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Process for the production of cellular plastics

The invention relates to the production of shaped polyurethane-based plastics from polyether-polyols and isocyanate prepolymers using water as the blowing agent and
5 using a specific catalysis with an improved gas yield and improved reaction properties.

The production of optionally cellular shaped PUR-based plastics with a compact surface has long belonged to the prior art, such as US-A 40 65 410, US-A 42 18 543, 37 26 952, 13 65 215, 40 33 912, 40 24 090, 40 58 492, 40 98 731, 44 77 602, EP-A
10 17 928, 44 481, DE-A 31 33 859.

These shaped plastics have also been used for years for the production of shoe soles. Dispensing with the use of certain halogen-containing blowing agents such as monofluorotrichloromethane (R 11) or the secondary products R 141b and R 134a and
15 blowing with water results in technical problems, which to date have not been solved completely.

In particular, the following difficulties arise if water is used:

Mould residence time with the background of dimensional stability due to the
20 tendency to expand or grow, since the mouldings at the formerly conventional times cannot yet be subjected to load; this can be compensated by longer mould residence times, but as a result the productivity falls.

Another variable is the narrower compression ratio, i.e. the quotient of the moulding
25 bulk density and free foam bulk density. While degrees of compression of up to 2.8 were previously processed, experience shows that the ratio for water is between 1.7 and 2.1. At higher values expansion results, and at lower values problems with filling the mould result.

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It has now been found that, with certain metal catalysts, a high gas yield can be achieved with water as the blowing agent, and good mechanical properties exist early on.

5 The invention provides a process for the production of cellular shaped plastics based on polyether-polyurethane by foam moulding a reaction mixture of

A) at least one higher molecular weight polyether- and/or polyester-polyol component,

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B) an isocyanate component,

C) chain lengtheners,

15 D) blowing agents,

E) amine and metal activators and

F) further known auxiliary substances and additives

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maintaining a characteristic index of 70 to 130, characterized in that the blowing component D) used is water, optionally with the addition of organic blowing agents, and the activator component E) comprises a tin compound of the formula (I)

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in which

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R^1, R^2 denote identical or different C_1 - to C_{10} -alkyl radicals, or C_6 - to C_{10} -aryl radicals

or aralkyl radicals and

n denotes a number from 1 to 4, preferably 1, 2, 3 or 4.

5 The higher molecular weight polyether-polyol component A) has an average OH functionality of 1.95 to 2.95, and is preferably a mixture of

Aa) at least one polyether-polyol of the OH number range 21 to 112, which is obtained by alkoxylation of a bifunctional starter, e.g. with propylene oxide and ethylene oxide, with predominantly primary OH groups
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and

Ab) at least one polyether-polyol of the OH number range 20 to 56 and with a starter functionality of 2.5 to 3.5, which is obtained by alkoxylation of corresponding starters or starter mixtures, e.g. with propylene oxide and ethylene oxide, with predominantly primary OH end groups.
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These polyols can comprise conventional fillers, such as are obtained by grafting with styrene/acrylonitrile or, in the form of polyurea dispersions, by addition of diamines and diisocyanates in polyols.
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The polyisocyanate component B) is a prepolymer with an NCO content of 10 to 25 wt.%. It is prepared by reaction of i) diisocyanatodiphenylmethane with ii) a polyol component of the OH number range 20 to 112 and with an average OH functionality of 2.0 to 2.5, it being possible for component i) to contain carbodiimide groups.
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Glycols, such as 1,2-ethanediol and 1,4-butanediol etc., are used as component C).

30 Possible activators D) are, on the amine side, triethylenediamine, N-methylimidazole and N,N-dimethylbenzylamine, which can also be partly neutralized, and the similarly

known Sn(II) or Sn(IV) carboxylates, or mercaptides.

Examples which may be mentioned of further auxiliary substances and additives F) which are optionally to be used are surface-active substances, foam stabilizers, cell
5 regulators, internal release agents, dyestuffs, pigments, hydrolysis stabilizers, fungistatic and bacteriostatic substances, light and oxidation stabilizers or antistatics.

For carrying out the process according to the invention, the starting materials are employed in amounts which correspond to an isocyanate characteristic index of 70 to
10 130, in particular 90 to 110. "Isocyanate characteristic index" here is to be understood as the quotient of the number of isocyanate groups and the number of groups which are reactive towards isocyanate groups, multiplied by 100.

The procedure for carrying out the process according to the invention is analogous to
15 the known processes of the prior art. In general, this means that components A) and C) to F) are combined to give a "polyol component" and are reacted with one another with the polyisocyanate component B) in one stage in a closed mould, for example a closed mould of metal or plastic, the usual two-component mixing units being used. The amount of reaction mixture introduced into the mould and also the amount of water
20 used as the blowing agent is chosen within the above-mentioned limits such that shaped foams having a bulk density of 150 to 1,000 kg/m³ result. The process products according to the invention are semi-rigid foams with a compact surface, i.e. their Shore A hardness according to DIN 53 505 is in the range from 15 to 75.

25 Their most important field of use lies in the production of shoes, for example for foamed shoe soles or built-in parts of shoes.

Examples

In the following examples, an isocyanate characteristic index of 100 was maintained. The mechanical properties were determined on test specimens having the dimensions
5 20 x 20 x 1 cm. All the percentage data relate to percentages by weight.

Starting materials

- 10 A) Polyether-polyols
- A1) Polyether-polyol of OH number 28 with 70% propylene oxide and 30% ethylene oxide and predominantly primary OH groups and propylene glycol as the starter
- 15 A2) Polyether-polyol of OH number 25 with 80% propylene oxide and 20% ethylene oxide and predominantly primary OH groups with trimethylolpropane as the starter
- 20 A3) Polyether-polyol of OH number 56 of propylene oxide with propylene glycol as the starter
- A4) Polyether-polyol of OH number 56 of propylene oxide with trimethylolpropane as the starter
- 25 B) Polyisocyanate
- B1) Prepolymer prepared by reaction of 56 parts by wt. 4,4'-diisocyanatodiphenylmethane (MDI) and 2 parts by wt. modified MDI with an NCO content of 30%, prepared by partial carbodiimidation,
30 and a polyol mixture of 37 parts by wt. polyol A3) and 5 parts by wt. polyol A4), an NCO content of 17.5% being obtained.

C) Catalyst according to the invention

Dibutyltin sulfide

- 5 12.45 g dibutyltin oxide are added to a solution of 24 g $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and 200 ml water and 5 ml ethanol, and 12 g acetic acid are then added dropwise. The mixture is stirred at room temperature for one hour, 100 ml methylene chloride are added, the mixture is extracted by shaking and the phases are separated. After concentration, 9.8 g dibutyltin sulfide are obtained.

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Analysis: S found: 12.5; calc.: 12.3%, molecular weight 795 g/mole (osmometric);
 $n = 3$; monomer molecular weight 264 g.

Table 1

Component/example	1	2	3	4	5	6	7	8	9
Polyol A1	76.5							>	
Polyol A2	10							>	
1,4-Butanediol	12							>	
1,2-Ethanediol	1							>	
Triethylenediamine	0.3							>	
Stabi. DC 190 (Air Products)	0.2							>	
Water	0.35	0.3	0.35	0.35	0.3	0.35	0.35	0.35	0.40
Dibutyltin sulfide (according to the invention)	0.03	0.03	-	-	-	0.06	0.09	-	-
Dibutyltin mercaptide	0.02	0.02	0.02	0.04	0.04	0.02	0.02	0.08	0.02
Prep. B1	90	88	90	90	88	90	90	90	92
Bulk density (free) (kg/m ³)	284	304	340	340	360	268	260	340	283
Bulk density (mould) (kg/m ³)	550							>	>
Comp. ratio	1.93	1.8	1.62	1.62	1.52	2.05	2.1	1.62	1.94
Shore A	52	52	50	51	52	51	50	50	49
Release from mould after 3 min	-	-	-	-	-	+	+	-	-
4 min	+	+	-	-	-	+	+	-	-
5 min	+	+	-	-	+	+	+	+	-
6 min	+	+	+	+	+	+	+	+	+
without sheet fracture (+) with sheet fracture (-)									
Cream time s	19	18	19	16	17	18	18	15	19
Setting time s	37	32	37	36	32	35	35	30	38
Rising time s	50	50	50	48	50	50	50	50	55
Pulling time s*	75	70	90	90	78	65	63	75	98

* Time until an elongation at break of at least 300%, which is usual for the finished elastomer, exists.

The catalyst according to the invention, dibutyltin sulfide, gives an exceptionally high gas yield, the cream time remaining practically unchanged even at higher concentrations. The preferred progress of the blowing reaction even also allows a reduction in the amount of water, without the free foam bulk density increasing
5 markedly in comparison with catalysis without dibutyltin sulfide. As a result, a compression ratio of approx. 2.0, which is ideal for water-blown sole systems, can be set. Problems such as dimensional stability or mould filling properties can consequently now also be controlled. The polymer build-up ends early, with the cream time unchanged, so that overall shorter mould release times are rendered possible,
10 without the cream time critical for the formulation being reduced. This is always to be found with the conventional activators to date. Thus, Examples 2, 6 and 7 show a constant cream time, that is to say a latent behaviour of the activation according to the invention, despite an increase in the amount of dibutyltin sulfide.

15 The suitability of the catalysis according to the invention is further demonstrated by Tables 2 and 3 below.

The aim of a reliable production, for example, of shoe soles should be a tolerance range for a shrinkage (contraction) of the sole of at best 0, maximum 0.5%, since the
20 tools are set to that value. If water is used as the blowing agent, an opposite effect occurs above a certain amount of water (approx. 0.35 parts), namely growth (expansion) of the moulding. This delay often results in the sole's being unusable, since the growth is different in the longitudinal and transverse directions.

25 Table 2

Shrinkage a desired tolerance range of 0 to a maximum of 0.5%

Example	1	2	3	4	5	6	7	8	9
after 3 min	no	no	no	no	no	yes	yes	no	no
after 4 min	yes	yes	no	no	no	yes	yes	no	no

Table 3

Enlargement of the moulding by 0.5% after a mould residence time of 6 minutes

Example	1	2	3	4	5	6	7	8	9
5	no								yes

Examples 6 and 7 show in particular the exceptionally good overall yield and, moreover, can be released from the mould after 3 minutes with dimensional stability, the shrinkage already corresponding to the ideal.

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A conventional catalysis as in Example 9 still exhibits growth (expansion) of the sole after a moulding time in the mould of 6 minutes.

Patent claims

1. A process for the production of cellular shaped plastics having a bulk density of 150 to 1,000 kg / m³ based on polyether- polyurethane by foam moulding a reaction mixture of

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A) at least one higher molecular weight polyether- and/or polyester-polyol component,

B) an isocyanate component,

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C) chain lengtheners,

D) blowing agents,

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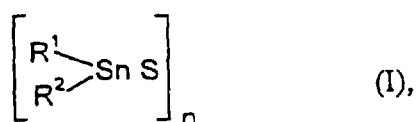
E) amine and metal activators and

F) further known auxiliary substances and additives

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characterized in that the blowing component D) used is water, optionally with the addition of organic blowing agents, and the activator component E) comprises a tin compound of the formula (I)

25



in which

R¹, R² denote identical or different C₁- to C₁₀-alkyl radicals, C₆- to C₁₀-aryl radicals or aralkyl radicals and

30

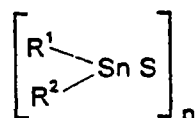
n denotes a number from 1 to 4,

the starting materials being reacted with an NCO index of 70 to 130 being maintained.

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2. A process according to claim 1, characterized in that the blowing agent D) used is water or water and organic blowing agents, and the activator component E) comprises compounds of the formula

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in which

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R¹ and R² denote identical or different C₁-C₆-alkyl radicals and

n denotes a number from 1 to 4.