

The present invention relates to the use of 3-methyl-but-3-en-1-ol for the stabilisation of mixtures which contain chlorofluoroalkanes and amines, aminoalcohols and/or polyols containing amino groups, and which, for example, are used for the production of polyurethane foams, a process for the stabilisation of such mixtures, the mixtures themselves and stabiliser-containing chlorofluoroalkanes.

In the production of polyurethane foams, isocyanates are reacted with multivalent alcohols to form polymers of high molecular weight which contain the polyurethane link. If foamed polymers are desired, a blowing agent, often a chlorofluoroalkane, is added to the isocyanate or the multivalent alcohol (polyol) or both. The blowing agent is evaporated by the reaction heat resulting during polymerisation and thus a foamed product of low density is obtained.

If the compounds required for the production of polyurethane foamed materials are mixed together directly before the reaction, a foamed material with good properties can easily be produced. For practical reasons, often only the diisocyanate constituent is stored separately until foaming. All other constituents required for the production of foamed material, such as catalysts, e.g. amine catalysts, emulsifying agents and the blowing agent or blowing agent mixture are premixed with the polyol. These pre-mixtures have to be able to be stored for relatively long periods before using,

without a reaction or decomposition occurring, which would adversely affect the quality of the foamed material produced.

5 However, such a method can only be carried out well with non-amine polyols, i.e. polyols which only contain carbon, hydrogen and oxygen as elements, provided that the pre-formulated mixtures are not subjected to extreme temperatures during storage. In the case of amines, aminoalcohols and the polyols based on amines, i.e. 10 polyols which contain nitrogen in addition to the stated elements carbon, hydrogen and oxygen, and which represent e.g. amine- or alkanolamine-started polyethers with free hydroxyl groups, however, there takes place a reaction between the amine, the aminoalcohol or the 15 amine-based polyol on the one hand and the chlorofluoroalkanes used as blowing agents on the other hand. This leads to a decrease in the pH value by the formation of hydrochloric acid and connected therewith to a decrease in the storage stability of the liquid mixtures. 20 Furthermore, the solution becomes darker, its viscosity increases, only poor-quality foamed materials can be produced or the mixtures even become unusable for the production of foamed materials.

25 It is known from German Patent 1 207 626 that these mixtures which contain amine-based polyols in addition to chlorofluoroalkanes can have unsaturated compounds - such as butadiene, isoprene, styrene, α -methylstyrene or 1-alkenes with 4 to 18 carbon atoms - added as stabilisers, whereas unsaturated oxygen-containing 30 compounds such as vinyl acetate or methyl vinylketones are described as ineffective for the same purposes.

The use of unsaturated organic compounds such as α -methylstyrene, dipentene, anethole, indole, dimethyl hexadiene, piperylene, p-mentha-1,5-diene, m-diisopropyl benzene, 1,3,5-triisopropenyl benzene, 1-(p-methoxyphenyl)-2-nitro-1-propene or 1-methoxy-1,3-butadiene for the stabilisation of trichlorofluoromethane, trichlorotrifluoroethane or tetrachlorodifluoroethane with respect to a reaction with primary or secondary alcohols is known from FR-A-1 420 190.

It is known from German Patent 1 518 461 that in addition to α -methylstyrene also anethole (= 1-(p-methoxyphenyl)-propene-1), m-diisopropenyl benzene, 1,3,5-triisopropenyl benzene and 1-(p-methoxyphenyl)-2-nitro-propene-1 can also be used for stabilisation.

Furthermore, German Patent 1 618 291 describes the use of p-isopropenyl-toluene (p-methyl- α -methylstyrene), and German Patent 3 139 401 the use of an isomeric mixture of 2,4-diphenyl-4-methyl-pentenenes ("dimeric α -methylstyrene") to inhibit the reaction of the amines, the aminoalcohols or the polyol containing amino groups with the chlorofluoroalkane.

In this case it is a drawback that the stated compounds fulfil their stabilising effect only for relatively short storage times and even then in some cases only unsatisfactorily. If a certain storage time is exceeded, reactions increasingly start to occur between the amine, the aminoalcohol or the amine-based polyol and the chlorofluoroalkane. Just as with non-stabilised mixtures, these reactions lead to a lowering of the pH value and to an increase in viscosity via the formation of hydrogen chloride. The mixtures change their colour,

become cloudy and additionally less reactive due to the precipitation of hydrochlorides. Such aged mixtures exhibit prolonged starting times on foaming, prolonged setting times and prolonged times for becoming free of tackiness. In addition they yield poor-quality foamed materials, i.e. dark-coloured foamed materials with non-uniform cells which are often too large, or they can even no longer be used for the production of foamed materials.

A further drawback consists in that metals present may catalyse and accelerate the ageing process, which additionally reduces the maximum storage time upon the usual storage of the pre-produced polyol mixtures in steel plate containers or metal drums. In this case, the corrosion of the containers which is promoted by the ageing of the mixtures causes additional problems.

The object of the invention therefore consists in overcoming the drawbacks of the prior art. A particular object is to provide better-stabilised mixtures containing chlorofluoroalkanes and amines, including the aminoalcohols and/or polyols containing amino groups, and which are suitable as premix for the production of foamed material. The objects are achieved by the uses, methods and products according to the invention.

It has now been found that by using 3-methyl-but-3-en-1-ol an advantageous stabilising effect is achieved. According to the invention, 3-methyl-but-3-en-1-ol is used for stabilising compositions which contain chlorofluoroalkanes and amines, including the aminoalcohols, and/or polyols containing amino groups.

The effective structural unit in 3-methyl-but-3-en-1-ol is the combination of a terminal double bond with a hydroxyl group which is placed in the β -position relative to this double bond.

5 3-methyl-but-3-en-1-ol is used according to the invention for stabilising compositions containing chlorofluoroalkanes and amines, including the aminoalcohols, and/or polyols containing amino groups. The stabilisers according to the invention are used in
10 quantities of 0.05 to 5% weight, preferably 0.3 to 1.5% weight, relative to the chlorofluoroalkane. In an example of the invention, the proportion by weight of 3-methyl-but-3-en-1-ol is 0.75% weight relative to the chlorofluoroalkane.

15 Chlorofluoroalkanes in the spirit of the invention are compounds known per se as blowing agents, e.g. perhalogenated C_1 to C_2 -alkanes, particularly trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1,1-trichloro-2,2,2-trifluoroethane,
20 tetrachloro-1,2-difluoroethane, tetrachloro-2,2-difluoroethane and mixtures of two or more of these compounds. Trichlorofluoromethane is particularly suitable.

25 As amines within the scope of the present invention, known amine catalysts can be used, such as saturated or unsaturated aliphatic, cycloaliphatic or heterocyclic amines. Examples are triethylamine, methyl-bis-dimethyl aminoethyl-amine, N,N,N',N'-tetramethyl ethylenediamine, triethylenediamine, dimethyl cyclohexylamine, N,N,N',N'-
30 tetramethyl-1,3-butanediamine, 1,1,3,3-tetramethylguanidine, 1,2,4-trimethylpiperazine, N-

cyclohexylpiperidine, 4-dimethylaminopyridine, N-methyl-morpholine or morpholine.

Furthermore, other conventional amines, such as N-ethyl-morpholine, N,N'-dimethyl benzylamine, N,N-dimethyl-
5 (N,N'-dimethylamino)piperazine, N,N-dimethyl piperazine, hexadecyldimethylamine, diethylcyclohexylamine, N-phenylcyclohexylamine may also be used.

In addition, known aminoalcohols, e.g. dimethyl-ethanolamine, diethanolamine, N-methyl diethanolamine, triethanolamine, diisopropanolamine or N,N,N',N'-tetra-
10 kis(2-hydroxypropyl)ethylenediamine, may be used as amines in the spirit of the invention. Furthermore, other conventional aminoalcohols, such as diethyl ethanolamine or 1,4-bis-(2-hydroxypropyl)-2-methyl-
15 piperazine, may also be used.

Polyols containing amino groups in the spirit of the invention are understood to be polyethers started with amines, alkanolamines or aromatic amines, with a remaining content of hydroxyl groups. Such polyols
20 based on amines are e.g. reaction products of ethylene oxide and/or propylene oxide with amines such as diethylene triamine, ethylene diamine, triethanolamine or toluylene diamine. It will be understood that in addition to the above cited polyol systems other
25 conventional polyols may also be used in the spirit of the invention. Suitably, an amine-based polyol with a hydroxyl number of 485 to 515 is used.

The invention also comprises a method for stabilising compositions comprising a chlorofluoroalkane and amines,
30 including the aminoalcohols, and/or polyols containing amino groups. In this case, 0.05 to 5% weight 3-methyl-

but-3-en-1-ol is worked into the mixture. In an example of the present invention, 0.75% weight 3-methyl-but-3-en-1-ol is added, the proportions by weight of the stabilisers being relative to the chlorofluoroalkane.

5 Furthermore, the invention comprises compositions which comprise chlorofluoroalkane, amines, including the aminoalcohols, and/or polyols containing amino groups, and 3-methyl-but-3-en-1-ol as stabiliser. In an example of the compositions according to the invention,
10 3-methyl-but-3-en-1-ol is contained as the stabilising compound.

Moreover, the invention also comprises chlorofluoroalkanes or their mixtures which contain 3-methyl-but-3-en-1-ol in a quantity sufficient for the stabilisation
15 of compositions which comprise these chlorofluoroalkanes and amines, including the aminoalcohols, and/or polyols containing amino groups.

The compositions according to the invention which are stabilised by 3-methyl-but-3-en-1-ol have advantageous
20 properties. The compositions are stable over very long periods of time, i.e. the pH value and the viscosity of the mixtures change only slightly. This is true even in the presence of boiler steel and is particularly important because of conventional storage in steel plate
25 containers or metal drums. The compositions according to the invention are superior to the compositions stabilised in a known manner with conventionally used compounds of the prior art in their stability and good storage properties.

30 Furthermore, they prove to be surprisingly well suited for the production of high-quality foamed materials.

To demonstrate the superiority of the compounds used as stabilisers according to the invention, the effect of 3-methyl-but-3-en-1-ol was compared with that of "dimeric α -methylstyrene" (known from German Patent 3 139 401), as is explained in greater detail in the Examples.

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

Examples

The composition I (containing 3-methyl-but-3-en-1-ol) according to the invention and the comparison composition II (containing "dimeric α -methylstyrene") were used for the following experiments:

Composition No.	I	II
amine-based polyether (parts by wt.)	100.0	100.0
polysiloxane (Si copolymer) "	0.8	0.8
dimethylcyclohexylamine "	2.0	2.0
water "	1.0	1.0
trichlorofluoromethane stabilised with 0.75% wt. dim. α -methylstyrene "	--	30.0
trichlorofluoromethane stabilised with 0.75% wt. 3-methyl-but-3-en-1-ol "	30.0	--

The compositions were stored in glass containers in the presence of boiler steel at +50°C for 8 weeks at first and then characterised by the determination of the parameters compiled in the Table below. The storage of

the mixtures for 8 weeks at +50°C in this case corresponds to a storage time of about 10 months at 20°C.

	Time (weeks)	Composition no.	
		I	II
pH value	0 8	10.8 9.2	10.9 8.5
viscosity (mPa s)	0 8	128 138	120 169
starting time (s)	0 8	17 17	17 30
setting time (s)	0 8	75 85	80 135
time for becoming free of tackiness (s)	0 8	110 110	115 180

Claims for the following contracting states: AT, BE, CH, DE, FR, GB, GR, IT, LU, NL, SE

1. The use of 3-methyl-but-3-en-1-ol for the stabilisation of compositions which contain chlorofluoroalkanes and amines and/or polyols containing amino groups.

2. The use according to Claim 1, characterised in that 3-methyl-but-3-en-1-ol is used in quantities of 0.05 to 5% by weight, preferably of 0.3 to 1.5% by weight, relative to the chlorofluoroalkane.

3. The use according to Claim 1, characterised in that the amines are amine catalysts, such as saturated or unsaturated aliphatic, cycloaliphatic or heterocyclic amines, preferably triethylamine, methyl-bis-dimethyl aminoethyl-amine, N,N,N',N'-tetramethyl ethylenediamine, triethylenediamine, dimethylcyclohexylamine, N,N,N',N'-tetramethyl-1,3-butanediamine, 1,1,3,3-tetramethylguanidine, 1,2,4-trimethylpiperazine, N-cyclohexylpiperidine, 4-dimethylaminopyridine, N-methylmorpholine or morpholine.

4. The use according to Claim 1, characterised in that the amines are aminoalcohols, preferably dimethylethanolamine, diethanolamine, N-methyl diethanolamine, triethanolamine, diisopropanolamine or N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine.

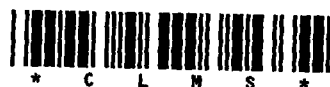
5. The use according to Claim 1, characterised in that the polyols containing amino groups are amine- or



alkanolamine-started polyethers with a residual content of hydroxyl groups.

5 6. A method for the stabilisation of compositions containing chlorofluoroalkanes and amines and/or polyols containing amino groups, characterised in that 0.05 to 5% weight 3-methyl-but-3-en-1-ol is worked into the composition.

10 7. Compositions containing chlorofluoroalkanes and amines and/or polyols containing amino groups and 3-methyl-but-3-en-1-ol as stabiliser.



Claims for the following contracting state: ES

1. A method for the stabilisation of compositions which contain chlorofluoroalkanes and amines and/or polyols containing amino groups, characterised in that 3-methyl-but-3-en-1-ol is used.

2. A method according to Claim 1, characterised in that 3-methyl-but-3-en-1-ol is used in quantities of 0.05 to 5% by weight, preferably of 0.3 to 1.5% by weight, relative to the chlorofluoroalkane.

3. A method according to Claim 1, characterised in that the amines are amine catalysts, such as saturated or unsaturated aliphatic, cycloaliphatic or heterocyclic amines, preferably triethylamine, methyl-bis-dimethyl aminoethyl-amine, N,N,N',N'-tetramethyl ethylenediamine, triethylenediamine, dimethylcyclohexylamine, N,N,N',N'-tetramethyl-1,3-butanediamine, 1,1,3,3-tetramethylguanidine, 1,2,4-trimethylpiperazine, N-cyclohexylpiperidine, 4-dimethylaminopyridine, N-methyl-morpholine or morpholine.

4. A method according to Claim 1, characterised in that the amines are aminoalcohols, preferably dimethyl-ethanolamine, diethanolamine, N-methyl diethanolamine, triethanolamine, diisopropanolamine or N,N,N',N'-tetra-kis(2-hydroxypropyl)ethylenediamine.

5. A method according to Claim 1, characterised in that the polyols containing amino groups are amine- or alkanolamine-started polyethers with a residual content of hydroxyl groups.



* C L N S *

6. A method according to Claim 1, characterised in that 0.05 to 5% weight 3-methyl-but-3-en-1-ol is worked into the composition.

5

7. Compositions containing chlorofluoroalkanes and amines and/or polyols containing amino groups and 3-methyl-but-3-en-1-ol as stabiliser.



* C L M S *