

Description

This invention relates to improved polymer foams and foaming agents by the use of blocking agents. More specifically, the invention relates to combinations of a hydrogen bond forming blocking agent and a hydrogen-containing fluorocarbon and a method of using the same in closed cell polymer foams to reduce permeation of air and/or hydrohalocarbon, thereby maintaining low thermal conductivity and improved thermal insulation value of the foam.

It is generally known and an accepted commercial practise to add a blowing agent to various polymeric materials during fabrication such as to produce a cellular (expanded foam) material. Typically, the blowing agent can be either a reactive solid or liquid that evolves a gas, a liquid that vaporizes, or a compressed gas that expands during final fabrication producing the desired polymeric foam. Such foams are categorically either closed cell (i.e. non-porous, continuous polymer phase with discontinuous gas phase dispersed therein) or open cell (porous) foams which are advantageously employed in various end use applications and exhibit various advantages associated with the particular type of foam produced. In describing the closed cell foam as involving a discontinuous gas phase, it should be appreciated that this description is an over simplification. In reality the gas phase is dissolved in the polymer phase and there will be a finite substantial presence of gas (blowing agent) in the polymer. Furthermore and as generally known in the art, the cell gas composition of the foam at the moment of manufacture does not necessarily correspond to the equilibrium gas composition after aging or sustained use. Thus, the gas in a closed cell foam frequently exhibits compositional changes as the foam ages leading to such known phenomenon as increase in thermal conductivity or loss of insulation value.

Closed cell foams are usually employed for their reduced thermal conductivity or improved thermal insulation properties. Historically, insulating polyurethane and polyisocyanurate foams have been made using trichlorofluoromethane, CCl_3F (CFC-11), as the blowing agent. Similarly, insulating phenolic foam is known to be made from phenol-formaldehyde resins (typically via an intermediate resole mixture involving a phenol-formaldehyde oligomer condensate) using blends of 1,1,2-trichlorotrifluoroethane, $\text{CCl}_2\text{FCClF}_2$ (CFC-113), and CFC-11 as the blowing agent. Also, insulating thermoplastic foam such as polystyrene foam is commonly manufactured using dichlorodifluoromethane, CCl_2F_2 (CFC-12), as the blowing agent.

The use of a chlorofluorocarbon as the preferred commercial expansion or blowing agent in insulating foam applications is in part based on the resulting k-factor (i.e., the rate of transfer of heat energy by conduction through one square foot of one inch thick homogenous material in one hour where there is a difference of one degree Fahrenheit perpendicularly across the two surfaces of the material) associated with the foam produced. Thus, it is generally known and accepted that a chlorofluorocarbon gaseous phase within the closed cell is a superior thermal barrier relative to other inexpensive gases such as air or carbon dioxide. Conversely, the natural intrusion of air into the foam over time and to a lesser extent the escape of the chlorofluorocarbon from the cell is deleterious to the desired low thermal conductivity and high insulative value of the foams. Also, the escape of certain chlorofluorocarbons to the atmosphere is now recognized as potentially contributing to the depletion of the stratospheric ozone layer and contributing to the global warming phenomenon. In view of the environmental concerns with respect to the presently used chlorofluorocarbon blowing agents, it is now generally accepted that it would be more desirable to use hydrochlorofluorocarbons or hydrofluorocarbons rather than the chlorofluorocarbons. Consequently, the need for a method or way of inhibiting the permeation of air and blowing agent through the polymer phase of the polymeric foam exists and hopefully any such solution to the problem would be effective in inhibiting the permeation of the proposed alternative halocarbons.

Historically, various methods and compositions have been proposed, with varying degree of success, to alleviate and/or control problems associated with permeation of gases into and out of polymeric foams. For example, in U.S. Patent 4,663,361 the problem of shrinkage (lack of dimensional stability) associated with using any blowing agent other than 1,2-dichlorotetrafluoroethane in the manufacture of foamed polyethylene is addressed. In this reference, a stability control agent is used in either a homopolymer or copolymer of ethylene wherein the blowing agent is isobutane or isobutane mixed with another hydrocarbon or a chlorocarbon, fluorocarbon or chlorofluorocarbon. The stability control agent is either partial esters of long chain fatty acids with polyols, higher alkyl amines, fatty acid amides, olefinically unsaturated carboxylic acid copolymers, or polystyrene.

In U.S. Patent 4,243,717 a Fischer-Tropsch wax is added to expanded polystyrene beads to produce a stable cell structure in the foam, without specific reference to the permeation of blowing agent or air. In Canadian Patent 990,900 the use of a barrier material or blocking agent is disclosed to alleviate the problem of gas migration through the cell wall specifically at the time of foaming. The particular problem addressed in this Canadian patent is the rupture and total collapse of the cell walls that frequently occur in the

manufacture of closed cell polyethylene foam. This problem is attributed to the fact that the cell walls for such foams are permeable to the rapidly expanding gas under the influence of the heat liberated by the exothermic polymer crystallization. The specific solution disclosed in this reference is to use a blend of polyethylene and polypropylene along with a barrier resin such as an elastomer containing polystyrene or acrylic resin which are intended to contribute high melt strength to the cell wall at the foaming temperature. An inert nucleant is also employed along with at least two gaseous propellants of substantially different vapor pressures.

In US Patent 4,795,763, the use of at least 2 percent carbon black as a filler uniformly dispersed in a polymeric foam is shown to reduce the aged k-factor of the foam to below the aged k-factor of the corresponding unfilled foam.

Thus, according to the present invention the effective rate of permeation of air and/or hydrohalocarbon across the polymeric phase of the foam is substantially reduced by virtue of the presence of a blocking agent. Further, according to the present invention, a blocking agent capable of hydrogen bond formation with the hydrogen-containing fluorocarbon is incorporated into the polymeric foam and thus tends to form hydrogen bonds with the blowing agent. This in turn dramatically reduces the permeation rate of the hydrogen-containing blowing agent retaining it in the foam. The presence of the blocking agent also functions to reduce entry of air into the polymer foam. By reducing the entry of air into insulating foam and simultaneously reducing the permeation of blowing agents out of insulating foam, the blocking agents according to the present invention produce foams which better maintain their insulating characteristics relative to foams made without these hydrogen bond forming agents.

EPA-001791 describes a polymer foaming composition, a closed cell foam and a method of manufacturing such a foam using ester of saturated fatty acid and certain fluorocarbon blowing agents. This document does not disclose the use of a hydrogen bond forming blocking agent which bonds or associates with the fluorocarbon to reduce permeation of air into the foam and loss of blowing agent from the foam.

EPA-305084 describes a process for producing a phenolic closed cell foam by using a mixture of a resole resin and a gel-forming ethylene oxide block copolymer. This document does not disclose the use of hydrogen-containing fluorocarbon blowing agents.

Thus, according to one aspect the present invention provides a closed cell thermoplastic or thermoset insulating polymer foam comprising a continuous polymeric phase and a discontinuous gaseous phase, characterised by:

a gaseous phase comprising at least one hydrogen-containing fluorocarbon, wherein said fluorocarbon comprises:

CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; and/or CH_2FCF_3 ; and

a hydrogen bond forming blocking agent wherein said agent associates or bonds with said fluorocarbon thereby reducing the permeation of air into the foam and slow down the escape of blowing agent from the foam.

Preferably the hydrogen bond forming blocking agent is present in the range of from 0.1 to 20 weight percent based on the total weight of foam.

Since the blocking agent according to the present invention can often be conveniently incorporated, marketed and used in combination with the blowing agent, the present invention further provides a polyol-containing foaming composition for a closed-cell insulating thermoset polymer foam comprising:

(a) a hydrogen-containing fluorocarbon wherein said fluorocarbon comprises:

CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; and/or CH_2FCF_3 ; and

(b) an effective amount of a polyol to produce a thermoset foam when reacted with an isocyanate containing component, and a hydrogen bond forming blocking agent which associates or bonds with said fluorocarbon, thereby simultaneously reducing the permeation of air into the foam and slow down the escape of blowing agent from the foam, during said reaction.

The invention also includes a method of manufacturing a closed cell thermo-plastic or thermoset insulating foam wherein a blowing agent expands as the polymeric phase solidifies, the method comprising:

selecting a hydrogen-containing fluorocarbon as the blowing agent, wherein said fluorocarbon comprises:

CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; and/or CH_2FCF_3 and

adding a hydrogen bond forming blocking agent, wherein said agent associates or bonds with said fluorocarbon, thereby reducing the permeation of air into the foam and slowing down the escape of blowing agent from the foam.

The invention further includes the use in the formation of a closed cell insulating polymer foam from a polyol, and an isocyanate or resole of a hydrogen-containing fluorocarbon blowing agent comprising CH_2F_2 , CHF_2CF_3 ; CHF_2CHF_2 and/or CH_2FCF_3 and a hydrogen bond forming blocking agent, wherein said agent

associates or bonds with said hydrogen-containing fluorocarbon blowing agent, thereby reducing the permeation of air into the foam and slowing down the escape of said blowing agent from the foam.

A further aspect of the invention comprises a thermoset polymer closed-cell insulating foam composition produced by reacting an isocyanate containing component in the presence of a hydrogen-containing fluorocarbon; and an effective amount of a polyol to produce a thermoset foam and a hydrogen bond forming blocking agent which associates or bonds with said fluorocarbon, thereby simultaneously reducing the permeation of air into the foam and slowing down the escape of blowing agent from the foam, wherein said fluorocarbon comprises:

CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; and/or CH_2FCF_3 ; and wherein said polyol comprises:

polyethylene glycol, polypropylene glycol, ethylene oxide/propylene oxide copolymer, sucrose polyol and/or a polyol containing ether, ester or ketone groups.

An additional blowing agent may be employed in the foaming composition, the blowing agent being selected from CCl_2FCH_3 , CClF_2CH_3 , CF_3CH_3 , $\text{CH}_2\text{FCH}_2\text{F}$, CHF_2CH_3 , CO_2 , hydrocarbons, and methyl formate.

It is an object of the present invention to provide a blocking agent that when incorporated into a polymeric foam will reduce or prevent the intrusion of air into the foam and/or the permeation or escape of blowing agent from the foam. It is a further object of the present invention to provide such a blocking agent that is particularly useful with the hydrogen-containing chlorofluorocarbons and hydrogen-containing fluorocarbons (i.e., the HCFCs and HFCs) in that the blocking agent will hydrogen bond with the hydrohalomethanes and hydrohaloethanes, thus significantly reducing their rate of permeation and escape from a closed cell polymeric foam. It is an associated object of the present invention to provide insulating foam containing a blocking agent and a method of manufacturing the same that exhibits preservation of the insulating properties over longer periods of times relative to the absence of the blocking agent. Fulfillment of these objects and the presence and fulfillment of additional objects will be apparent upon complete reading of the specification and the claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Polymer foams typically involve a continuous or at least a contiguous phase in a cellular structure. This cellular structure can be either flexible or rigid and is categorically either an open cell structure (i.e., the individual cells are ruptured or open producing a soft, porous "sponge" foam which contains no blowing agent gas) or a closed cell structure (i.e., the individual cells contain blowing agent gas surrounded by polymeric sidewalls with minimum cell-to-cell gas flow). Thermally insulating foams are closed cell structures containing a blowing agent gas (i.e., a gas formed in situ during the foam manufacturing process). Preferably the blowing agent gas should have a low vapor thermal conductivity (VTC) so as to minimize conduction of heat through the insulating foam. Thus, the vapor thermal conductivities for halocarbons such as CFC-11, CFC-12 and hydrochlorodifluoromethane, CHClF_2 (HCFC-22), at 25°C (i.e., 45.1, 55.7 and 65.9 $\text{Btu}\cdot\text{ft}^{-1}\cdot\text{hr}^{-1}\cdot^\circ\text{F}^{-1} \times 10^4$, respectively) compare favorably to the VTC for air at 25°C (i.e., 150.5 $\text{Btu}\cdot\text{ft}^{-1}\cdot\text{hr}^{-1}\cdot^\circ\text{F}^{-1} \times 10^4$). From these data, it can readily be seen that the presence of a halocarbon blowing agent is required for optimum thermal insulation properties with both thermoplastic and thermoset foams.

A problem with hydrogen-containing alternative blowing agent HCFC-22 is its rapid migration from thermoplastic foams. For example, in the case of one grade of polystyrene, the permeation rate at 25°C for CFC-12 vs. HCFC-22 was 4.2×10^{-9} g/hr vs. 6.5×10^{-8} g/hr (i.e., HCFC-22 diffused 15.5 times faster than CFC-12). Without some way to prevent or slow down the rate of HCFC-22 permeation from polystyrene foam, this blowing agent is unacceptable for producing good insulation foam, using this particular grade of polystyrene.

HCFC-22 is also known to diffuse rapidly from some polyurethane/polyisocyanurate foam formulations. Techniques for slowing/preventing this blowing agent migration are required if the halocarbon is to be useful in preparing these thermoset insulating foams.

In addition to the undesirable degradation of foam insulation value caused by permeation losses of blowing agent, the effect of air entry from the atmosphere into the foam cells is at least equally significant. As air enters the foam cells, the vapor thermal conductivity of the cell gas increases and the insulation value drops.

The blocking agents of this invention unexpectedly function to reduce air entry into foams and/or to reduce the permeation of hydrogen-containing blowing agents such as HCFC-22 from the foam cells,

* 1 $\text{Btu ft}^{-1}\text{ hr}^{-1}\cdot^\circ\text{F}^{-1} = 1.73 \cdot 10^3 \text{ W/m}^\circ\text{K}$

thereby producing more effective/economical insulation foams.

For the purposes of the present invention, the term "blocking agent" is used herein to denote hydrogen bond forming compounds which contain ether, ester or ketone groups or the like. These hydrogen bond forming compounds can bond or associate with hydrogen-containing halocarbon blowing agents such as HCFC-22 and thereby reduce their rates of permeation from the foam.

Unexpectedly, HCFC-22, difluoromethane (CH_2F_2 , HFC-32), pentafluoroethane (CHF_2CF_3 , HFC-125), 1,1,2,2-tetrafluoroethane (CHF_2CHF_2 , HFC-134), and 1,1,1,2-tetrafluoroethane (CH_2FCF_3 , HFC-134a) have been observed to associate or hydrogen bond with compounds containing ether, ester or ketone groups. Glycols and other polyhydroxy compounds tend to form intra- or inter-molecular hydrogen bonds with themselves and thus do not associate strongly with HCFC-22. HCFC-22, with hydrogen bonding esters, ketones or ethers, exhibits dramatically reduced vapor pressure as a result of the association. Furthermore, when these hydrogen bonding compounds are present in thermoplastic polymers such as polystyrene, the permeation of HCFC-22 is reduced/slowed as the result of the mutual association which occurs between these compounds. The hydrogen bond forming agents additionally function to improve the solubility of blowing agents such as HFC-134a in thermoplastic polymers such as polystyrene.

Also, the mutual solubility of HCFC-22 and HCFC-123 with several hydrogen bond forming compounds further provides evidence of an unexpected association between these materials. CFC-12 does not share this unexpected solubility characteristic. Because of the solubility of many of the hydrogen bond forming compounds in HCFC-22, these compounds are suitable for dissolving in HCFC-22 and, thus, can be made commercially available in this convenient form.

For purposes of the present invention and as previously mentioned, the blocking agent can broadly be any compound that contains either an ether, ester or ketone group or combinations of the same and is capable of hydrogen bonding or the equivalent strong association or complexing with hydrogen-containing halocarbons. For example, but not by way of limitation, the following table lists examples of ether, ester or ketone groups containing compounds which associate or hydrogen bond with hydrogen-containing halocarbons such as HCFC-22.

HYDROGEN BONDING AGENTS

- (1) Polyethylene oxide polymers
- (2) Ethylene oxide/propylene oxide copolymers
- (3) Polypropylene oxide polymers
- (4) Polyethylene glycol mono- and dioleates
- (5) Polyethylene glycol monostearates
- (6) Alkylphenoxy polyethoxy ethanols
- (7) Polyethylene oxide sorbitan monostearates and tristearates
- (8) Polyethylene oxide fatty acid amides
- (9) Primary and secondary alcohol ethoxylates
- (10) Glyme, diglyme, triglyme and tetraglyme
- (11) Mono-, di- and tripropylene glycol methyl ethers and ether acetates
- (12) Dimethyl adipate, succinate and glutarate
- (13) Ethylene oxide/propylene oxide adducts with a sucrose
- (14) Ketones and polyketone polymers.

The use of hydrogen-containing blowing agents such as HCFC-22 with ether, ester or ketone hydrogen bond forming compounds in polymer foams does not preclude the simultaneous incorporation of blowing agents such as 1,1-dichloro-1-fluoroethane (CCl_2FCH_3 , HCFC-141b), 1-chloro-1,1-difluoroethane (CClF_2CH_3 , HCFC-142b), 1,1,1-trifluoroethane (CF_3CH_3 , HFC-143a), 1,2-difluoroethane ($\text{CH}_2\text{FCH}_2\text{F}$, HFC-152), and 1,1-difluoroethane (CHF_2CH_3 , HFC-152a) which do not tend to form strong hydrogen bonds. It should be further appreciated that 1,1,1-trifluoro-2,2-dichloroethane (CHCl_2CF_3 , HCFC-123), 1,1,2-trifluoro-1,2-di-chloroethane (CHClFCClF_2 , HCFC-123a), 1,1,1,2-tetra-fluoro-2-chloroethane (CHClFCF_3 , HCFC-124), and various CFCs may also be present as a component of a blowing agent mixture useful according to the present invention and that the present invention is applicable when CO_2 , C_3 - C_6 hydrocarbons or methyl formate are components of the blowing agent gas. Similarly, various additives such as stabilizers, dyes, and fillers can be present in the blowing agent.

In addition to reducing the entry of air into and/or the migration of hydrogen-containing blowing agents such as HCFC-22 from thermoplastic foams, the hydrogen bond forming agents may provide other functions to the foam manufacturing process. For example, compounds such as the polyethylene oxide polymers may provide lubricity and thereby increase the extrusion throughput or production rate. Further-

more, these compounds are contemplated as potentially useful as polymer plasticizers and may contribute advantageously to other properties.

The hydrogen bond forming agents of this invention are suitable for use with thermoplastics such as polystyrene, polyethylene, polypropylene, and polyvinyl chloride, to prevent loss of hydrogen-containing blowing agents; however, they can also be used with thermoset polymer foams such as polyurethane, polyisocyanurate, and phenolic resin foams. Since these hydrogen bond forming agents associate with blowing agents such as HCFC-22, they will function to reduce/prevent permeation of the blowing agent in any compatible polymer foam system. Furthermore, these hydrogen bond forming agents will function in the presence of other additives normally used in polymer foams, such as stabilizers, dyes, and fillers.

The blowing agent concentration used to prepare most conventional thermoplastic and thermoset polymer foams is generally in the range of 5 weight percent to 30 weight percent (based on total weight of the foam). To reduce migration of hydrogen-containing blowing agents such as HCFC-22, the effective use concentration of hydrogen bond forming agent is at least 0.1 weight percent and preferably from 1.0 to 20 weight percent (based on total formulation weight), most preferably 0.5 weight percent to 10 weight percent.

Typically, the improved polymer foaming composition will contain from 1 to 100 parts by weight hydrogen bond forming blocking agent for every 100 parts of hydrogen-containing halocarbon blowing agent.

The actual method by which the blocking agent according to the present invention is to be incorporated into the closed cell foam can vary according to the specific application and composition being employed. In the broadest sense, the blocking agent can be treated as any other foam additive as generally known in the art. As previously stated, the blocking agent in certain applications imparts beneficial effects to the polymer phase in addition to reducing permeability and in such cases the blocking agent can be added to the polymer. Since the blocking agent is categorically a hydrogen bond forming compound, it may be advantageously added to the blowing agent or preblended into the polymer (e.g., polystyrene) prior to extrusion or other method of fabrication. In the case of thermoset foams (e.g., polyurethane/polyisocyanurate foams) the hydrogen bond forming agents can be added to the foam in the isocyanate (A-side) or the polyol (B-side) or added with the blowing agent at the mixing head where the A-side and B-side are combined (i.e., third-streamed). For purposes of the present invention the term "A-side" is used to specify the isocyanate containing component of a conventional two component precursor foam system. The term "B-side" is used to specify the polyol containing component. It should be appreciated that this nomenclature may be reversed particularly in certain European literature. It should be further appreciated that these precursor components to foams typically contain other ingredients, additives, agents, and diluent all as generally known in the art. Thus for example, but not by way of limitation, the B-side will typically contain, in addition to the polyol, a surfactant, a catalyst and one or more blowing agents. If the hydrogen bond forming agent used contains free hydroxyl groups, this must be taken into account when calculating the hydroxyl equivalent for the B-side system. In the case where the blocking agent is preferentially more soluble in one of the foam components, it is preferably added to that component. For example, addition of the blocking agent to the polyol component of two-component thermoset resin is preferred. Of course, the addition to more than one component or either component is also contemplated. In the case of phenolic foams, the hydrogen bond forming agents can be added to the foam by preblending into the resole or added separately at the mixing head prior to the foam laydown. The most preferred method of adding the blocking agent is to mix it with the blowing agent and as such the admixture of HCFC or HFC and blocking agent is contemplated as being a commercially attractive product, per se. Again, since the blocking agent is categorically a hydrogen bond forming compound, in the case of the thermoset foams (e.g., polyurethane/polyisocyanurate foams) not only can a polyol be added as the blocking agent but the polyol (B-side) can be viewed as the blocking agent. Thus, as previously stated if the hydrogen bond forming agent used contains free hydroxyl groups they must be taken into account when calculating the hydroxyl equivalent for the B-side system. Conversely, the ether and ester groups of the polyol found in the B-side should also be viewed as contributing as the hydrogen bond forming blocking agent. As such, in cases where there are ether and/or ester groups present in the polyol, the polyol should be considered as a blocking agent.

The following examples are presented to further illustrate specific critical properties of various specific embodiments of the present invention, including vapor pressure, boiling point and permeation data, as well as similar properties, for comparison purposes, of systems and compositions outside the scope of the invention. Any term appearing in capital letters and between " " marks is a trademark for a particular product.

EXAMPLE 1

The solubilities of several representative hydrogen bond forming agents in HCFC-22 were determined for 10 wt. % solutions at ambient temperature (approximately 21°C). The solutions were prepared by combining the hydrogen bond forming agents with HCFC-22 in 30 ml. plastic-coated pressure bottles. Solubility was determined by visual examination. Table I lists ten hydrogen bond forming compounds which are soluble to > 10 wt. % in HCFC-22. These hydrogen bond forming agents are soluble in HCFC-22, HCFC-123 and HCFC-123a because of their bonding or association; whereas, they are generally insoluble in CFC-12. The hydrogen bond forming agents are also soluble in HCFC-141b.

Table I**Hydrogen Bonding Agent Solubility in HCFC-22**

The following hydrogen bonding agents are soluble at ambient temperature in HCFC-22 to > 10 wt. %:

Hydrogen Bonding Agents***"PLURONIC" F-108****"CARBOWAX" 3350****"WITCONOL" H35A****"TRITON" X-67****Polypropylene Glycol 2025****"ETHOFAT" 0/20****"ETHOMID" HT/60****"TERGITOL" 15-S-20****"ETHOX" DO-9****"TERGITOL" NP-40**

* Solubilities determined at ambient temperature (approximately 21°C). Similar solubilities have been observed for HCFC-123, HCFC-123a, and HCFC-141b even though HCFC-141b is not a strong hydrogen bond forming HCFC.

EXAMPLE 2

Vapor pressure data were obtained for mixtures of CFC-12 and HCFC-22, respectively, with hydrogen bonding agents. In these tests, 30 grams of blowing agent was combined with 70 grams of hydrogen bond forming agent in a 30 ml plastic-coated pressure bottles. After thermostating the bottles at 21°C, the vapor pressures were determined using a pressure gauge accurate to 1.0 kPa. Although HCFC-22 by itself has considerably higher vapor pressure at 21°C than CFC-12 (937 kPa vs. 584 kPa, the formation of hydrogen bonds between the hydrogen bond forming agents and HCFC-22 resulted in dramatic vapor pressure depressions to values much lower than for CFC-12. The vapor pressure data are summarized in Table II.

Boiling point data were obtained for a 30/70 blend of HCFC-123/DBE. The data in Table I A show an elevation in boiling point (relative to the value calculated from Raoult's Law) of 17°C as the result of the association or hydrogen bonding which occurs between these materials. Similar boiling point elevations

were observed for 30/70 blends of HCFC-123/DPM and HCFC-123/DPMA.

Table IIB shows vapor pressure data for HFC-32, HCFC-124, HFC-125, HFC-134 and HFC-134a with DBE, acetone, and 2-pentanone. Each hydrogen bond forming agent depresses the vapor pressure of the blowing agents.

Table II
Effect of Hydrogen Bonding Agents
on Vapor Pressure of HCFC-22

Bonding Agent	Blowing Agent	Vapor at 21° C.	Pressure kPa
	Wt. %	CFC-12	HCFC-22
None	100.0	584	937
"CARBOWAX" 3350	30.0	584	495
"PLURONIC" F-108	30.0	584	483
"WITCONOL" H35A	15.0	404	238
	30.0	584	362 (*)
"TRITON" X-67	15.0	584	304
	30.0	584	383
"TWEEN" 61	30.0	584	586
Polypropylene Glycol 2025			
	30.0	440 (*)	371 (*)

	"ETHOFAT" 0/20	30.0	497 (*)	342 (*)
	"ETHOMID" HT/60	15.0	584	228
5		30.0	584	300
	"CARBOWAX" 8000	30.0	584	521
	Polyethylene Glycol			
10	Cpd 20M	30.0	584	481
	"POLYOX" WSRN-10	30.0	584	490
	"TERGITOL" 15-S-20	15.0	584	204
		30.0	584	283 (*)
15	"TERGITOL" 24-L-92	30.0	508 (*)	314 (*)
	"TERGITOL" NP-40	30.0	584	404
	Polypropylene Glycol			
20	425	30.0	473 (*)	356 (*)
			(876 at 54° C)	(741 at 54° C)
25	"PLURACOL" 975	15.0	418 (*)	218 (*)
			(858 at 54° C)	(438 at 54° C)
30		30.0	584	449 (*)
			(2 phases)	
	"ETHOX" DO-9	30.0	471(*)	323 (*)
35	Diglyme	30.0	280 (*)	149 (*)
	Glyme	30.0	211	118 (*)
	DBE	30.0	411 (*)	249 (*)
	"ARCOSOLV" PM	30.0	342 (*)	235 (*)
40	Acetone	30.0	235 (*)	141 (*)
	2-Pentanone	30.0	380 (*)	200 (*)
	Polymethylvinyl Ketone	30.0	521 (*)	414 (*)

(* solution)

Table IIA

Boiling Point Elevation Data		
Compound	Boiling Point, °C	
	Actual	Raoult's Law
HCFC-123*	27.6	--
DBE	196	--
30/70 HCFC-123/DBE	81	64
DPM	188	--
30/70 HCFC-123/DPM	88	67
DPMA	200	--
30/70 HCFC-123/DPMA	93	60

* Commercial grade; typically including up to about 10 percent HCFC-123a.

Table IIB

Effect of Hydrogen Bonding Agents on Vapor Pressures of HCFC-124, HFC-125, HFC-134, HFC-134a and HFC-32			
Bonding Agent	Blowing Agent	Blowing Agent Wt. %	Vapor Pressures at 21 °C, kPa
None	CFC-114	100.0	189
DBE	CFC-114	30.0	188 (*)
None	HCFC-124	100.0	336
DBE	HCFC-124	30.0	109 (*)
Acetone	HCFC-124	30.0	101 (*)
2-Pentanone	HCFC-124	30.0	113 (*)
None	HFC-125	100.0	1229
DBE	HFC-125	30.0	273 (*)
Acetone	HFC-125	30.0	169 (*)
None	HFC-134a	100.0	661
DBE	HFC-134a	30.0	206 (*)
Acetone	HFC-134a	30.0	125 (*)
2-Pentanone	HFC-134a	30.0	183 (*)
None	HFC-134	100.0	515
DBE	HFC-134	30.0	149 (*)
Acetone	HFC-134	30.0	101 (*)
None	HFC-32	100.0	1453
Acetone	HFC-32	30.0	383 (*)

(* solution)

COMPARATIVE EXAMPLE 3

For comparison purposes, HCFC-22 was combined with non-hydrogen bonding agents, such as stearyl stearamide ("KEMAMIDE" S-160) and glycerol monostearate ("WITCONOL" MST), and the vapor pressure of HCFC-22 showed slight, if any, depression. Thus, compounds which form strong hydrogen bonds with themselves, e.g., glycerol monostearate, do not associate with HCFC-22 and do not reduce the measured vapor pressure. The vapor pressure data are shown in Table III.

Table III

Vapor Pressure for HCFC-22 with Non-Hydrogen Bonding Agents			
	Blowing Agent	Vapor Pressure at 21 °C, kPa	
Additive	Wt. %	CFC-12	HCFC-22
None	100.0	584	937
"KEMAMIDE" S-180	30.0	584	937
"WITCONOL" MST	30.0	584	914
"ALKAMIDE" HTDE	30.0	584	824
"ARMID" O	30.0	584	914
"SPAN" 60	30.0	584	848
Glycerin	30.0	584	937
"SELAR" OH 3007	30.0	584	937
"SELAR" PA 7426	30.0	584	937
"SURLYN" 8396-2	30.0	584	937
Polyacrylonitrile A-7	30.0	584	933
"SOLEF" 1008-1001	30.0	584	937
"ELVANOL" 90-50	30.0	584	937

EXAMPLE 4

The permeation of nitrogen and HCFC-22 through polystyrene film was measured for polymer films with and without blocking agents.

The permeation data was obtained on 15-20 mil thick polystyrene films which were prepared as follows:

(a) Hydrogen bond forming agents and polystyrene were passed through a twin screw extruder three times at 205 °C to ensure good blending of components. The extruder used was a 28 mm Werner and Pfleider, Stuttgart, Model 20S-K-28 twin screw.

(b) After pelletizing the extruded polymer, 15-20 mil thick films (in 15 cm x 15 cm) were pressed at about 241,250 kPa pressure using a Barber-Coleman press.

(c) The 15 cm x 15 cm sheets of 15-20 mil film were cut into 47 mm diameter circles or discs with a polymer die punch.

Permeation tests were run on polystyrene films containing various blocking agents to determine the permeation of air and blowing agents in polystyrene foam. Such film closely simulates polystyrene foam cell walls and the permeation data are predictive of foam blowing agent retention and susceptibility to air intrusion. Studies were made with HCFC-22 and nitrogen (simulating air).

Polystyrene Film Preparation**(A) Mixing Polystyrene/Additives by Extrusion**

Samples of polystyrene (2500 grams) plus blocking agents were hand mixed and passed through a screw extruder three times at about 205 °C. Three passes were used to ensure uniform blending of components. Since the polymer mixes were extruded into a water tank for cooling prior to pelletizing (between the passes through the extruder and after the third extrusion), the pelletized samples were dried about 16 hours in a vacuum oven at 80-95 °C. The extruder used was a 28 mm Werner and Pfleider, Stuttgart, Model 20S-K-28 twin screw.

(B) Film Pressing of Polystyrene/Additive Mixtures

Using a Barber-Coleman press, 30 gram samples of polystyrene/additive mixes (as pellets) were pressed into 15 cm x 15 cm sheets of film with 15-20 mil thickness. The pressing was done at 205 °C and at a pressure of about 241,250 kPa (maintained for 5 minutes).

(C) Film Discs for Permeation Tests

Discs (15-20 mil thickness) were cut from 15 cm x 15 cm sheets of film. Five discs of 47 mm diameter were made from each sheet. The discs were cut or stamped at ambient temperature using a die punch made of A-2 type steel (hardened).

Permeation Test Procedure

The permeation tests on the polystyrene film containing blocking agents were conducted by a modification of ASTM D1434-82, "Standard Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting". This modified procedure is described in the Master of Chemical Engineering Thesis, P. S. Mukherjee, Widener University, Chester, PA, February 1988, entitled "A Study of the Diffusion and Permeation Characteristics of Fluorocarbons Through Polymer Films".

Test Conditions

- (1) All tests were run at a 138 kPa pressure differential between the high pressure side and the low pressure side of the permeation cell.
- (2) Permeation tests were run at 60 to 120°C, with tests for each blocking agent/polystyrene/gas combination being run at two or more temperatures. Data for other temperatures were calculate from the equation:

$$\ln P = \frac{A}{T} + B$$

where P is permeation coefficient, T is °K (°C + 273.2) and A and B are constants determined from the permeation coefficients calculated from the following equation:

$$P = \frac{(\text{Rate of Permeation}) (\text{Film Thickness})}{(\text{Film Area}) (\text{Pressure drop across film})}$$

- (3) The permeation rates are based on a 1 cm² by 1 cm thick film with a 7 kPa pressure drop across the film.

The permeation rate and permeation coefficient data for nitrogen in polystyrene containing blocking agents are summarized in Table IV. Data for HCFC-22 in polystyrene containing blocking agents are shown in Table V. The units for permeation rate are g/hr and for permeation coefficient are cm³(STP)·cm/sec·cm²·cmHg. The data summarized in Tables IV and V are calculated at 25°C from data measured at other temperatures.

Table IV
Permeation Data

Polymer: Polystyrene* Temperature: 25° C

<u>Gas</u>	<u>Blocking Agent</u>	<u>Wt. % in Polymer</u>	<u>Permeation Coeff.</u>	<u>Permeation</u>	<u>% Change In</u>
			<u>cm³ gas at STP cm</u> <u>sec cm² (cm Hg)</u>	<u>Rate</u> <u>g/hr</u>	<u>Permeation</u> <u>Rate</u>
Nitrogen	None	-	8.00×10^{-11}	1.86×10^{-9}	-
Nitrogen	"WITCONOL"	5.0	5.50×10^{-11}	1.28×10^{-9}	-31.2
	H35A				
Nitrogen	"TRITON" X-67	5.0	4.49×10^{-11}	1.04×10^{-9}	-44.1
Nitrogen	Polypropylene	5.0	4.72×10^{-11}	1.10×10^{-9}	-40.9
	Glycol 2025				
Nitrogen	"TWEEN" 61	5.0	4.672×10^{-11}	1.07×10^{-9}	-42.5

* "DYLENE" 8 polystyrene (Melt Index 6-7), Arco Chemical Company.

Table V
Permeation Data

Polymer: Polystyrene* Temperature: 25° C

<u>Gas</u>	<u>Blocking Agent</u>	<u>Wt. % in Polymer</u>	<u>Permeation Coefficient</u>	<u>Permeation%</u>	<u>Change In</u>
			<u>cm³ gas at STP cm</u> <u>sec cm² (cm Hg)</u>	<u>Rate</u> <u>g/hr</u>	<u>Permeation</u> <u>Rate</u>
HCFC-22	None	-	5.41×10^{-12}	3.89×10^{-10}	-
HCFC-22	"WITCONOL"	5.0	2.21×10^{-12}	1.58×10^{-10}	-59.4
	H35A				

* "DYLENE" 8 polystyrene (Melt Index 6-7), Arco Chemical Company.

50 EXAMPLE 5

In a manner analogous to Example 2, vapor pressure data were obtained for mixtures of HCFC-22 in polyols and for a mixture of HFC-134a in a polyol. The vapor pressure data are summarized in Table VI.

Table VI
Effect of Polyols as
Hydrogen Bonding Agents
on Vapor Pressure
of HCFC-22 and HFC-134a

	Blowing Agent	Vapor Pressure at 21° C. kPa	
		FOUND HCFC-22*	RAOULT'S LAW
Hydrogen Hydrogen Bonding	Wt. %		
STEPANPOL PS-2502	2.9	101	205
	5.4	194	291
	7.8	218	356
	17.9	400	545
	20.6	542	569
PLURACOL P-410	2.0	101	176
	4.0	101	243
	6.0	121	300
	8.0	145	351
	10.0	163	396
	12.0	174	438
PLURACOL TP-440	2.1	130	181
	4.0	154	243
	6.4	183	311
	9.9	228	394
	12.0	267	369
PLURACOL 1016	1.8	106	151
	4.0	65	206
	6.0	156	114

8.2	204	298
10.1	218	329
12.1	242	371

5

Blocking Agent	Wt. %	FOUND	RAOULT'S LAW
Bonding Agent	HFC-134A*		
10 PLURACOL PT-440	2.5	101	147
	5.0	128	188
	7.6	183	225
	10.0	232	255

15

* WT% blowing agent in hydrogen bonding agent

20 EXAMPLE 6

To further verify the differences in behavior between the conventional chlorofluorocarbon blowing agents and the hydrogen-containing halocarbons, the solubility of HCFC-134a was compared to that of CFC-12. The CFC-12 was found to be miscible at 25 °C in 150 SUS (32cs at 38 °C) oils including paraffinic
 25 oils, naphthenic oils, alkylated benzene oils and PAG oils. In contrast, the HFC-134a was found to be insoluble (<1 wt. percent) in the paraffinic oils, naphthenic oils and alkylated benzene oils. However, HFC-134a was found to be miscible in PAG oils at 25 °C.

30 EXAMPLE 7

Closed cell polyurethane thermoset foams were produced using CFC-11, HCFC-22 and HFC-134a as the primary blowing agent and CO₂ produced in situ by addition of water. The K-factor for the respective foams were measured and compared to vapor thermal conductivity data corresponding to the blowing agents. The respective recipe for both the A-side and the B-side components and the resulting data are
 35 presented in Table VII along with the vapor thermal conductivity data.

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55

* UCON oils (n-butyl alcohol + propylene oxide or EO/PO)

Table VII

Foams co-blown with water:

A-Side	270 gms	PAPI 580
B--Side	100 gms	STEPAPNOL PS-2502
	2.3 gms	DC 193
	5 gms	HEXCEM 977
	.35 gms	POLYCAT 8
	2.5 gms	water

(see below) halocarbon

Foam Index** 250

Blowing Agent type	B-side		B.A.	Volume of gas		Density kg/m ³	K-factor* age in days at R.T. 5 6
	g	vap. pres. kPa		MOLES CO ₂	total		
CFC-11	12	101	0.09	0.14	0.23	54.8	0.0247
CFC-11	22	101	0.16	0.14	0.30	51.9	0.0234
CFC-11	32.6	101	0.24	0.14	0.38	53.0	0.0218
HCFC-22	12	328	0.14	0.14	0.28	47.4	0.0234
HFC-134a	12	225	0.12	0.14	0.26	47.6	0.0248

Foams blown without water:

A-Side	158 gms	PAPI 580
B--Side	100 gms	STEPAPNOL PS-2502
	1.7 gms	DC 193
	1.35 gms	HEXCEM 977
	.17 gms	POLYCAT 8
	0.0 gms	water

(see below) halocarbon

Blowing Agent type	B-side vap. pres.		B.A.	Volume of gas		Density kg/m ³	*K-factor age in days at R.T. 10
	g	psig		MOLES CO ₂	total		
CFC-11	41	0	0.30	0.00	0.30	40.0	0.0206
HCFC-22	26	0	0.30	0.00	0.30	44.9	0.0234

VAPOR THERMAL CONDUCTIVITY DATA

BLOWING AGENT	VTC, mW/m ² K	
	25° C	60° C

CFC-11	7.81	9.17
CFC-22	11.42	12.95
HFC-134a	14.50	17.66
CO ₂	16.50	19.16

* W/m²K

**(equivalents of isocyanate/equivalents of hydroxyl) X100

The primary property of halocarbon blowing agents in insulating foam is to provide good thermal insulation by virtue of their low vapor thermal conductivity in the foam cells. By comparing the accompanying vapor thermal conductivity data (VTC) for CFC-11, and HFC-134a or CFC-22, it is apparent that conductivity of HFC-134a and CFC-22 is almost twice that of CFC-11. Thus it is to be expected that an insulating foam made with HFC-134a or CFC-22 would be a much poorer insulator than a foam made with CFC-11. On the contrary and as seen in the k-factor data, the insulation performance for the HFC-134a/CO₂ and CFC-22/CO₂ foam, is unexpectedly and essentially the same as that for the CFC-11/CO₂ foam, wherein the HCFC-134a/CO₂ and CFC-22/CO₂ foam produced in the presence of the blocking agent exhibited extremely fine closed cell structure.

The chemicals used in the previous Examples and tests are identified structurally and by source as follows:

<u>Designation</u>	<u>Structure</u>	<u>Source</u>
"CARBOWAX" 3350	Polyethylene	Union Carbide Corp.
"CARBOWAX" 8000	Polyethylene glycol	Union Carbide Corp.
"Pluronic" F-108	Ethylene oxide/propylene oxide copolymer	BASF Wyandotte Corp.

	oxide copolymer	
"WITCONOL" H35A	Polyethylene glycol (400)	Witco Corp.
	stearate	
"WITCONOL" MST	Glycerol monostearate	Witco Corp.
"TRITON" X-67	Alkylpoly-ethoxy ethanol	Rohm and Haas Co.
"TWEEN" 61	POE (4) sorbitan stearate	ICI Americas, Inc.
Polypropylene Glycol 2025	Polypropylene glycol	Union Carbide Corp.
"ETHOFAT" 0/20	Polyethylene oxide oleate	Akzo Chemie America
"ETHOMID" HT/60	Polyethylene oxide fatty acid amide	Akzo Chemie America
Polyethylene Glycol Cpd 20M	Polyethylene glycol	Union Carbide Corp.
"POLYOX" WSRN-10	Polyethylene oxide	Union Carbide Corp.
"TERGITOL" 15-S-20	Linear alcohol/ethylene oxide	Union Carbide Corp.
"TERGITOL" 24-L-92	Linear alcohol/ethylene oxide	Union Carbide Corp.
"TERGITOL" NP-40	Nonylphenol/ethylene oxide	Union Carbide Corp.
Polypropylene Glycol 425	Polypropylene glycol	Union Carbide Corp.
"PLURACOL" 975	Sucrose polyol	BASF Wyandotte Corp.
"PLURACOL" P-410	Polypropylene glycol	BASF Wyandotte Corp.

2 5
 "PLURACOL" P-440 Trifunctional BASF Wyandotte Corp.
 polyol based
 upon Polypropylene
 glycol

10
 "PLURACOL" 1016 Trifunctional BASF Wyandotte Corp.
 amino polyol

15
 "STEPANPOL" PS-2502 Difunctional Stepan Company
 polyol based
 upon Phthalic
 anhydride

20
 "PAPI" 580 Methylene DOW Chemicals
 diisocyanate

25
 "DC" 193 Silicone DOW Chemicals
 surfactant

30
 "HEXCEM" 977 Potassium Mooney Chemicals
 octanoate

35
 "POLYCAT" 8 N,N-dimethyl- Air Products and
 cyclohexylamine Chemicals, Inc. --

40
 "ETHOX" DO-9 Polyethylene Ethox Chemicals Inc.
 glycol dioleate

45
 Glyme Ethylene Aldrich Chemical Co.
 glycol di-
 methylether

50
 Diglyme 2-Methoxy- Aldrich Chemical Co.
 ethyl ether

55
 DBE Mixture of Du Pont Co.
 dimethyl adipate,
 dimethyl gluta-
 rate and di-
 methyl succinate*

"ARCOSOLV" PM Propylene Arco Chemical Co.
 glycol mono-
 ethyl ether

"ARCOSOLV" DPM Dipropylene Arco Chemical Co.
 glycol mono-

		methyl ether	
5	"ARCOSOLV" DPMA	Dipropylene glycol mono-methyl ether acetate	Arco Chemical Co.
10	"KEMAMIDE" S-180	Stearyl stearamide	Witco Corp.
	Acetone	---	Fisher Scientific
	2-Pentanone	Methyl propyl ketone	Pfaltz and Bauer, Inc.
15	"ALKAMIDE" HTDE	stearic diethanolamide	Alkaril Chemicals, Ltd.
20	"ARMID" O	Oleamide	Akzo Chemie America
	"SPAN" 60	Sorbitan stearate	ICI Americas, Inc.
	Glycerin	---	Aldrich Chemical Co.
25	"SELAR" OH 3007	Ethylene/vinyl alcohol copolymer	Du Pont Co.
30	"SELAR" PA 7426	Amorphous nylon	Du Pont Co.
	"SURLYN" 8396-2	Ethylene/methacrylic acid copolymer	Du Pont Co.
35	Polymeric Acrylonitrile A-7	Acrylonitrile/methyl acrylate copolymer	Du Pont Co.
40	"SOLEF" 1008-1001	Polyvinylidene fluoride	Soltex Polymer Corp.
45	"ELVANOL" 90-50	Polyvinyl alcohol	Du Pont Co.
	"DYLENE" 8	Polystyrene	Arco Chemical Co.
50	Polymethylvinyl Ketone (8919)	---	Monomer-Polymer Laboratories, Inc.

	CFC-12	Dichlorodifluoro- methane	Du Pont Co.
5	CFC-114	1,2-dichlorotetra- fluoroethane	Du Pont Co.
	HCFC-22	Chlorodifluoro- methane	Du Pont Co.
10	HCFC-123	1,1,1-trifluoro-2,2 -dichloroethane	Du Pont Co.
15	HCFC-123a	1,1,2-trifluoro-1,2 -dichloroethane	Du Pont Co.
	HCFC-124	1,1,1,2-tetrafluoro- chloroethane	Du Pont Co.
20	HFC-125	Pentafluoroethane	Du Pont Co.
	HFC-32	Difluoromethane	Du Pont Co.
	HFC-134	1,1,2,2-tetrafluoro- ethane	Du Pont Co.
25	HFC-134a	1,1,1,2-tetrafluoro- ethane	Du Pont Co.
30	HCFC-141b	1-fluoro-1,1-di- chloroethane	Du Pont Co.
	* 17/66/16.5 mixture of esters		

35

Claims

- 40 1. A closed cell thermoplastic or thermoset insulating polymer foam comprising a continuous polymeric phase and a discontinuous gaseous phase, characterised by:

 - a gaseous phase comprising at least one hydrogen-containing fluorocarbon, wherein said fluorocarbon comprises:
 CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; and/or CH_2FCF_3 ; and
 - a hydrogen bond forming blocking agent wherein said agent associates or bonds with said

45 fluorocarbon thereby reducing the permeation of air into the foam and slow down the escape of blowing agent from the foam.
- 50 2. A method of manufacturing a closed cell thermoplastic or thermoset insulating foam wherein a blowing agent expands as the polymeric phase solidifies, the method comprising:

 - selecting a hydrogen-containing fluorocarbon as the blowing agent, wherein said fluorocarbon comprises:
 CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; and/or CH_2FCF_3 and
 - adding a hydrogen bond forming blocking agent, wherein said agent associates or bonds with said

55 fluorocarbon, thereby reducing the permeation of air into the foam and slowing down the escape of blowing agent from the foam.
3. Use in the formation of a closed cell insulating polymer foam from a polyol, and an isocyanate or resole of a hydrogen-containing fluorocarbon blowing agent comprising CH_2F_2 , CHF_2CF_3 , CHF_2CHF_2 and/or



	CFC-12	Dichlorodifluoro-	Du Pont Co.
		methane	
5	CFC-114	1,2-dichlorotetra-	Du Pont Co.
		fluoroethane	
	HCFC-22	Chlorodifluoro-	Du Pont Co.
10		methane	
	HCFC-123	1,1,1-trifluoro-2,2	Du Pont Co.
		-dichloroethane	
15	HCFC-123a	1,1,2-trifluoro-1,2	Du Pont Co.
		-dichloroethane	
	HCFC-124	1,1,1,2-tetrafluoro-	Du Pont Co.
		chloroethane	
20	HFC-125	Pentafluoroethane	Du Pont Co.
	HFC-32	Difluoromethane	Du Pont Co.
	HFC-134	1,1,2,2-tetrafluoro-	Du Pont Co.
25		ethane	
	HFC-134a	1,1,1,2-tetrafluoro-	Du Pont Co.
		ethane	
30	HCFC-141b	1-fluoro-1,1-di-	Du Pont Co.
		chloroethane	
	* 17/66/16.5 mixture of esters		

35

Claims

1. A closed cell thermoplastic or thermoset insulating polymer foam comprising a continuous polymeric phase and a discontinuous gaseous phase, characterised by:
 - a gaseous phase comprising at least one hydrogen-containing fluorocarbon, wherein said fluorocarbon comprises:

CH₂F₂; CHF₂CF₃; CHF₂CHF₂; and/or CH₂FCF₃; and

a hydrogen bond forming blocking agent wherein said agent associates or bonds with said fluorocarbon thereby reducing the permeation of air into the foam and slow down the escape of blowing agent from the foam.
2. A method of manufacturing a closed cell thermoplastic or thermoset insulating foam wherein a blowing agent expands as the polymeric phase solidifies, the method comprising:
 - selecting a hydrogen-containing fluorocarbon as the blowing agent, wherein said fluorocarbon comprises:

CH₂F₂; CHF₂CF₃; CHF₂CHF₂; and/or CH₂FCF₃ and

adding a hydrogen bond forming blocking agent, wherein said agent associates or bonds with said fluorocarbon, thereby reducing the permeation of air into the foam and slowing down the escape of blowing agent from the foam.
3. Use in the formation of a closed cell insulating polymer foam from a polyol, and an isocyanate or resole of a hydrogen-containing fluorocarbon blowing agent comprising CH₂F₂, CHF₂CF₃, CHF₂CHF₂ and/or



CH_2FCF_3 and a hydrogen bond forming blocking agent, wherein said agent associates or bonds with said hydrogen-containing fluorocarbon blowing agent, thereby reducing the permeation of air into the foam and slowing down the escape of said blowing agent from the foam.

4. Use according to claim 3 wherein an additional blowing agent is employed selected from CCl_2FCH_3 , CClF_2CH_3 , CF_3CH_3 , $\text{CH}_2\text{FCH}_2\text{F}$, CHF_2CH_3 , CO_2 , hydro-carbons, and methyl formate.
5. A polyol-containing foaming composition for a closed-cell insulating thermoset polymer foam comprising:
 - (a) a hydrogen-containing fluorocarbon wherein said fluorocarbon comprises: CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; and/or CH_2FCF_3 ; and
 - (b) an effective amount of a polyol to produce a thermoset foam when reacted with an isocyanate containing component, and a hydrogen bond forming blocking agent which associates or bonds with said fluorocarbon, thereby simultaneously reducing the permeation of air into the foam and slow down the escape of blowing agent from the foam, during said reaction.
6. A thermoset polymer closed-cell insulating foam composition produced by reacting an isocyanate containing component in the presence of a hydrogen-containing fluorocarbon; and an effective amount of a polyol to produce a thermoset foam and a hydrogen bond forming blocking agent which associates or bonds with said fluorocarbon, thereby simultaneously reducing the permeation of air into the foam and slowing down the escape of blowing agent from the foam, wherein said fluorocarbon comprises: CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; and/or CH_2FCF_3 ; and wherein said polyol comprises: polyethylene glycol, polypropylene glycol, ethylene oxide/propylene oxide copolymer, sucrose polyol and/or a polyol containing ether, ester or ketone groups.
7. A closed-cell thermoplastic or thermoset polymer foam of claim 1 or a foam composition of claim 5 or 6, wherein said hydrogen bond forming blocking agent is present in the range of from 1.0 to 20 weight percent of said foam or composition.
8. A closed-cell thermoplastic or thermoset polymer foam of claim 1 or 6, or a composition of claim 5 or 6, wherein said blocking agent comprises:
 - Polyethylene oxide polymers;
 - Ethylene oxide/propylene oxide copolymers;
 - Polypropylene oxide polymers;
 - Polyethylene glycol mono- and dioleates;
 - Polyethylene glycol monostearates;
 - Alkylphenoxy polyethoxy ethanols;
 - Polyethylene oxide sorbitan monostearates and tristearates;
 - Polyethylene oxide fatty acid amides;
 - Primary and secondary alcohol ethoxylates;
 - Glyme (A), diglyme (B), triglyme (C) and tetraglyme (D);
 - Mono-, di- and tripropylene glycol methyl ethers and ether acetates;
 - Dimethyl adipate, succinate and glutarate;
 - Ethylene oxide/propylene oxide adducts with a sucrose;
 - Ketones and polyketone polymers; or mixtures thereof.
 - (A) = (ethylene glycol dimethyl ether)
 - (B) = (2-methoxy-ethyl ether)
 - (C) = (triethylene glycol dimethyl ether)
 - (D) = (tetraethylene glycol dimethyl ether)
9. A thermoset polymer foaming composition of claim 5, wherein said polyol comprises: polyethylene glycol, polypropylene glycol, ethylene oxide/propylene oxide copolymer, sucrose polyol, polyol containing ether, ester or ketone groups or mixtures thereof.
10. A closed-cell thermoplastic or thermoset polymer foam of claim 1 wherein said blocking agent comprises:
 - polyethylene glycol, polypropylene glycol, ethylene oxide/propylene oxide copolymer, sucrose polyol, polyol containing ether, ester or ketone groups or mixtures thereof.



11. A closed-cell thermoplastic or thermoset polymer foam of claims 1 or 7, or a composition of claims 5 or 6 which additionally contains a blowing agent selected from CCl_2FCH_3 , CClF_2CH_3 , CF_3CH_3 , $\text{CH}_2\text{FCH}_2\text{F}$, CHF_2CH_3 , CO_2 , hydrocarbons, and methyl formate.

5 Patentansprüche

1. Geschlossenzelliger thermoplastischer oder warmgehärteter polymerer Isolierschaum, umfassend eine kontinuierliche polymere Phase und eine diskontinuierliche Gasphase, gekennzeichnet durch:
eine Gasphase, die wenigstens einen wasserstoffhaltigen Fluorkohlenstoff umfaßt, worin der Fluorkohlenstoff umfaßt:
10 CH_2F_2 , CHF_2CF_3 , CHF_2CHF_2 und/oder CH_2FCF_3 und ein Wasserstoffbrückenbindung-bildendes Blockierungsmittel, worin sich das Mittel mit dem Fluorkohlenstoff zusammenlagert oder verbindet, wodurch das Eindringen von Luft in den Schaum verringert und das Entweichen von Blähmittel aus dem Schaum verlangsamt wird.
- 15 2. Verfahren zur Herstellung eines geschlossenzelligen thermoplastischen oder warmgehärteten Isolierschaums, worin sich ein Blähmittel ausdehnt, wenn sich die polymere Phase verfestigt, wobei das Verfahren umfaßt: Auswählen eines wasserstoffhaltigen Fluorkohlenstoffes als Blähmittel, worin der Fluorkohlenstoff CH_2F_2 , CHF_2CF_3 , CHF_2CHF_2 und/oder CH_2FCF_3 umfaßt, und Zugeben eines Wasserstoffbrückenbindung-bildenden Blockierungsmittels, worin sich das Mittel mit dem Fluorkohlenstoff zusammenlagert oder verbindet, wodurch das Eindringen von Luft in den Schaum verringert und das Entweichen von Blähmittel aus dem Schaum verlangsamt wird.
- 20 3. Verwendung zur Bildung eines geschlossenzelligen polymeren Isolierschaums aus einem Polyol und einem Isocyanat oder Resol eines wasserstoffhaltigen Fluorkohlenstoff-Blähmittels, umfassend CH_2F_2 , CHF_2CF_3 , CHF_2CHF_2 und/oder CH_2FCF_3 , und ein Wasserstoffbrückenbindungbildendes Blockierungsmittel, worin sich das Mittel mit dem wasserstoffhaltigen Fluorkohlenstoff-Blähmittel zusammenlagert oder verbindet, wodurch das Eindringen von Luft in den Schaum verringert und das Entweichen des Blähmittels aus dem Schaum verlangsamt wird.
- 25 4. Verwendung nach Anspruch 3, bei der ein zusätzliches Blähmittel eingesetzt wird, ausgewählt aus CCl_2FCH_3 , CClF_2CH_3 , CF_3CH_3 , $\text{CH}_2\text{FCH}_2\text{F}$, CHF_2CH_3 , CO_2 , Kohlenwasserstoffen und Methylformiat.
- 30 5. Polyolhaltige Schaumzusammensetzung für einen geschlossenzelligen warmgehärteten polymeren Isolierschaum, umfassend:
(a) einen wasserstoffhaltigen Fluorkohlenstoff, worin der Fluorkohlenstoff umfaßt:
 CH_2F_2 , CHF_2CF_3 , CHF_2CHF_2 und/oder CH_2FCF_3 , und
(b) eine wirksame Menge eines Polyols zur Herstellung eines warmgehärteten Schaumes, wenn eine Umsetzung mit einer isocyanathaltigen Komponente erfolgt, und ein Wasserstoffbrückenbindung-bildendes Blockierungsmittel, das sich mit dem Fluorkohlenstoff zusammenlagert oder verbindet, wodurch gleichzeitig das Eindringen von Luft in den Schaum verringert und das Entweichen von Blähmittel aus dem Schaum während der genannten Reaktion verlangsamt wird.
- 35 6. Warmgehärtete geschlossenzellige polymere Isolierschaumzusammensetzung, hergestellt durch Reaktion einer isocyanathaltigen Komponente in Gegenwart eines wasserstoffhaltigen Fluorkohlenstoffes und einer wirksamen Menge eines Polyols zur Herstellung eines warmgehärteten Schaumes, und ein Wasserstoffbrückenbindung-bildendes Blockierungsmittel, das sich mit dem Fluorkohlenstoff zusammenlagert oder verbindet, wodurch gleichzeitig das Eindringen von Luft in den Schaum verringert und das Entweichen von Blähmittel aus dem Schaum verlangsamt wird, worin der Fluorkohlenstoff umfaßt:
40 CH_2F_2 , CHF_2CF_3 , CHF_2CHF_2 und/oder CH_2FCF_3 , und
worin das Polyol umfaßt:
Polyethylenglycol, Polypropylenglycol, Ethylenoxid/Propylenoxid-Copolymer, Saccharose-Polyol und/oder polyolhaltige Ether-, Ester- oder Ketogruppen.
- 45 7. Geschlossenzelliger thermoplastischer oder warmgehärteter Polymerschaum nach Anspruch 1 oder eine Schaumzusammensetzung nach Anspruch 5 oder 6, worin das Wasserstoffbrückenbindung-bildende Blockierungsmittel im Bereich von 1,0 bis 20 Gew.-% des Schaumes oder der Zusammensetzung vorhanden ist.
- 50
- 55



8. Geschlossenzelliger thermoplastischer oder warmgehärteter Polymerschaum nach Anspruch 1 oder 6 oder eine Zusammensetzung nach Anspruch 5 oder 6, worin das Blockierungsmittel umfaßt:
 Polyethylenoxid-Polymere,
 Ethylenoxid/Propylenoxid-Copolymere,
 Polypropylenoxid-Polymere,
 Polyethylenglycol-mono- und -dioleate,
 Polyethylenglycol-monostearate,
 Alkylphenoxypolyethoxyethanole,
 Polyethylenoxid-sorbitanmonostearate und -tristearate,
 Polyethylenoxid-Fettsäureamide,
 primäre und sekundäre Alkoholethoxylate,
 Glyme (A), Diglyme (B), Triglyme (C) und Tetraglyme (D), Mono-, Di- und Tripropylenglycolmethylether und Etheracetate,
 Dimethyladipat, -succinat und -glutarat,
 Ethylenoxid/Propylenoxid-Addukte mit einer Saccharose, Ketone und Polyketon-Polymere oder Gemische davon.
 (A) = (Ethylenglycoldimethylether)
 (B) = (2-Methoxy-ethylether)
 (C) = (Triethylenglycoldimethylether)
 (D) = (Tetraethylenglycoldimethylether)
9. Warmgehärtete polymere Schaumzusammensetzung nach Anspruch 5, worin das Polyol umfaßt: Polyethylenglycol, Polypropylenglycol, Ethylenoxid/Propylenoxid-Copolymer, Saccharosepolyol, polyolhaltige Ether-, Ester- oder Ketogruppen oder Gemische davon.
10. Geschlossenzelliger thermoplastischer oder warmgehärteter Polymerschaum nach Anspruch 1, worin das Blockierungsmittel umfaßt: Polyethylenglycol, Polypropylenglycol, Ethylenoxid/Propylenoxid-Copolymer, Saccharosepolyol, polyolhaltigen Ether, Ester- oder Ketogruppen oder Gemische davon.
11. Geschlossenzelliger thermoplastischer oder warmgehärteter Polymerschaum nach den Ansprüchen 1 oder 7 oder eine Zusammensetzung nach den Ansprüchen 5 oder 6, die zusätzlich ein Blähmittel enthält, ausgewählt aus CCl_2FCH_3 , CClF_2CH_3 , CF_3CH_3 , $\text{CH}_2\text{FCH}_2\text{F}$, CHF_2CH_3 , CO_2 , Kohlenwasserstoffen und Methylformiat.

35 Revendications

1. Une mousse polymère isolante thermoplastique ou thermodurcie à cellules fermées, comprenant une phase polymère continue et une phase gazeuse discontinue, caractérisée par :
 une phase gazeuse comprenant au moins un fluorocarbure hydrogéné, ledit fluorocarbure comprenant :
 CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; et/ou CH_2FCF_3 ; et
 un agent de blocage formateur de liaison hydrogène, lequel agent s'associe ou se lie audit fluorocarbure en ayant ainsi pour effet de réduire la pénétration d'air dans la mousse et de ralentir le dégagement d'agent gonflant à partir de la mousse.
2. Un procédé de fabrication d'une mousse isolante thermoplastique ou thermodurcie à cellules fermées, dans lequel un agent gonflant se dilate tandis que la phase polymère se solidifie, le procédé comprenant :
 le choix d'un fluorocarbure hydrogéné comme agent gonflant, ledit fluorocarbure comprenant :
 CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; et/ou CH_2FCF_3 ; et
 l'addition d'un agent de blocage formateur de liaison hydrogène, lequel agent s'associe ou se lie audit fluorocarbure en ayant ainsi pour effet de réduire la pénétration d'air dans la mousse et de ralentir le dégagement d'agent gonflant à partir de la mousse.
3. Utilisation, dans la formation d'une mousse polymère isolante à cellules fermées à partir d'un polyol et d'un isocyanate ou Résol, d'un agent gonflant fluorocarboné hydrogéné comprenant CH_2F_2 , CHF_2CF_3 , CHF_2CHF_2 et/ou CH_2FCF_3 et un agent de blocage formateur de liaison hydrogène, lequel agent s'associe ou se lie audit agent gonflant fluorocarboné hydrogéné en ayant ainsi pour effet de réduire la



pénétration d'air dans la mousse et de ralentir le dégagement dudit agent gonflant à partir de la mousse.

4. Utilisation selon la revendication 3, dans laquelle on utilise un agent gonflant supplémentaire choisi parmi CCl_2FCH_3 , CClF_2CH_3 , CF_3CH_3 , $\text{CH}_2\text{FCH}_2\text{F}$, CHF_2CH_3 , CO_2 , des hydrocarbures et le formiate de méthyle.
5. Une composition moussante contenant un polyol pour produire une mousse polymère isolante thermodurcie à cellules fermées, comprenant :
 - (a) un fluorocarbure hydrogéné, ledit fluorocarbure comprenant : CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; et/ou CH_2FCF_3 ; et
 - (b) une quantité efficace d'un polyol pour produire une mousse thermodurcie par réaction avec un composant contenant un isocyanate, et un agent de blocage formateur de liaison hydrogène qui s'associe ou se lie audit fluorocarbure pendant ladite réaction en ayant ainsi simultanément pour effet de réduire la pénétration d'air dans la mousse et de ralentir le dégagement d'agent gonflant à partir de la mousse.
6. Une composition de mousse polymère isolante thermodurcie à cellules fermées produite en faisant réagir un composant contenant un isocyanate en présence d'un fluorocarbure hydrogéné ; et une quantité efficace d'un polyol pour produire une mousse thermodurcie et un agent de blocage formateur de liaison hydrogène qui s'associe ou se lie audit fluorocarbure en ayant ainsi simultanément pour effet de réduire la pénétration d'air dans la mousse et de ralentir le dégagement d'agent gonflant à partir de la mousse, dans laquelle fluorocarbure comprend :
 CH_2F_2 ; CHF_2CF_3 ; CHF_2CHF_2 ; et/ou CH_2FCF_3 ; et
 dans laquelle ledit polyol comprend :
 un polyéthylène-glycol, un polypropylène-glycol, un copolymère oxyde d'éthylène/oxyde de propylène, un polyol à base de saccharose et/ou un polyol contenant des groupes éther, ester ou cétone.
7. Une mousse polymère thermoplastique ou thermodurcie à cellules fermées de la revendication 1 ou une composition de mousse de la revendication 5 ou 6, dans laquelle ledit agent de blocage formateur de liaison hydrogène est présent en une proportion de 1,0 à 20 pour cent en poids de ladite mousse ou composition.
8. Une mousse polymère thermoplastique ou thermodurcie à cellules fermées de la revendication 1 ou 6, ou une composition de la revendication 5 ou 6, dans laquelle ledit agent de blocage comprend :
 des poly(oxyde d'éthylène) ;
 des copolymères oxyde d'éthylène/oxyde de propylène ;
 des poly(oxyde de propylène) ;
 des mono- et dioléates de polyéthylène-glycol ;
 des monostéarates de polyéthylène-glycol ;
 des alkylphénoxy-polyéthoxy-éthanols ;
 des monostéarates et tristéarates de polyoxyéthylène-sorbitanne ;
 des amides d'acides gras polyoxyéthylés ;
 des éthoxylats d'alcools primaires et secondaires ;
 le glyme (A), le diglyme (B), le triglyme (C) et le tétraglyme (D) ;
 les éthers et éther-acétates méthyliques de mono-, di- et tripropylène-glycols ;
 l'adipate, le succinate et le glutarate de diméthyle ;
 des produits d'addition d'oxyde d'éthylène/oxyde de propylène avec un saccharose ;
 des cétones et polymères polycétoniques ; ou des mélanges d'entre eux ;
 (A) = (éther diméthylique d'éthylène-glycol)
 (B) = (éther de 2-méthoxyéthyle)
 (C) = (éther diméthylique de triéthylène-glycol)
 (D) = (éther diméthylique de tétraéthylène-glycol).
9. Une composition moussante pour mousse polymère thermodurcie de la revendication 5, dans laquelle ledit polyol comprend :
 un polyéthylène-glycol, un polypropylène-glycol, un copolymère oxyde d'éthylène/oxyde de propylène, un polyol à base de saccharose, un polyol contenant des groupes éther, ester ou cétone, ou un



mélange d'entre eux.

10. Une mousse polymère thermoplastique ou thermodurcie à cellules fermées de la revendication 1, dans laquelle ledit agent de blocage comprend :

un polyéthylène-glycol, un polypropylène-glycol, un copolymère oxyde d'éthylène/oxyde de propylène, un polyol à base de saccharose, un polyol contenant des groupes éther, ester ou cétone, ou un mélange d'entre eux.

11. Une mousse polymère thermoplastique ou thermodurcie à cellules fermées des revendications 1 ou 7, ou une composition des revendications 5 ou 6, qui contient de plus un agent gonflant choisi parmi CCl_2FCH_3 , CClF_2CH_3 , CF_3CH_3 , $\text{CH}_2\text{FCH}_2\text{F}$, CHF_2CH_3 , CO_2 , des hydrocarbures et le formiate de méthyle.