

Use of polyether PUR for safety clothing

This invention relates to the use of cellular to solid moulded plastics made from polyether PUR for the production
5 of safety clothing, preferably safety shoe soles.

The production of moulded polyurethane-based plastics has been known prior art for many decades. These moulded plastics may be produced in a wide range of densities and
10 hardnesses for various applications, for example as protective clothing.

The principal application for polyurethanes in safety clothing is as protective shoes. On the basis of existing
15 standards (the EN 344 series), which lay down the structure and properties of safety shoes, the selection of materials has hitherto been restricted to the use of polyester PUR. The principal reason for excluding polyether PUR is its inadequate resistance to oil and petrol (EN 344, point
20 4.8.9, resistance to fuel).

However, polyester PUR or the components required for the production thereof by reaction injection moulding exhibit the following disadvantages:

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- elevated viscosities of the components in the ready-to-process state results in unfavourable reproduction of shapes
- 30 • the elevated temperature of the components in the ready-to-process state, which is necessary for processing, reduces their pot life
- unsatisfactory resistance to hydrolysis and microbial
35 attack, especially in agricultural use or in areas with a hot and humid climate, which also results in a restricted storage life of finished safety shoes

- poor low temperature flexibility of standard polyester PUR

The production of polyether PUR using the reaction casting
5 process or reaction injection moulding process, like
polyester PUR processing, is part of the prior art.
Depending upon requirements, polyester PUR is used at
various densities and hardnesses in both single and double
layer moulded sole and direct soling processes for the
10 production of walking, leisure and sports shoes.

In connection with new developments of polyether-based PUR,
such a PUR has surprisingly been found which exhibits
sufficient fuel resistance for use in safety shoe
15 applications.

The present invention provides the use of cellular to solid
moulded polyether-based plastics by foam moulding to
produce safety clothing.

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Safety clothing complying with EN 344 series standards
(fuel resistance in isooctane < 12 vol.%) are, for example,
safety shoes, boots, aprons etc..

25 This fuel resistance is achieved at outsole bulk densities
of $\geq 800 \text{ kg/m}^3$ with the polyester PUR system raw materials
stated below by way of example.

The cellular to solid polyether polyurethane based moulded
30 plastics are produced by foam moulding a reaction mixture
prepared, for example, from

- a) a relatively high molecular weight polyether polyol
component,
- 35 b) a polyisocyanate component

- c) chain extenders,
- d) optionally blowing agents,
- 5 e) activators and optionally
- f) further auxiliary substances and additives,

wherein the starting materials are reacted while
10 maintaining an isocyanate index of 70 to 130.

The relatively high molecular weight polyether polyol
component a) has a hydroxyl functionality of 2.00 or
substantially comprises a mixture having an average
15 hydroxyl functionality of 2.02 to 2.95 prepared from

aa) at least one polyether diol of the hydroxyl value
range from 10 to 115, which was produced by
propoxylating a difunctional starter and subsequently
20 ethoxylating the propoxylation product while
maintaining a weight ratio of propylene oxide to
ethylene oxide of 60:40 to 85:15 and

ab) at least one polyether triol of the hydroxyl value
25 range from 12 to 56, optionally containing fillers
based on styrene/acrylonitrile copolymers, polyureas
or polyhydrazocarbonamides in a quantity of up to 20
wt.%, relative to the total weight of component a),
which polyether triol was produced by propoxylating a
30 trifunctional starter and subsequently maintaining a
weight ratio of propylene oxide to ethylene oxide of
60:40 to 85:15.

Polyisocyanate component b) is a semi-prepolymer containing
35 isocyanate groups and having an NCO content of 10 to 25
wt.%, produced by reacting (i) 4,4'-di-isocyanato-diphenyl-
methane with (ii) a polyether component of the hydroxyl

value range of 10 to 115 and an (average) hydroxyl functionality of 2.0 to 2.5, consisting of at least one polyether diol, produced by propoxylating a difunctional starter and optionally subsequently ethoxylating the
5 propoxylation product using up to 40 wt.% of ethylene oxide, relative to the weight of the polyether diol, or a mixture of at least one such diol with at least one polyether triol, produced by propoxylating a trifunctional starter and optionally subsequently ethoxylating the
10 propoxylation product using up to 40 wt.% of ethylene oxide, relative to the weight of the polyether triol and/or a polyester component of the hydroxyl value range from 28 to 115 and an average functionality of 2.0 to 2.5, wherein component (i) was optionally added before the reaction or
15 to the reaction product with polypropylene glycols of the molecular weight range from 134 to 700 and/or by carbodiimidising a proportion of the isocyanate groups of liquefied 4,4'-diisocyanatodiphenylmethane in a quantity of up to 10 wt.%, relative to the weight of component (i).

20 1,2-Ethanediol and/or 1,4-butanediol and/or diethylene glycol and/or triethanolamine and/or diethyltolylenediamine are used as component c),

25 while water and/or a physical blowing agent, for example R 134a® (hydrofluoroalkane mixture), are optionally used as component d).

Activators e) which may be considered are the compounds
30 known *per se* from polyurethane chemistry, such as for example tert. amines such as triethylenediamine, N,N-dimethylbenzylamine or organotin compounds, such as for example dibutyltin dilaurate or tin(II) octoate.

35 Further optionally used auxiliary substances and additives f) which may be mentioned by way of example are surface-active substances, foam stabilisers, cell regulators,

internal release agents, dyes, pigments, hydrolysis stabilisers, fungistatically and bacteriostatically active substances, light stabilisers, anti-oxidants and anti-static agents (quaternary ammonium compounds).

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The polyurethanes are produced in accordance with the known prior art. This means in general that components a) and c) to f) are combined to produce a "polyol component" and reacted in a single stage with the polyisocyanate component
10 b) in a closed mould, for example a closed metal or plastic mould, wherein conventional two-component mixing units are used. The quantity of the reaction mixture introduced into the mould and the quantity of the water optionally used as the blowing agent and/or of a physical blowing agent, for
15 example R 134[®], are calculated in this process in such a manner that moulded foams of a bulk density of $\geq 800 \text{ kg/m}^3$ are obtained. The most important area of application is in shoe production, according to the invention for the production of cellular to solid outsoles for safety shoes.
20 These shoes preferably have an outsole bulk density of $\geq 800 \text{ kg/m}^3$ and, in a particular embodiment, are associated with a throughsole having a bulk density of $\geq 400 \text{ kg/m}^3$.

Examples

The following Example illustrates formulation constituents for use in outsoles for safety shoes. An isocyanate index of 100 was maintained in all the Examples. Test sheets of dimensions 20x20x1 cm were taken as test specimens for determining mechanical properties and resistance to petrol (EN 344, point 4.8.9).

10 **Starting materials**

Polyhydroxyl compounds a)

- a₁ polyether diol, OH value 28, PO/EO weight ratio 70:30
- 15 a₂ polyether diol, OH value 28, PO/EO weight ratio 77:23

Polyisocyanate b)

- Reaction product of 4,4'-diisocyanatodiphenylmethane (MDI)
- 20 with tripropylene glycol, NCO content 23%.

Example:

The formulations for Examples 1 to 3 are shown in Table 1 below, while mechanical properties and petrol resistance are shown in Table 2.

Table 1 (all figures are parts by weight)

	Example 1	Example 2	Example 3
Component a ₁	90.00	79.27	71.55
Component a ₂	---	10.00	20.00
1,4-Butanediol	6.00	7.50	---
1,2-Ethanediol	---	0.50	---
Diethyltolylenediamine	---	---	6.00
Triethylenediamine	1.80	0.60	0.20
Dibutyltin dilaurate	0.05	0.03	0.05
Triethanolamine	0.15	---	0.20
Water	---	0.10	---
Tetraalkylammonium sulfate (Catafor CA 100)	2.00	2.00	2.00
Polyisocyanate b)	33	44	26

Table 2: Mechanical properties

		Example 1	Example 2	Example 3
Bulk density DIN 54320	(kg/m ³)	1100	900	1080
Hardness DIN 53505	(Shore A)	60	60	70
Tensile strength DIN 53504	(MPa)	16	8	12
Elongation at break DIN 53504	(%)	800	600	610
Tear propagation strength DIN 53516	(kN/m)	18	10	20
Fuel resistance EN 344	(% change in volume)	9.5	10.5	11.5



Patent Claims

1. Use of cellular to solid moulded polyether-based plastics for the production of safety clothing by
5 mould foaming.
2. Use according to claim 1 as a safety shoe sole.
3. Use according to claim 2, characterised in that the
10 outsole bulk density is $\geq 800 \text{ kg/m}^3$.
4. Use according to claim 2, characterised in that the outsole is associated with a throughsole having a bulk density of $\geq 400 \text{ kg/m}^3$.