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Release-friendly polyurethane moulding foam systems

5 The invention relates to polyurethane moulding foams which contain esters of mono- to penta-unsaturated fatty acids and polyhydric alcohols as internal release agents.

10 The production of moulding plastics based on polyurethane has been state of the art for decades (G. Oertel (ed.): "Kunststoff-Handbuch", Volume VII, "Polyurethane", 2nd edition, Carl-Hanser-Verlag, Munich, Vienna 1983). The production of compact, cellular, elastic or rigid moulded bodies has in the meantime gained great technical importance, the property of good adhesion to other materials being used as an advantage in many cases. In the production of mouldings that property is more of a disadvantage, because adhesion to the surface of the mould (which in most cases is made of aluminium) is also very pronounced.

15 In order to avoid that adhesion and prevent mechanical damage to moulds and mouldings, external release agents are predominantly used, but internal release agents have also been proposed several times. In EP-A 153 639 there are used in the production of moulded bodies by the RIM method reaction products of a mixture of
20 montanic acid (mixture of saturated fatty acid glycerides having from 24 to 32 carbon atoms) and a further aliphatic carboxylic acid, for example decanoic acid or its higher homologues, of at least difunctional alkanolamines, polyols and/or polyamines; US-A 4 519 965 teaches the use of zinc carboxylates with carboxylate radicals consisting of from 8 to 24 carbon atoms. DE-A 36 31 842 describes
25 ketimines, aldimines, enamines and/or Schiff's bases in the presence of a metal salt of organic acids having from 8 to 24 carbon atoms as internal release agents which prove to be effective especially in the production of compact and hard self-skinning foams but markedly slow down the polyaddition reaction. For the production of elastic, substantially compact PUR moulded bodies there is used as internal release
30 agent according to DE-A 39 04 810 a mixture of at least one organic amine, a metal salt of stearic acid and at least one ketimine in combination with at least one organic

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carboxylic acid. A disadvantage of that method is the occurrence of shortened flow times, which make it difficult to fill complex moulds having narrow openings. EP-A 666 880 and DE-A 195 46 097 disclose alkali and alkaline earth salts of alkyl- and alkylene-succinic acid and the mono- and/or poly-amides and -imides thereof, and mixtures thereof, as internal release agents for the production of cellular to solid PUR moulded bodies.

Despite the work that has been going on in this field for many years, internal release agents have been able to become established in only a few applications and hitherto could not be used successfully in the production of half-hard elastic PUR mouldings.

The object of the invention was, therefore, to find a suitable internal release agent for that field of application which fulfills the following requirements:

- separation- and ageing-resistant formulation,
- good release properties with respect to standard mould surfaces,
- preservation of system reactivity,
- adhesion to composite components (e.g. to leather or other PUR components),
- mouldings can be lacquered without additional pre-treatment (e.g. with trichloroethane).

Those requirements could be fulfilled by the use of esters of mono- to penta-unsaturated fatty acids with polyhydric alcohols, which are added to the polyol and/or to the isocyanate in each case as an individual component or in the form of a mixture.

Accordingly, the invention provides polyurethane moulding foams that contain esters of mono- to penta-unsaturated fatty acids and polyhydric alcohols as internal release agent. In a particular embodiment of the invention, the foams are self-releasing cellular to solid polyurea polyurethanes optionally containing reinforcing

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agents, which polyurea polyurethanes are obtained by reacting a reaction mixture consisting of:

- a) an organic polyisocyanate,
- b) an at least bifunctional compound containing active hydrogen atoms and having
5 a number-average molecular weight of from 300 to 8000, preferably from 1000 to 6000, especially from 2000 to 4000,
- c) a chain-lengthening agent,
- d) an internal mould release agent,
- e) optionally blowing agents, reinforcing agents and auxiliary agents,
- 10 f) optionally catalysts,

the starting materials being reacted while maintaining an isocyanate number of from 70 to 130.

There are used as component a) preferably the technically readily accessible
15 polyisocyanates, such as diisocyanatodiphenylmethane, toluene diisocyanate, and mixtures thereof with partially carbodiimidised isocyanates in pre-lengthened form having an NCO content of from 5 to 30 wt.%. For pre-lengthening there are used polyethers or polyesters or mixtures of at least bifunctional compounds containing active hydrogen atoms and having a number-average molecular weight of from 500
20 to 8000, which have a hydroxyl functionality of from 2 to 2.5.

The polyol component b) has a hydroxyl functionality of at least 2.0. It preferably consists of one or more compounds having a hydroxyl functionality of 2.0 or of a mixture having a mean hydroxyl functionality of from 2.02 to 2.95, consisting of:

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either

- ba) at least one polyether diol having an OH number of from 10 to 115, which has been prepared by propoxylation of a difunctional starter and subsequent

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ethoxylation of the propoxylation product while maintaining a weight ratio of propylene oxide to ethylene oxide of from 60:40 to 85:15, and

5 bb) at least one polyether triol having an OH number of from 12 to 56 and optionally containing fillers based on styrene-acrylonitrile copolymers or polyureas in an amount of up to 20 wt.%, based on the total weight of component b), which polyether triol has been prepared by propoxylation of a trifunctional starter and subsequent ethoxylation of the propoxylation product while maintaining a weight ratio of propylene oxide to ethylene oxide of from
10 60:40 to 85:15,

or alternatively

15 bc) at least one polyester polyol having an OH number of from 28 to 112 and an OH functionality of from 2 to 3, which polyester polyol is obtained from adipic, succinic, glutaric, phthalic, isophthalic and/or terephthalic acid by reaction with 1,4-butanediol, isobutyl glycol, propanediol, methylpropanediol, diethylene glycol, ethylene glycol, hexanediol, neopentyl glycol, glycerol and/or trimethylolpropane;

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or mixtures of these components.

There are used as component c) the NH- and/or OH-functional chain lengtheners known to the person skilled in the art, such as ethanediol, diethylene glycol, butanediol, methylpropanediol, neopentyl glycol, hexanediol, propylene glycol, triethanolamine, trimethylolpropane, glycerol, diethyltoluenediamine, toluenediamine, diaminodiethylbenzene, dimethylthiotoluenediamine or mixtures of
25 those compounds.

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According to the invention there are used as internal release agents d) esters, amides or imides which are obtainable from mono- to penta-unsaturated fatty acids by reaction with polyhydric alcohols or amines. The fatty acids used are unsaturated carboxylic acids having from 8 to 30 carbon atoms, such as linoleic, linolenic, 5 palmitoleic, oleic, arachidonic, elaeostearic, clupanodonic or erucic acid, which are esterified by polyhydric alcohols, such as ethanediol, trimethylolpropane, triethanolamine, glycerol or pentaerythritol, or are amidated by polyhydric amines, such as ethylenediamine, diethylenetriamine, pentaethylenetriamine, polyoxyethylenedi- or -tri-amine. Reaction products whose acid number is in the 10 range of from 0.5 to 5 are suitable. Preference is given to the mentioned polyester compounds. The compounds which can be employed as internal mould release agents may be used both individually and in the form of mixtures. The content of internal mould release agent and the composition thereof may vary according to the mouldings to be produced and the starting materials used for the polyaddition 15 reaction. They can readily be optimised for the particular case in question. Adaptation to the given peripheral conditions can be made in a simple manner by determining the forces necessary for removing the moulding from the mould by means of a "peeling test". To that end, the base of the mould, which consists of individual aluminium plates, is detached from the moulding at one side by means of 20 a pneumatic cylinder arranged perpendicular to the moulding. If the forces measured during that operation are less than 0.4 N/cm^2 , then mouldings can be produced without the use of additional external mould release agents.

In component e), there are optionally used as blowing agent water and/or a physical 25 blowing agent (e.g. R134a, a hydrofluoroalkane mixture). The activators known from the literature, for example tertiary amines, tin compounds, titanium compounds, may be employed as the catalysts and auxiliary agents and additives which may optionally be used concomitantly. In addition, according to the profile of requirements, it is also possible to add surface-active substances, foam stabilisers, 30 cell regulators, colourings, pigments, hydrolysis inhibitors, substances having

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fungistatic and bacteriostatic activity, oxidising agents, light stabilisers and antistatics.

5 The polyurethanes are prepared in the manner known in principle to the person skilled in the art. In general, that means that components b) to e) are combined to form a polyol component and are reacted with the isocyanate component a) in one step, conventional two-component mixing units being used. Component d) can be a constituent both of the polyol component and of the isocyanate component. The polyurethanes may, however, also be prepared by the so-called prepolymer process.
10 The foams may be produced in an open mould or a closed mould.

Surprisingly, it has been found that the internal release agents according to the invention have a positive effect on the wear resistance of the polyurethane material. In the test of the wear resistance of PUR test specimens according to DIN 53516, a
15 reduction in wear by from 50 to 70% was determined for the polyurethanes according to the invention.

It has been possible to establish, likewise surprisingly, that the coefficient of static friction on steel (according to DIN EN 344) is increased by the use of the
20 compounds used according to the invention as internal mould release agents, which is an advantage especially in the field of shoe-soling materials.

A further positive effect of the internal release agents according to the invention is the matt appearance of the soles. In the conventional procedure, the PUR mouldings
25 mostly have a pronounced lustre, which is interpreted as "plastic-like" by many customers and is not readily accepted. The "dry feel" of rubber is increasingly in demand, and the solution described herein comes very close thereto.

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The polyurethane moulding foams according to the invention are suitable especially for the production of shoe soles, but also for a variety of applications in the field of motor vehicle interiors or furniture, for example armrests, headrests or castors.

Examples

Examples 1-6

5 Starting materials

Polyhydroxyl compounds A:

A1: polyester diol (linear polyadipate, OH number 56);

10 A2: polyether diol/triol mixture (EO-PO ether, OH number 28, functionality
2.1)

Release agent C:

Example 2: glycerol trilinolate;

Example 3: glycerol trioleate;

Examples 4 and 6: pentaerythritol tetraoleate

15 Isocyanate D:

D1: 4,4'-methylenediphenyl diisocyanate partially pre-lengthened with a
polyadipate (A1), NCO content approximately 19.5 wt.%;

D2: 4,4'-methylenediphenyl diisocyanate partially pre-lengthened with an EO-
PO polyether (OH number 28), NCO content approximately 20.0 wt.%

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Description of the test

25 According to the details given in Table 1, components A1 to C were mixed and
reacted with the isocyanates D1 or D2 in a conventional two-component mixing and
metering unit according to the low-pressure process, and the mixture was introduced
into an aluminium mould whose surface had not been additionally treated or was
provided with external release agents. After a reaction time of from 2.5 to 4 minutes,
the moulding was removed. The physical properties were determined 48 hours at the
earliest after manufacture of the test plates (200 x 200 x 10 mm³), from which the

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conventional test specimens described in the standards (DIN 53504 S1 rod, DIN 53507 tear strength, wear DIN 53516) were prepared.

5 The wear resistance of the PUR test specimens was tested in accordance with DIN 53516. The coefficient of friction μ was measured according to DIN EN 344, using a tractive machine, as the quotient of the force acting horizontally and vertically (10 kN). The results of the measurements are summarised in Table 1.

Table 1

Component	Example 1*		Example 2		Example 3		Example 4		Example 5*		Example 6	
Polyester A1 [parts by wt.]	100	100	94	94	94	94	94	94	--	--	--	--
Polyether A2 [parts by wt.]	--	--	--	--	--	--	--	--	88	92	82	86
1,4-Butanediol [parts by wt.]	--	--	--	--	--	--	--	--	11.2	7.5	11.2	7.5
Ethanediol [parts by wt.]	9.9	8.6	9.9	8.6	9.9	8.6	9.9	8.6	--	--	--	--
Dabco [parts by wt.]	1.0	0.6	1.0	0.6	1.0	0.6	1.0	0.6				
Dabco/DBTDL [parts by wt.]									0.52	0.52	0.52	0.52
Water [parts by wt.]	0.1	0.4	0.1	0.4	0.1	0.4	0.1	0.4	0.3	--	0.3	--
Release agent C [parts by wt.]	--	--	6	6	6	6	6	6	--	--	6	6
Isocyanate D1 [parts by wt.]	82	81	80	78	80	79	81	78	--	--	--	--
Isocyanate D2 [parts by wt.]	--	--	--	--	--	--	--	--	77	60	75	58
Parting force [N/cm ²]	>1	>1	0.25	0.45	0.25	0.33	0.28	0.38	>1	>1	0.65	0.55
Apparent density [kg/m ³]	850	600	850	600	850	600	850	600	600	950	600	950
Hardness [Shore A]	65	55	65	55	65	55	65	55	60	60	60	58
Wear [mg]	50	80	25	40	30	45	15	30	250	150	50	40
Coefficient of dynamic friction μ	1.5	n.d.	n.d.	n.d.	n.d.	n.d.	2.5	n.d.	n.d.	n.d.	n.d.	n.d.
*comparison example not according to the invention												
n.d. - not determined												
Dabco - diazabicyclooctane												
DBTDL - dibutyltin dilaurate												

**Patent Claims**

1. Polyurethane moulding foam which contains esters of mono- to penta-unsaturated fatty acids and polyhydric alcohols as internal release agent.
- 5 2. Moulded body containing polyurethane moulding foam according to claim 1.
3. Shoe sole containing polyurethane moulding foam according to claim 1.
- 10 4. Process for the production of polyurethane moulding foams according to claim 1, in which esters of mono- to penta-unsaturated fatty acids and polyhydric alcohols are added to the polyisocyanate component.
- 15 5. Process for the production of polyurethane moulding foams according to claim 1, in which esters of mono- to penta-unsaturated fatty acids and polyhydric alcohols are added to the polyol component.
6. Use of esters of mono- or poly-unsaturated fatty acids with polyhydric alcohols as internal release agent in the production of PUR mouldings.