. It may contain, for example, a liquid or pressure-liquefied physical foaming agent as additional liquid component. Halogenated foaming agents are highly suitable; halogen-free foaming agents are often environmentally compatible and to be preferred. According to a particularly advantageous variant, liquid CO₂ is contained as the sole foaming agent, and the liquid additional component is formed by a liquid flame retardant from the group of esters of phosphoric acid or the esters of phosphonic acid.

10 Any customary liquid physical foaming agents, namely readily volatile organic compounds such as ethers, acetone, hydrocarbons such as pentane, heptane, hexane, gasoline mixtures, halogenated hydrocarbons or halogenated ethers are possible as additional liquid components in addition to the pressure-liquefied carbon dioxide. Also gases liquefied under pressure, such as propane or butane, may be used in addition to the liquefied carbon dioxide.

20 Preferably the foaming agent compositions according to the invention contain more than 5% by weight, in particular 5 to 50, e.g. 5 or 10 to 30% by weight, liquefied carbon dioxide.

30 Foaming agent compositions which contain 10 to 50 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one foaming agent which is liquid or has been liquefied under pressure and is selected from the group consisting of ethers having a total of 2 to 4 carbon atoms, ketones having 3 to 5 carbon atoms,



aliphatic hydrocarbons having 2 to 12 carbon atoms, halogenated hydrocarbons having 1 to 5 carbon atoms and halogenated ethers having a total of 2 to 6 carbon atoms or consist of such a mixture are preferred.

5 Examples of aliphatic hydrocarbons are pentane, hexane, heptane and gasoline fractions, in particular light gasolines having a boiling point in the range of 15 to 80°C. Preferably the low-boiling fractions, such as propane and/or butane, are used in pressure-liquefied
10 form. Examples of cyclic hydrocarbons are cyclopropane, cyclopentane and cyclohexane.

"Halogenated hydrocarbons" are understood to mean hydrogen-containing fluorochlorohydrocarbons or fluoro-
hydrocarbons. Possible fluorochlorohydrocarbons are
15 e.g. chlorodifluoromethane (R22), 1,1-dichloro-1-fluoroethane (R141b), 1-chloro-1,1-difluoroethane (R142b) and 1,3-dichloro-1,1,2,2,3,3-hexafluoropropane (R216a). Examples of fluorohydrocarbons are trifluoromethane (R23), pentafluoroethane (R125),
20 1,1,1,2-tetrafluoroethane (R134a), 1,1,1-trifluoroethane (R143a), 1,1,2-trifluoroethane (R143), 1,1-difluoroethane (R152a), 1,1,1,3,3-pentafluoropropane (R245fa), octafluoropropane (R218) and 1,1,1,3,3,-pentafluorobutane (R365mfc). "Halogenated
25 ethers" are understood to mean hydrogen-containing fluorochloroethers or fluoroethers, such as difluoromethoxy-2,2,2-trifluoroethane (E245). Examples of possible ethers are dimethyl ether or diethyl ether. Of the ketones, acetone is particularly preferred.

30 The foaming agent compositions according to the invention may be free of halogenated foaming agents and consist only of liquefied carbon dioxide as the sole foaming agent component. Blends which contain or consist of liquefied carbon dioxide in a quantity of 20
35 to 30 parts by weight and butane or a propane/butane mixture in a quantity of 50 to 60 parts by weight

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and/or acetone in a quantity of 5 to 15 parts by weight are preferred. A customary mixture, for example a mixture having a vapour pressure of approximately 3.7 bar (absolute) can be used as the propane/butane mixture.

Also preferred are foaming agent compositions according to the invention which contain or consist of 10 to 50 parts by weight liquefied carbon dioxide and 10 to 90 parts by weight of a halogenated hydrocarbon or a halogenated ether. In this case, foaming agent compositions which contain or consist of 10 to 30 parts by weight liquefied carbon dioxide and of the halogenated hydrocarbons 10 to 90 parts by weight 1,1-difluoroethane (R152a) and/or 1,1-dichloro-1-fluoroethane (R141b) are particularly preferred. Among the compositions according to the invention containing halogenated ethers, those foaming agent compositions which contain or consist of 15 to 40 parts by weight liquefied carbon dioxide and 10 to 20 parts by weight difluoromethoxy-2,2,2-trifluoroethane (E245) are particularly preferred.

In another particularly preferred variant, the foaming agents according to the invention may contain phosphate esters or phosphonates customary as flame retardants in addition to pressure-liquefied carbon dioxide as liquid components. Phosphate or phosphonic esters which contain three C1 - C4 alkyl groups, which are optionally substituted by one or more halogen atoms are particularly suitable, such as tris-chloroisopropyl phosphate, tris-chloroethyl phosphate, trichloroethyl phosphate, trichloropropyl phosphate, tris-chloropropyl phosphate, triethyl phosphate, dimethylethyl phosphate, tris-dichloroisopropyl phosphate or dimethylmethyl phosphonate. Expediently, the concentrations are 10 to 50 parts by weight liquefied carbon dioxide and 80 to

100 parts by weight phosphate ester or phosphonate. Preferably tris-chloropropyl phosphate is used. These particularly preferred foaming agent compositions are free of foaming agents other than CO₂ and are therefore particularly environmentally compatible.

The foaming agent compositions according to the invention are suitable for the production of all PU foams known hitherto from pressurised vessels, in particular for foaming 1C and 2C PU foamed materials.

The foaming agent compositions according to the invention can also be used for the production of multi-component PU foamed materials in which the foam-forming agents with more than one reactive component are poured separately into a pressurised vessel. The foaming agent compositions according to the invention can also be used for the production of so-called 1.5C PU foams, in which, in contrast to the 2C foams, a quantity of a polyol component which is insufficient for reaction of the isocyanate groups is added to the prepolymer shortly before application.

The foaming agent compositions according to the invention have proved very advantageous for the production of 1C or 2C PU foamed materials.

The 1C PU foamed material mixture to be foamed in known manner may in known manner contain a polyol component, a polyisocyanate component, a catalyst and also optionally as auxiliary a flame retardant as additional constituents in addition to the foaming agent composition according to the invention.

Glycerol, glycols or polyether polyols which were obtained as addition products of propylene oxide or ethylene oxide to polyvalent alcohols, water or ethylene diamine, or polyester polyols which were

obtained as polycondensation products from polyols with dicarboxylic acids or their anhydrides, or mixtures thereof may for example be contained in the 1C PU foam mixture as the polyol component. A typical polyol

component may for instance be a mixture of a brominated polyether polyol (for instance diol or triol) with a hydroxyl number of 200 to 350 and a polyether polyol (e.g. a diol) with a hydroxyl number of 110.

Furthermore, modified vegetable oils having an OH number in the range of 100 to 300, e.g. castor oil, are also possible.

Examples of polyisocyanate components which can be used are diphenylmethane-4,4'-diisocyanate, diisocyanato-toluene, 1,5-diisocyanato-naphthalene, triisocyanato-triphenylmethane, 1,6-diisocyanatohexane, preferably diphenylmethane-4,4'-diisocyanate, or mixtures thereof.

Typical catalysts in 1C PU foam mixtures which can be foamed in the method according to the invention with a foaming agent composition according to the invention are organic amines, aminoalcohols or aminoethers, e.g. 2-dimethylaminoethyl-3-dimethylaminopropyl ether, diethanolamine, dimethylcyclohexylamine, 2-dimethyl-aminoethyl ether, or morpholine compounds, such as 2,2-dimorpholinodiethyl ether, N,N-dimethylaminoethyl morpholine, N-methyl morpholine. The morpholine compounds, in particular 2,2-dimorpholinodiethyl ether, are preferred.

Tris-chloroisopropyl phosphate, trichloroisopropyl phosphate, tris-chloroethyl phosphate, trichloroethyl phosphate, tris-chloropropyl phosphate, trichloropropyl phosphate, dimethylethyl phosphate, tris-dichloro-isopropyl phosphate, dimethylmethyl phosphonate and dimethylene ethyl phosphate, preferably tris-chloro-

propyl phosphate, may be used as customary flame retardants.

Copolymers of siloxane are for example suitable as stabilisers.

5 A 1C PU foam mixture which is to be foamed contains, relative to the foam mixture as 100% by weight, for example 20 to 30% by weight of a polyol component, 40 to 60% by weight of a polyisocyanate component, 0.1 to 3% by weight catalyst, optionally 10 to 15% by weight
10 of a flame retardant, and optionally 1 to 2% by weight foam stabiliser in addition to 15 to 35% by weight of a foaming agent composition according to the invention. A typical 1C PU foam mixture, which can advantageously be foamed with the aid of the foaming agent composition according to the invention thus consists for example of
15 approximately 22.5% by weight of a polyol component, e.g. of a mixture of a brominated polyether polyol with a hydroxyl number of 200 to 350 and a polyether polyol with a hydroxyl number of 110 in a mixture ratio of
20 1:1, approximately 42.5% by weight of a polyisocyanate component, e.g. diphenylmethane-4,4'-diisocyanate, approximately 0.5% by weight of a catalyst substance such as 2,2-dimorpholinodiethyl ether, approximately 1.5% by weight silicone foam stabiliser, approximately
25 13% by weight of a flame retardant such as tris-chloro-propyl phosphate, and a content of approximately 20% by weight of a foaming agent composition according to the invention. A single-component foamed material having a uniform, fine-celled structure and low bulk density,
30 e.g. a bulk density of approximately 23 to 25 kg/m³, can be produced from such a 1C PU foam mixture.

The 1.5C and 2C PU foamed materials differ from the single-component foamed materials in that the polyol component required for hardening the foam is kept

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5 separate from the prepolymer composition in the
pressurised vessel and is not added to the prepolymer
until immediately before foaming. All the polyol
components already mentioned may be used as the second
component. For more rapid hardening, the second
component may furthermore contain a conventional
catalyst, for example the afore-mentioned amine or
morpholine compounds or alternatively organometallic
compounds, such as tin dioctoate, cobalt naphthenate,
10 dibutyl tin dilaurate or iron acetylacetonate.

15 The 1C or multi-component PU foamed materials produced
with the foaming agent composition according to the
invention possess very good heat insulation properties
and are therefore well suited for insulation purposes,
e.g. in the construction or housing field. The foaming
agent compositions according to the invention are also
suitable for the production of polyurethane-based spray
adhesives.

20 Furthermore, the invention comprises a method for
producing a 1C or 2C PU foamed material, in which a PU
foamed material is produced from a pressurised vessel
which contains a PU foam mixture consisting of a polyol
component, a prepolymer containing isocyanate groups, a
catalyst and optionally additional conventional
25 auxiliaries and also one of the foaming agent
compositions described above by relieving the excess
pressure in the pressurised vessel to atmospheric
pressure through a valve. Appropriate pressurised
vessels and valves suitable for foaming are generally
30 known.

Furthermore, the invention relates to 1C or multi-
component PU foamed material mixtures for producing a
PU foamed material from pressurised vessels which

contain one of the foaming agent compositions described above.

Another subject of the invention is a method for producing a foaming agent composition for the production of PU foamed materials from pressurised vessels, in which liquefied carbon dioxide is used as a foaming agent component. In the method according to the invention, the physical foaming agent component which is liquid or has been liquefied under pressure is placed in a pressurised vessel in the desired parts by weight, and liquefied, usually pressure-liquefied, carbon dioxide is forced in in the desired amount in known manner. This foaming agent composition produced according to the invention can then be injected in the desired quantity into a pressurised vessel (aerosol can) which already contains the prepolymer and optionally all the other components. The quantity of carbon dioxide is then only regulated by the pressure permitted for aerosol cans (10 to 18 bar).

According to the invention, it is then possible to produce pressurised vessels containing PU foamed material mixtures which may contain approximately 20 to 30 g carbon dioxide per 1 kg can. According to methods used hitherto, in which carbon dioxide was always used in gaseous form, it was hitherto only possible to introduce only approximately 3 to 5 g carbon dioxide per 1 kg can. Advantageously, according to the invention it is now possible to reduce further the content of combustible physical foaming agents which are liquid or have been liquefied under pressure in the production of PU foamed materials from pressurised vessels. Also from the point of view of cost, reduction of the liquid or pressure-liquefied physical foaming agents customary hitherto is extremely advantageous. 1C or multi-component PU foamed

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materials produced with the foaming agent composition according to the invention have a predominantly closed-celled, very uniform, fine-celled structure and very high heat insulation properties. Accordingly, PU foamed materials which have been produced with a foaming agent composition according to the invention are particularly suitable for insulation purposes in the field of construction and housing.

The following examples are intended to explain the invention in greater detail, but without restricting its scope.

Examples

1. Production of a polystyrene foamed material

a) Liquefied carbon dioxide/R152a as foaming agent:

200 kg polystyrene (melt index 3.0-110) were mixed with 2 kg talcum as nucleation agent and this mixture was metered into a conventional extruder and melted. Approximately 6% by weight of a foaming agent according to the invention, relative to polystyrene, was metered into the melting zone of the extruder via an injection nozzle into the polystyrene melt. The foaming agent composition according to the invention contained 14 parts by weight liquefied carbon dioxide and 86 parts by weight R152a. The vapour pressure of this foaming agent composition was approximately 14 bar at 20°C.

In the mixing zone, the polystyrene melt was mixed homogeneously with the foaming agent composition according to the invention and then the resulting mixture was extruded via a nozzle. A closed-celled foamed material of uniform, fine-celled structure was obtained.

Both polystyrene foam films and polystyrene foam sheets were produced according to the invention. A polystyrene foam film produced according to the invention had a density of approximately 35 kg/m³, and a polystyrene foam sheet produced according to the invention had a density of approximately 33 kg/m³.

b) Liquefied carbon dioxide/R152a/ethanol as foaming agent:

As described under Example 1a), approximately 8.5% by weight of a foaming agent according to the invention, relative to polystyrene, was metered into a polystyrene melt. The foaming agent composition according to the invention contained 14 parts by weight liquefied carbon dioxide, 57 parts by weight R152a and 29 parts by weight ethanol. The vapour pressure of these foaming agent compositions was approximately 15 bar at 20°C.

A polystyrene foam film produced according to the invention had a density of approximately 36 kg/m³, and a polystyrene foam sheet produced according to the invention had a density of approximately 34 kg/m³.

2. Production of a polyethylene foam material

a) Liquefied carbon dioxide/R152a/R141b as foaming agent:

200 g polyethylene (melt index 3.5-150) were extruded under identical conditions as described in Example 1 for polystyrene foamed material. Approximately 6% by weight of a foaming agent mixture, relative to polyethylene, was metered in. According to the invention, a foaming agent composition consisting of 14 parts by weight liquefied carbon dioxide, 50 parts by

weight R152a and 36 parts by weight R141b was used. A fine-celled polyethylene foamed material of low shrinkage was obtained. The polyethylene foam tube produced according to the invention had a density of approximately 40 kg/m³.

3. Production of a PU foamed material

For production of the PU foamed material a polyol mixture, consisting of 40 parts by weight of an ethylene diamine/propylene oxide polyether (OH number 480), 60 parts by weight of a sorbitol/glycerol/propylene oxide polyether (OH number 490), 1 part by weight foam stabiliser (type DC193 by Dow Corning Corporation) and 1.5 parts by weight dimethyl-cyclohexylamine were used as one of the starting components. Diphenylmethane diisocyanate was used as the isocyanate component in a stoichiometric quantity increased by 10% by weight. The PU foamed materials were produced on a low-pressure installation having an output rate of approximately 8 kg/min, with which metering of 3 components is possible. A static mixer served as the mixing unit.

a) Liquefied carbon dioxide/R141b/water as foaming agent:

According to the invention, a foaming agent composition was used in a quantity of 30 parts by weight. The foaming agent composition consisted of 13.9 parts by weight liquefied carbon dioxide, 85.1 parts by weight R141b and additionally 1 part by weight water. With this foaming agent composition according to the invention, a PU rigid foam material having a fine-celled structure and a density of approximately 24 kg/m³ was produced.

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b) Liquefied carbon dioxide/n-pentane/water as foaming agent:

Furthermore, a PU foamed material containing 18 parts by weight of a foaming agent composition was produced. This foaming agent composition consisted according to the invention of 13.9 parts by weight liquefied carbon dioxide and 85.1 parts by weight n-pentane and additionally 1 part by weight water. With this foaming agent composition, a PU rigid foam material having a fine-celled structure and a density of approximately 25.4 kg/m³ was obtained.

c) Liquefied carbon dioxide/E245 as foaming agent:

Furthermore, a PU foamed material was produced with 35 parts by weight of a foaming agent composition. This foaming agent composition consisted according to the invention of 14 parts by weight liquefied carbon dioxide and 85 parts by weight E245. With this foaming agent composition, a PU rigid foam having a fine-celled structure and a density of approximately 33.5 kg/m³ was obtained.

4. Liquefied carbon dioxide/propane/butane/acetone as foaming agent for 1C PU foamed materials:

a) 247 g of an initial polyol mixture, consisting of

73 g polyether polyol (diol), brominated, hydroxide number approximately 240,

73 g polyether polyol (diol), hydroxide number approximately 110,

89 g tris-chloropropyl phosphate,

5 g silicone foam stabiliser,

7 g dimorpholinodiethyl ether,

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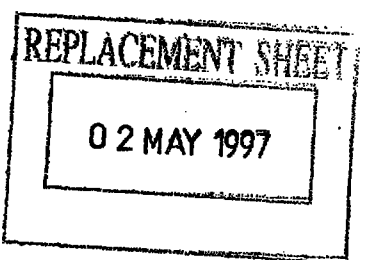
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was poured into an aluminium aerosol can having a volume of 1000 cm³. 356 g diphenylmethane-4,4-diisocyanate were added and the aerosol can was closed by a foam aerosol valve. A foaming agent composition according to the invention was produced by placing 62 g pressure-liquefied propane/butane and 10 g acetone in a pressurised vessel and adding 28 g pressure-liquefied carbon dioxide with mixing. 99 g of this foaming agent composition according to the invention was then injected via a conventional aerosol filling device into the aerosol can containing the foam components. The aerosol can was briefly shaken and allowed to stand for approximately 24 hours in order to form the prepolymer. Once this time had ended, the 1C PU foam mixture was ready for use.

The 1C PU foam mixture was expelled from the aerosol can by means of the foaming agent composition according to the invention. A PU foamed material having a bulk density of approximately 23 kg/m³ of uniform, fine-celled structure was obtained. The shrinkage of the PU foamed material after 7 days' storage at an atmospheric humidity of approximately 90% was about 5 percent length on average.

b) As described under a), a polyol blend and a polyisocyanate were poured into an aerosol can of the same volume. A composition of 50 g propane/butane, 7.5 g acetone and 20 g liquefied carbon dioxide was used as foaming agent composition according to the invention. The foaming agent composition was produced and poured into the aerosol can as described under a).

The PU foamed material produced with this foaming agent composition according to the invention had a bulk density of approximately 25 kg/m³.



5. Liquefied carbon dioxide/propane/butane/R141b as foaming agent for 1C PU foamed materials:

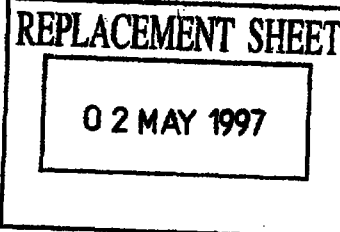
5 A polyol blend and a polyisocyanate were poured into an aerosol can having a volume of 1000 cm³ as described in Example 4. A composition of 62 g propane/butane, 10 g R141b and 28 g liquefied carbon dioxide was used as the foaming agent composition according to the invention. The foaming agent composition was produced and poured into the aerosol can as described in Example 4.

10 The PU foamed material produced with this foaming agent composition had a bulk density of approximately 25 kg/m³.

6. Liquefied carbon dioxide/trichloropropyl phosphate/R141b as foaming agent for 1C PU foamed materials:

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20 214 g of a polyol blend and 356 g polyisocyanate were poured into an aerosol can having a volume of 1000 cm³ as described in Example 4. A composition according to the invention was produced by placing 100 g tris-chloropropyl phosphate and 10 g R141b in a pressurised vessel and adding 28 g pressure-liquefied carbon dioxide with mixing. 99 g of this foaming agent composition was poured into the aerosol can as described in Example 4.



Claims

1. A foaming agent composition for the production of foamed plastics and for the production of single-component or dual-component polyurethane foamed materials from pressurised vessels, characterised in that it contains 0.5 to 50% by weight liquefied carbon dioxide.
2. A foaming agent composition according to Claim 1, characterised in that it contains 5 to 50% by weight liquefied CO₂.
3. A foaming agent composition according to Claim 2, characterised in that it contains 10 to 50% by weight liquefied CO₂.
4. A foaming agent composition according to Claim 3, characterised in that it contains 10 to 20% by weight liquefied CO₂.
5. A foaming agent composition according to any one of Claims 1 to 4 for the production of foamed plastics, characterised in that it contains 10 to 20 parts by weight liquefied carbon dioxide and 30 to 90 parts by weight of at least one physical foaming agent which is liquid or has been liquefied under pressure and is selected from the group consisting of alcohols with 1 to 5 carbon atoms, aliphatic hydrocarbons with 2 to 12 carbon atoms, cyclic hydrocarbons with 3 to 12 carbon atoms, halogenated hydrocarbons with 1 to 5 carbon atoms and halogenated ethers with a total of 2 to 6 carbon atoms.
6. A foaming agent composition according to any one of Claims 1 to 4 for the production of single-component or dual-component polyurethane foamed materials from



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pressurised vessels, characterised in that it contains
10 to 50 parts by weight liquefied carbon dioxide and
30 to 90 parts by weight of at least one foaming agent
which is liquid or has been liquefied under pressure
and is selected from the group consisting of ethers
having a total of 2 to 4 carbon atoms, ketones having 3
to 5 carbon atoms, aliphatic hydrocarbons having 2 to
12 carbon atoms, cyclic hydrocarbons with 3 to 12
carbon atoms, halogenated hydrocarbons having 1 to 5
carbon atoms and halogenated ethers having a total of 2
to 6 carbon atoms.

7. A foaming agent composition according to any one
of Claims 1 to 4 for the production of single-component
or dual-component polyurethane foamed materials from
pressurised vessels, characterised in that it contains
10 to 50 parts by weight liquefied carbon dioxide and
80 to 100 parts by weight of at least one trialkyl
phosphate or trialkyl phosphonate selected from the
group consisting of triethyl phosphate, trichloro-
isopropyl phosphate, tris-chloroethyl phosphate, tris-
chloroisopropyl phosphate, tris-chloropropyl phosphate,
trichloroethyl phosphate, trichloropropyl phosphate,
tris-dichloroisopropyl phosphate, dimethylethyl
phosphate, dimethylmethyl phosphonate, diethylmethyl
phosphonate and diethylethyl phosphonate.

8. A halogen-free foaming agent composition according
to Claim 7, characterised in that it contains 20 to 30
parts by weight liquefied carbon dioxide and 50 to 60
parts by weight butane or a propane/butane mixture
and/or 5 to 15 parts by weight acetone.

9. A foaming agent composition according to Claim 7,
characterised in that it contains 20 to 40 parts by
weight liquefied carbon dioxide and 10 to 50 parts by
weight of a halogenated hydrocarbon selected from the



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group consisting of 1,1-dichloro-1-fluoroethane,
pentafluoroethane and 1,1-difluoroethane.

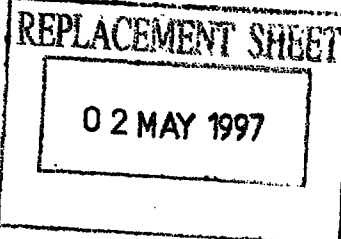
10. A foaming agent composition according to Claim 7,
characterised in that it contains 20 to 40 parts by
weight liquefied carbon dioxide and 10 to 50 parts by
weight difluoromethoxy-2,2,2-trifluoroethane.

11. A method for the production of foamed plastics
with the aid of foaming agents, characterised in that a
liquid foaming agent composition according to Claim 1
is used which contains 0.5 to 50% by weight liquefied
carbon dioxide.

12. A method according to Claim 11, characterised in
that a foaming agent composition is used which contains
10 to 20 parts by weight liquefied carbon dioxide and
30 to 90 parts by weight of at least one foaming agent
which is liquid or has been liquefied under pressure
and is selected from the group consisting of alcohols
with 1 to 5 carbon atoms, aliphatic hydrocarbons with 2
to 12 carbon atoms, cyclic hydrocarbons with 3 to 12
carbon atoms, halogenated hydrocarbons with 1 to 5
carbon atoms and halogenated ethers with a total of 2
to 6 carbon atoms.

13. A method according to Claim 12, characterised in
that a foaming agent composition is used which contains
10 to 20 parts by weight liquefied carbon dioxide and
30 to 90 parts by weight of at least one aliphatic or
halogenated hydrocarbon or halogenated ether.

14. A method according to Claim 13, characterised in
that a foaming agent composition is used which contains
10 to 20 parts by weight liquefied carbon dioxide and



30 to 90 parts by weight 1,1-difluoroethane and/or 30 to 90 parts by weight 1,1-dichloro-1-fluoroethane.

5 15. A method according to Claim 14, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight 1,1-dichloro-1-fluoroethane.

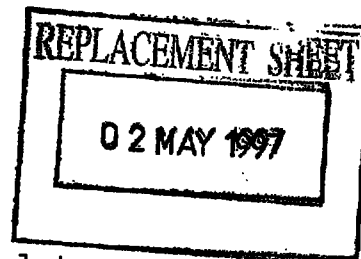
10 16. A method according to Claim 11, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide, 50 to 70 parts by weight 1,1-difluoroethane and 20 to 35 parts by weight ethanol.

15 17. A method according to Claim 13, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight difluoromethoxy-2,2,2-trifluoroethane.

20 18. A method according to Claim 13, characterised in that a foaming agent composition is used which contains 10 to 20 parts by weight liquefied carbon dioxide and 80 to 90 parts by weight n-pentane.

19. A method according to Claim 11, characterised in that foamed polyethylene, polystyrene or polyurethane plastics are produced.

25 20. A method for producing a single-component or dual-component polyurethane foamed material, characterised in that a polyurethane foamed material is produced from a pressurised vessel which contains a prepolymer containing isocyanate groups, optionally additional conventional auxiliaries and a foaming agent
30 composition according to any one of Claims 1 to 4 or 6 to 10 as foaming agent by pressure-relieving the excess



pressure prevailing in the pressurised vessel to atmospheric pressure via a suitable valve.

21. A method according to Claim 20, characterised in that a foaming agent composition is used in a quantity of 5 to 40% by weight, relative to the total mixture of prepolymer and foaming agent composition.

22. A method for producing a foaming agent composition according to Claim 1, characterised in that carbon dioxide which has been liquefied under pressure is introduced into an additional component which is liquid or has been liquefied under pressure or vice versa, so that the foaming agent composition contains 0.5 to 50% by weight liquid CO₂.

23. A method according to Claim 22, characterised in that the additional component is a foaming agent or a flame retardant.

24. A composition consisting of prepolymer and foaming agent for the production of a single-component or dual-component polyurethane foamed material, characterised in that it contains a foaming agent composition according to any one of Claims 1 to 4 or 6 to 10.

25. An arrangement for producing a single-component or dual-component polyurethane foamed material, characterised in that it contains a prepolymer containing isocyanate groups and a foaming agent composition according to any one of Claims 1 to 4 or 6 to 10 in a pressurised vessel provided with a valve.

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PCT
WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro
**INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)**

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(54) Title: FOAMING AGENTS CONTAINING LIQUID CARBON DIOXIDE			
(54) Bezeichnung: FLÜSSIGES KOHLENDIOXID ENTHALTENDE TREIBMITTEL			
(57) Abstract			
The invention concerns a process for preparing foamed plastics, wherein a liquid foaming agent composition containing carbon dioxide liquefied under pressure is used. In addition to the carbon dioxide liquefied under pressure, all conventional liquid physical foaming agents such as alcohols, aliphatic or cyclical hydrocarbons, halogenous hydrocarbons or halogenous ethers can be used. The process is suitable in particular for preparing foamed polyethylene, polystyrene or polyurethane plastics. Foaming agent compositions containing carbon dioxide liquefied under pressure are also suitable for producing single or multi-component polyurethane foamed materials. In addition to the carbon dioxide liquefied under pressure all conventional liquid physical foaming agents such as ethers, ketones, aliphatic or cyclical hydrocarbons, halogenous hydrocarbons or halogenous ethers can be used. The invention further concerns a process for preparing these foaming agent compositions.			
(57) Zusammenfassung			
Beschrieben wird ein Verfahren zur Herstellung geschäumter Kunststoffe, bei dem man eine flüssige Treibmittelzusammensetzung einsetzt, welche unter Druck verflüssigtes Kohlendioxid enthält. Neben dem unter Druck verflüssigtem Kohlendioxid können dabei alle üblichen flüssigen physikalischen Treibmittel wie Alkohole, aliphatische oder cyclische Kohlenwasserstoffe, halogenhaltige Kohlenwasserstoffe oder halogenhaltige Ether verwendet werden. Das Verfahren eignet sich insbesondere für die Herstellung geschäumter Polyethylen-, Polystyrol- oder Polyurethan-Kunststoffe. Treibmittelzusammensetzungen, welche unter Druck verflüssigtes Kohlendioxid enthalten, eignen sich auch zur Erzeugung von Einkomponenten- oder Mehrkomponenten-Polyurethan-Schaumstoffen. Neben dem unter Druck verflüssigtem Kohlendioxid können auch hier alle üblichen flüssigen physikalischen Treibmittel wie Ether, Ketone, aliphatische oder cyclische Kohlenwasserstoffe, halogenhaltige Kohlenwasserstoffe oder halogenhaltige Ether eingesetzt werden. Weiterhin wird ein Verfahren zur Herstellung dieser Treibmittelzusammensetzungen beschrieben.			