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(54) Titre : MELANGE COMPRENANT DU 1,1,1,3,3-PENTAFLUOROBUTANE ET DU 1,1,1,2,3,3,3-HEPTAFLUOROPROPANE

(54) Title: MIXTURES COMPRISING 1,1,1,3,3-PENTAFLUOROBUTANE AND 1,1,1,2,3,3,3-HEPTAFLUOROPROPANE

(57) Abrégé/Abstract:
The invention relates to advantageous blowing agent mixtures comprising HFC-365mfc and HFC-227 in addition to 1,1,1,3,3-pentafluoropropane and/or 1,1,2-tetrafluoroethane. The invention also relates to non-combustible polyetherpolyol and/or polyesterpolyol premixes for producing foam products, especially PU foam.

Abstract

The invention relates to advantageous blowing-agent mixtures with HFC-365mfc and HFC-227ea and also 1,1,1,3,3-pentafluoropropane and/or 1,1,1,2-tetrafluoroethane. Non-combustible polyether polyol and/or polyester polyol premixes for the production of foamed products, in particular PU foams, are also described.

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Mixtures with 1,1,1,3,3-pentafluorobutane and 1,1,1,2,3,3,3-heptafluoropropane

Description

The present invention relates to mixtures with 1,1,1,3,3-pentafluorobutane (R-365mfc) and at least two further fluorocarbons and their use in the production of foamed plastics.

It is already known to use partially fluorinated hydrocarbons as blowing gases for the production of foamed plastics.

International patent application WO 98/27145 discloses the use of blowing-agent mixtures which contain 1,1,1,3,3-pentafluorobutane and further fluorocarbon compounds and optionally further blowing agents such as carbon dioxide, in the context of the production of foams.

It is an object of the present invention to devise mixtures which are further improved with respect to the flashpoint, with which for example foamed plastics with advantageous quality properties can be produced in a more simple manner.

This object is achieved by the present invention.

Blowing-agent mixtures according to the invention which can be used as blowing gas for the production of foamed plastics, contain or consist of

A) 1,1,1,3,3-pentafluorobutane and

B) 1,1,1,2,3,3,3-heptafluoropropane and

C) 1,1,1,2-tetrafluoroethane and/or 1,1,1,3,3-pentafluoropropane,

with the following provisos:

a) per 100 parts by weight of the blowing-agent mixture, 65 to 85 parts by weight, preferably 75 to 85 parts by weight, are allotted to the total of constituents A) and B);

b) per 100 parts by weight of the total of the constituents A) and B) mentioned under a), with 80 to 95 parts by weight, preferably 83 to 90 parts by weight, being allotted to 1,1,1,3,3-pentafluorobutane, and the remainder of the total of A) and B) is formed by 1,1,1,2,3,3,3-heptafluoropropane;

c) per 100 parts by weight of the blowing-agent mixture, at least 15 parts by weight are allotted to constituent C).

Preferred blowing-agent mixtures are characterised in that they consist of constituents A), B) and C) , wherein per 100 parts by weight of the blowing-agent mixture 70 to 80 parts by weight are allotted to the total of constituents A) and B) and 20 to 30 parts by weight to constituent C).

1,1,1,3,3-pentafluorobutane lies at the limit of flammability; the mixtures according to the invention are also improved compared with known mixtures with HFC-365mfc with regard to flammability. They are particularly suitable for use as blowing gas for the production of foamed plastics with very good insulation values, but may also be used for other purposes such as for example as refrigerants, solvents or cleaning agents.

Particularly good blowing-agent mixtures consist of 80% by weight of a mixture of 87 parts by weight HFC-365mfc and 13 parts by weight HFC-227ea; the remaining 20% by weight consists of 1,1,1,3,3-pentafluoropropane, HFC-134a or a mixture of both.

The mixtures according to the invention are particularly suitable as blowing gas for the production of foamed plastics, for example also by the extrusion process. In this process, the thermoplastics containing the blowing agent are extruded directly to form foamed sheets, films or profiles. The plastics material foams immediately after leaving the nozzle. For example, XPS and XPE foamed materials (polystyrene- or polyethylene-based foamed materials, respectively) can be manufactured.

The mixtures according to the invention are particularly well suited for the production of foamed materials based on isocyanates. They are highly suitable in the production of in particular rigid, but also flexible foams based on isocyanate, also for integral foams.

The production of foamed materials based on isocyanate is known. Their production and the base materials usable therefor are disclosed for example in European patent application EP-A-0 381 986; in "Ullmann's Encyclopedia of Industrial Chemistry", 5th edition, volume A 21, pages 665 to 680; international patent applications WO 92/00345, 96/30439, 96/14354 and German Offenlegungschrift DE 44 22 714 A1.

Aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates for example with 2 to 4 isocyanate groups are used as starting constituents. They have an aliphatic hydrocarbon radical with up to 18 C atoms, a cycloaliphatic hydrocarbon radical with up to 15 C atoms, an aromatic hydrocarbon radical with 6 to 15 C atoms or an araliphatic hydrocarbon radical with 8 to 15 C atoms. Starting

constituents which are particularly preferred industrially are for example 2,4- and 2,6-toluylene diisocyanate, diphenylmethane diisocyanate, polymethylene polyphenyl isocyanate and mixtures thereof. Also what are called "modified polyisocyanates", which contain carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups, may be used.

Further starting constituents are compounds with at least 2 hydrogen atoms which are reactive with respect to isocyanates. These are in particular compounds with a molecular weight of 400 to 10,000, which preferably contain 2 to 8 hydroxyl groups and furthermore may contain amino groups, thiol groups or carboxyl groups. Polyethers, polyesters, polycarbonates and polyester amides which have 2 to 8 hydroxyl groups are particularly well suited.

Optionally also compounds which serve as chain extension agents or cross-linking agents and preferably have 2 to 8 hydrogen atoms which are reactive with respect to isocyanates may be used as starting constituents. Usually such agents have a molecular weight of 32 to 400. Instead of or in addition to hydroxyl groups, amino groups, thiol groups or carboxyl groups may also be present.

Optionally, further auxiliaries and additions may be jointly used. For example, additionally chemical blowing agents such as water may be used. Catalysts such as for example tertiary amines, such as dimethylcyclohexylamine, and/or organic metal compounds such as for example tin salts of carboxylic acids can also be used. Surface-active additions such as emulsifiers or foam stabilisers, for example siloxane polyether copolymers, reaction-delaying agents, cell regulators such as paraffins, fatty alcohols or dimethylpolysiloxanes, pigments, dyes, flameproofing agents such as phosphate esters or phosphonate esters, such as for example tris-chloroisopropyl phosphate, may be used.

Furthermore, stabilisers against the effects of ageing and the weather, plasticisers, fillers, dyes, antistatic agents, nucleating agents, pore-regulating substances or biocidal active substances can be used.

Suitable catalysts are for example mentioned in international patent application WO 96/14354. These include organic amines, aminoalcohols and aminoethers such as morpholine compounds, for example dimethylcyclohexylamine, diethanolamine, 2-dimethylaminoethyl-3-dimethylamino-propylether, 2-dimethylaminoethylether, 2,2-dimorpholino-diethylether, N,N-dimethylaminoethylmorpholine and N-dimethylmorpholine. Also organometallic compounds such as for example tin, cobalt or iron compounds can be used as catalyst. Examples which can be used are tin dioctoate, cobalt naphthenate, dibutyltin dilaurate and iron acetonylacetate.

The blowing agents may be used as such, i.e. without the above-mentioned auxiliaries and additions. According to one embodiment, the blowing agents are used together with one or more of the above auxiliaries and additions. A further subject of the invention is thus production constituents for the production of foamed plastics, which are based on a content of the mixture according to the invention which is effective for foaming as blowing gas and at least one of the above-mentioned auxiliaries and additions. The blowing agent according to the invention is then preferably contained in an amount of from 1 to 35% by weight, and the auxiliary(auxiliaries) and addition(s) as remainder to make up to 100% by weight.

One preferred production constituent is premixes consisting of blowing agent according to the invention and polyester polyols and/or polyether polyols. This embodiment will be explained further below.

It is conventional, in order to produce foams, first to produce what are called premixes from the different feed

materials, and these are then reacted with the isocyanate. For the production of the premix, polyols or polyethers, blowing agents, catalysts and optionally further additives are mixed together in the required amounts. The foams are then produced by bringing the premix into contact with the isocyanate or isocyanates.

If premixes are produced using the aforementioned blowing-agent mixtures, if a critical amount of blowing agent is exceeded surprisingly it may happen that the entire system has to be classified as combustible owing to the low flashpoint, although the blowing-agent mixture and polyol system per se are not combustible.

Premixes according to the invention contain polyol and also 1 to 35% by weight, preferably 5 to 20% by weight, of the blowing agent according to the invention. The premixes may consist of blowing agent and polyol, but also one or more of the above-mentioned auxiliaries and additions in an amount of from e.g. 10 to 30% by weight may be contained therein. Blowing agent, polyol and any auxiliaries and additions present add up to 100% by weight in the premix. Preferably polyether polyols or polyester polyols are used.

For example 10 to 20% by weight, preferably 10 to 15% by weight, of a phosphorus compound, preferably triethyl phosphate or tris-chloroisopropyl phosphate, may be contained in the premix.

The production constituent or polyol premix according to the invention is then brought into contact with the isocyanate or isocyanates in known manner and foamed.

The polyols are compounds with at least 2 hydrogen atoms which are reactive with respect to isocyanates. These are in particular compounds with a molecular weight of 400 to 10,000, which preferably contain 2 to 8 hydroxyl groups and

furthermore may contain amino groups, thiol groups or carboxyl groups.

The premix according to the invention is even safer compared with known premixes with respect to being flameproof. Thus simple storage and transport of the premix is possible.

A further subject of the invention is plastics foams produced using the blowing-agent mixture according to the invention.

The following examples are intended to explain the invention further, without limiting its scope.

Examples

Example 1:

Polyol mixture

Polyether polyol (Tercarol A350) was mixed with 10% by weight blowing agent (relative to polyol) and the flashpoint was determined. A ternary mixture consisting of 80 parts by weight HFC-365mfc and HFC-227ea (weight ratio 87:13) and 20 parts by weight 1,1,1,3,3-pentafluoropropane was used as blowing agent. Flashpoint according to DIN EN ISO 13736: 15°C.

Example 2:

Use of HFC-134a

A premix was produced analogously to Example 1 from polyether polyol (Tercarol A350) and 10% by weight ternary blowing-agent mixture. Instead of the fluoropropane, it contained HFC-134a. The flashpoint was determined in accordance with DIN EN ISO 13763. No flashpoint could be determined.

Claims

1. A blowing-agent mixture, containing or consisting of

A) 1,1,1,3,3-pentafluorobutane and
B) 1,1,1,2,3,3,3-heptafluoropropane and
C) 1,1,1,2-tetrafluoroethane and/or 1,1,1,3,3-pentafluoropropane,

with the following provisos:

a) per 100 parts by weight of the blowing-agent mixture, 65 to 85 parts by weight are allotted to the total of constituents A) and B);

b) per 100 parts by weight of the total of the constituents A) and B) mentioned under a), 80 to 95 parts by weight are allotted to 1,1,1,3,3-pentafluorobutane, and the remainder of the total of A) and B) is formed by 1,1,1,2,3,3,3-heptafluoropropane;

c) per 100 parts by weight of the blowing-agent mixture, at least 15 parts by weight are allotted to constituent C).

2. A blowing-agent mixture according to Claim 1, characterised in that it consists of the constituents A), B) and C), with 70 to 80 parts by weight being allotted to the total of constituents A) and B) and 20 to 30 parts by weight to constituent C) per 100 parts by weight of the blowing-agent mixture.

3. A production constituent for the production of plastics foams, characterised in that they contain a blowing-agent mixture according to one of Claims 1 and 2 in an amount of from 1 to 35 percent by weight and auxiliaries or intermediate products such as flameproofing agents or catalysts, as remainder to make up to 100% by weight.

4. A non-combustible polyether and/or polyester polyol premix for the production of plastics foams, characterised in that the premix contains 1 to 35% by weight of the blowing agent according to one of Claims 1 and 2.

5. A non-combustible polyether and/or polyester polyol premix according to Claim 4, characterised in that the premix contains 5 to 20% by weight of the blowing agent.

6. Plastics foams, obtainable using a blowing-agent composition according to one of Claims 1 or 2.