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(54) Title: A PROCESS FOR MOLDING MICROCELLULAR ELASTOMERIC POLYURETHANE ARTICLES AND MICROCELLULAR ELASTOMERIC POLYURETHANES THEREFOR

(57) Abstract

Described is a novel, particularly flexible, process for molding microcellular elastomer polyurethane articles. Described is furthermore the preparation of microcellular elastomer polyurethanes especially suitable for said molding process. The process according to the invention is particularly suitable for being automated by means of a processor.

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A PROCESS FOR MOLDING MICROCELLULAR ELASTOMERIC POLYURETHANE ARTICLES AND MICROCELLULAR ELASTOMERIC POLYURETHANES THEREFOR.

The instant invention relates to a novel process for molding articles of microcellular elastomeric polyurethane (hereinbelow indicated,for the sake of brevity, simply as M.E.P.). More particularly, the instant invention relates to a particularly flexible process for molding a microcellular elastomeric polyurethane.

It is an object of the instant invention to provide a molding process which allows to make a wide range - from the point of view of the physico-mechanicl characteristics - of M.E.P. articles without the need for changing or substituting the starting materials.

Another object of the instant invention is that of providing a process for making M.E.P.s particularly suitable for said molding process,in which starting materials are employed having a well defined composition.

A further object of the instant invention is that of providing a process for molding M.E.P. articles wherein the reaction for producing the polyurethane is driven in a step preceding the molding of the article in order to form bases with a controlled and stable structure.

A further object yet of the instant invention is that of providing a process for molding M.E.P. articles which allows

to make M.E.P.s having different physico-mechanical characteristics, only by means of cross-linking agents.

Another important object of the instant invention is to provide a process for molding M.E.P. articles which can be automated by means of a processor.

These objects and others yet will be more clearly illustrated by the description hereinbelow.

As it is known, M.E.P. is generally made by reacting stoichiometric quantities of a polyol and of a prepolymer.

Practically, said reagents are taken from tanks and conveyed to the mixing heads by means of dosing pumps. The blending takes place as a result of the rapid increase of the flow speed of the materials introduced into the head, where they flow into one only zone of relatively limited dimensions so that there is a very high probability that the molecules both of the reagents and of the catalyst may interact and that therefore the reaction product is sufficiently homogeneous notwithstanding the very high reaction speed. However, since for economic reasons very short withdrawal times are demanded in the industrial process, it was necessary to use considerable quantities of catalysts which, by remaining within the finished article, caused the deterioration of the latter's physico-mechanical characteristics.

Furthermore, since the polyols used for making M.E.P. do not consist of single components but instead of mixtures of different components,some of which are hardly or not at all soluble, this gives rise to the drawback of having to subject the polyol mixtures to homongenization before use: not only, but these mixtures must be constantly stirred during their use.

A further inconvenience of the state of the art processes lies in the fact that the quantity of reagents to be stocked for the molding process must not only be proportional to the quantity to be worked, but also to the type of article to be made. This implies the interruption of the production to allow for the change or the modification of one or both reagents (polyol, isocyanate) and/or the catalyst. These changes and/or modifications,besides lowering productivity, imply too the loss of starting materials and the use of solvents for washing the tanks and equipment. Last but not least, said changes and/or modifications almost always demand the re-adjustment of the operating conditions of the plant with consequent problems of adjusting the production to the market requirements.

Evident are the shortcomings of the state of the art processes from what has briefly been described hereinabove.

Consequently, the object of the instant invention is that of providing a process for molding M.E.P. articles, that does not present the shortcomings of the processes known from the art. It has now been found that when using strictly defined compounds (hereinafter called quasi-polyurethanes or, in short: Q-PUR), as the starting materials, instead of prepolymers and polyols, it is possible to make M.E.P. articles the specific gravity, surface hardness, elasticity, compressive strength and abrasion resistance of which can be modified by acting exclusively on the quantity of the starting materials.

According to the process of the instant invention, the basic components are polymerized to the highest degree compatible with the molding plant. This allows to attain Q-PURs by means of strictly timed reactions and not by random blending in the mixing head.

More precisely, the inventive process provides the use - instead of a prepolymer and of a polyol (which, as is known, is in actual fact a mixture of several polyols, sometimes of a not strictly defined composition) - of two bases or Q-PURs which not only do not contain foreign materials, be they dissolved or not, such as solvents or fillers of various kind, but they have a strictly defined chemical composition.

The first of these bases consists of a quasi-polyurethane (Q-PUR-1) with a molecular weight of between 600 and 2200, preferably between 650 and 1500 and even more,preferably between 700 and 1100, and a percentage of free isocyanate (-NCO) groups of between 14 and 3.8, preferably between 12.9 and 5.6 and even more preferably between 12 and 7.6. The second base consists of a quasi-polyurethane (Q-PUR-2) having a molecular weight of between 3000 and 8000, preferably between 3500 abd 5000 and even more preferably between 3750 and 4500 and with a percentage of free hydroxyl(-OH) groups of between 1.13 and 0.48, preferably of between 0.97 and 0.68 and even more preferably between 0.9 and 0.75.

In the blending step, the free -NCO groups of Q-PUR-1 are saturated with aqueous glycol solutions and glycol/catalyst solutions so as to make polyurethane polymers of different specific weight.

The chemical structure of the M.E.P. is modified, according to the process of the instant invention, by means of Q-PUR-2. More precisely, said chemical structure varies in proportion to the quantity of Q-PUR-2 employed.

According to the instant invention, the isocyanates and the resins are reacted in a vessel according to per se known processes which allow to steer the reaction in such a manner as to attain a regular distribution of the molecular weights.

In the course of the molding step,the glycol develops its chain-lengthening and cross-linking activity. In turn, the Q-PUR-2 (which at each extremity of the molecule has a free hydroxyl group)reacts with the Q-PUR-1,via the latter's free isocyanate groups,in order to form a longer straight chain. In this manner the inner plasticizing of the polymer structure is achieved.

The skilled artisan will immediately appreciate the advantage of using an inner rather than an external,i.e.an heterogeneous-phase plasticizing process as that which occurs when conventional (reactive or inert) plasticizers are used. Hence this is a further advantage offered by the process according to the instant invention.

As already mentioned hereabove,the Q-PUR-1s, suitable for the process according to the instant invention, preferably have a molecular weight of between 600 and 2200, preferably between 650 and 1500 and even more preferably between 700 and 1100 and a percentage of free isocyanate groups ranging between 14 and 3.8, preferably between 12.9 and 5.6 and even more preferably between 12 and 7.6. This polyurethane resin of the instant invention is preferably made by reacting a diphenylmethane diisocyanate with a saturated polyester,such as e.g. glycol adipate, having a molecular weight of between 1500 and 2500.

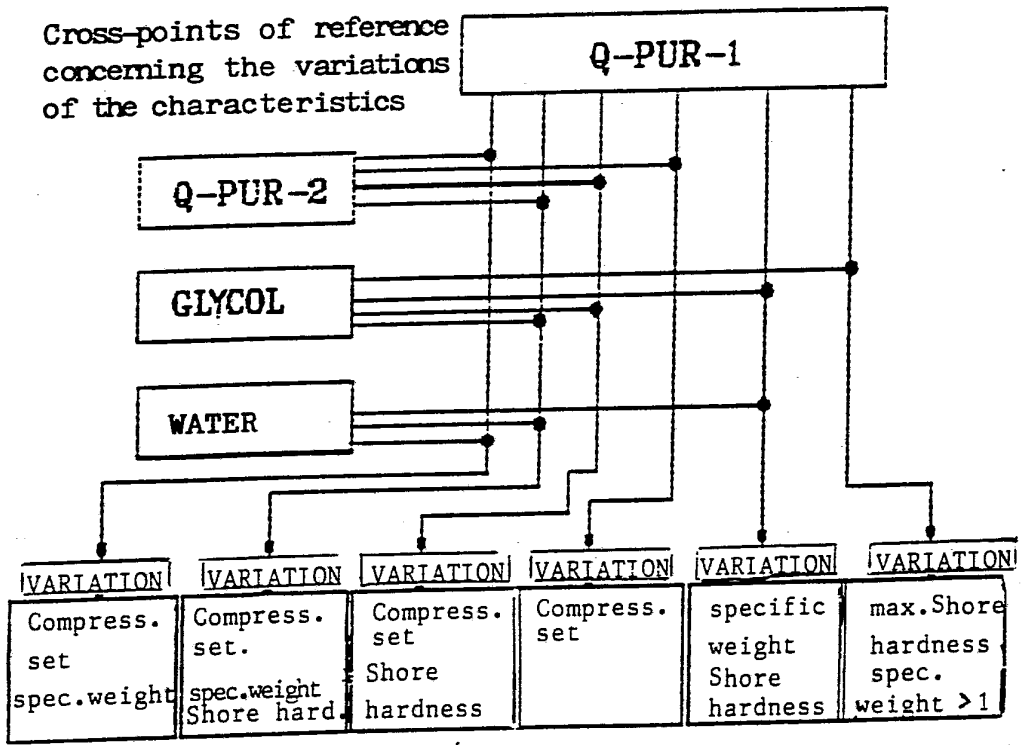
The Q-PUR-1 constitutes the basic component for the M.E.P. formulation and,contrary to what happens with conventional polymers, by saturating the isocyanate groups with glycols the whole cross-linking process of the system is completed, the final characteristics of which are predetermined by the type of saturated polyester used, by the molecular weight of Q-PUR-1 as well as by the type of glycol used. The reaction is catalyzed with triethylene diamine and the specific weight is determined by the water content.

On the other hand, Q-PUR-2 consists of a polyurethane resin having a molecular weight ranging between 3000 and 8000, preferably between 3500 and 5000 and even more preferably between 3750 and 4500, containing a percentage of free hydroxy groups ranging between 1.13 and 0.48, preferably between 0.97 and 0.68, and even more preferably between 0.9 and 0.75. Preferably, this resin is made by reacting, according to per se known methods,diphenylmethane diisocyanate with a saturated polyester having a molecular weight of 1500 to 2500, in the molar ratio of 1:2.

The Q-PUR-2 thus obtained constitutes the component capable of steering the M.E.P. characteristics. As already mentioned previously, one of the main advantages of the inventive process is represented by its flexibility. In fact,as it can be taken from the Table herebelow, depending upon how

the various components are combined, it is possible to obtain molecular structures that differ even very much the ones from the others, so much so that end products can be obtained having completely different physico-mechanical characteristics the ones from the others. It should not be overlooked that inside each main group it is possible to arrange for one of the physico-mechanical characteristics to prevail over another one.

TABLE 1



Considering that the reaction partners useful for the instant invention are all strictly defined materials as far as their chemical composition is concerned, the inventive process particularly lends itself to automation using a processor.

After having generally outlined the process according to the instant invention, it will now be better illustrated by way of some working examples which, for the sake of brevity, do not contemplate all the starting materials or the possible combinations of the reaction partners. This fact, however, shall not constitute a limitation of the scope of protection of the instant invention inasmuch - as appears evident to the skilled artisan - the forms of embodiment of the process according to the instant invention can vary widely, be it with regard to the starting materials as to the reaction conditions, so as to adapt them to the specific circumstances.

Once the skilled artisan has become acquainted with the fundamental principles on which the present process is based, he will have no difficulty whatsoever in adapting the parameters of the process so as to attain the M.E.P. having the desired characteristics, without thereby departing from the gist of the invention.

EXAMPLE 1

Preparation of a quasi-polyurethane using free -NCO groups (Q-PUR-1).

A 10,000 liter steel reaction vessel provided with stirrer, thermoregulator and suitable device for providing an inert environment, is fed with 3751 kg MDI (diphenylmethane diisocyanate) at a temperature of 38 to 42°C under stirring and in a dry nitrogen environment, to which is added 3,748 kg saturated polyester resin (made by reacting adipic acid with monoethylene glycol of m.w. = 1500, containing a percentage of water lower than 0.1 and with an acid number lower than 1 (AN < 1). This resin, at a temperature of 80°C, is fed to the MDI mass through a line (at the extremity of which is an anti-bubbling continuous flow device) dosed at a flow rate of 70-80 l/min by means of a metering pump.

Since the reaction is exothermic, the temperature of the reaction mass tends to increase, which must therefore be cooled so as not to exceed 90°C. After the addition of the resin has been completed, the reaction mass is stirred for 2 hours, between 85 and 90°C, taking care that the atmosphere is saturated with nitrogen. The reaction has been completed once the following values have been obtained:

free -NCO : 14%

molecular weight: 600

EXAMPLES 2 to 7

By operating in like manner to what is described in Example 1 but using the reagents indicated quali/quantitatively in the Table hereinbelow, are prepared the Q-PUR-1s having the characteristics as shown.

TABLE 2

	MDI kg	RESIN kg	RESIN (*)	RESIN (mol.weight)	%-NCO (final)	MOL.WEIGHT (final)
2)	3280	4219	monoeth.glycol/diethylene glycol	1750	12	700
3)	2499	5000	diethylene glycol 1/4 butane diol	2000	8,4	1000
4)	1748	5751	1/4 butane diol	2500	5,25	1600
5)	1532	5967	1/4 butane diol monoeth.glycol	3000	4,66	1800
6)	1322	6177	diethylene glycol monoeth.glycol/trimethylol propane	4000	4,2	2000
7)	1104	6395	diethylene glycol trimethylol propane	6000	3,8	2200

(*) Note: "RESIN" stands for a polyester resin made from adipic acid and the respectively indicated alcohol.

EXAMPLE 8

Preparation of a quasi-polyurethane using free -OH groups (Q-PUR-2)

A 10,000 liter steel reaction vessel provided with stirrer, thermoregulator and suitable device for providing an inert environment, is fed with 8,000 saturated polyester resin (made by reacting, at a temperature of 120°C, adipic acid with monoethylene glycol having a m.w. = 1500, containing a percentage of water lower than 0.1 and an AN <1). Under stirring and in a dry nitrogen environment is then added, very cautiously, 613 kg MDI, at a temperature of 38 to 42°C, while the flow capacity of the metering pump must not exceed 8 l/min; the blades of the stirrer must not thrust the MDI against the walls of the reaction vessel.

The environment must be carefully controlled and secured throughout the entire reaction. After the addition has been completed, the reaction mass is left to cool down to 60°C, still under stirring. The reaction has been completed once the following values are obtained:

free -OH : 1.13%

molecular weight : 3000.

EXAMPLES 9 to 14

By operating in like manner to what is described in Example 8 but using the reagents indicated quali/quantitatively

in the Table hereinbelow, are prepared the Q-PUR-2s having the characteristics as shown.

TABLE 3

	MDI kg	RESIN kg	RESIN (*)	RESIN (mol.weight)	%-OH (final)	MOL.WEIGHT (final)
9)	571	8000	monoeth.glycol/diethylene glycol	1750	0,9	3750
10)	500	8000	diethylene glycol 1/4 butane diol	2000	0,8	4250
11)	342	8000	1/4 butane diol	2500	0,75	4500
12)	266	8000	1/4 butane diol monoeth.glycol	3000	0,68	5000
13)	181	8000	diethylene glycol monoeth.glycol/trimethylol propane	4000	0,56	6000
14)	95	8000	diethylene glycol trimethylol propane	6000	0,48	7000

(*) NOTE: "RESIN" stands for a polyester resin made from adipic acid and the respectively indicated alcohol.

In Examples 1 thru 14 a polyester has always been employed. However, it is possible to use instead a polyether made - as is known to the skilled artisan - by polymerizing propylene oxide with monoglycols or polyglycols containing one or more reactive hydrogen atoms.

Generally, it has been found that the use of polyethers yields Q-PUR-1 and Q-PUR-2 having the same molecular weight, yet considerably less viscous than the corresponding quasi-

polyurethane originating from a polyester and, hence, having improved workability. At any rate, the choice depends on the physico-mechanical characteristics of the quasi-polyurethane desired.

Examples 15 to 17

Preparation of the "catalyst-foaming agent" solutions

Herebelow is given the composition (the parts are expressed in percent) of three typical solutions having a catalytic foaming activity, useful for the process of the instant invention for affecting the reaction velocity and/or physico-mechanical characteristics of the M.E.P.

COMPONENT	SOLUTION 1 (catalyst)	SOLUTION 2 (chain lengthener)	SOLUTION 3 (foaming agent)
Monoethylene glycol	70	100	70
Dabco	30	0	0
Water	0	0	30
% Total	100	100	100

The preparation of these solutions does not demand particular procedures, however the temperature must be kept at about 60°C and precaution must be taken to operate in a moisture free environment.

Dabco, as is known to the skilled artisan, is triethylene diamine.

The molding of M.E.P. according to the inventive process is illustrated in the Examples that follow.

Into a mixing head are fed all the reaction partners:

Q-PUR-1 (base 1)

Q-PUR-2 (base 2)

SOLUTION 1 (catalyst)

SOLUTION 2 (chain lengthener)

SOLUTION 3 (foaming agent)

The tanks containing the bases 1 and 2 are thermoregulated at a temperature of 50-60°C and provided with a moisture trap.

A gear pump, having a volume proportional to the quantity of product mass used per unit of time, maintains the base (1 or 2) in continuous and constant circulation between the tank and the mixing head.

The tanks containing the additives are thermoregulated at a temperature of 20-30°C and provided with moisture traps.

In this case too it will be a gear pump, yet having a volume twenty times lower than the previously cited one, that keeps the recycling in the head.

The flow rate of all these pumps is governed by a manager program of the molding cycle. The program, stored in a processor's memory, stabilizes, according to demand, the quantities of the various partners which take part in the reaction.

Shortly before injection, the speed of the motors connected to the pumps is adjusted by the processor's interfaced control cards to the r.p.m.s necessary for the specific situation. At the command START-INJECTION open up only the valves corresponding to the materials that have to take part in the reaction producing that given type of polyurethane. The valves remain open so as to interrupt recycling and to feed the reaction partners into the mixing zone for the time required to fill the mold.

The products crossing the mixing zone come into close contact thanks to a mechanical impeller.

The ejection from the head occurs through an orifice at the extremity of the head itself.

Once the injection is finished, the dedicated software redirects the output according to the program and the cycle concontinues, allowing for the production of a continuously differentiated series of M.E.P.

Example 18

An M.E.P. of low specific gravity, having sufficient compressive strength to permit its use for producing shoe bottoms.

DOSAGE OF THE COMPONENTS :

	flow rate (g/s)
SOLUTION 1 - Catalyst	0.32
SOLUTION 3 - Foaming Agent	0.26
SOLUTION 2 - Chain Lengthener	2.75
	3.33
BASE 1	45.50
BASE 2	0.00
TOTAL BASES	45.50
TOTAL FLOW RATE	48.83

This M.E.P. has the following chemical composition:

MD1	35.50
Polyester 1	57.67
Polyester 2	0.00
MEG (*)	6.47
Dabco	0.20
Water	0.16
TOTAL	100.00

EXAMPLE 19

An M.E.P. of low specific weight, with such characteristics of softness as to permit its use for producing innersoles for footwear.

DOSAGE OF THE COMPONENTS:

	flow rate g/s
SOLUTION 1 - Catalyst	0.23
SOLUTION 3 - Foaming Agent	0.37
SOLUTION 2 - Chain Lengtherener	0.01
Total Additives	0.61
BASE 1	13.65
BASE 2	14.74
TOTAL BASES	28.39
TOTAL FLOW RATE	29.00

This M.E.P. has the following chemical composition:

MDI	20.93
Polyester 1	29.14
Polyester 2	47.83
MEG (*)	1.48
Dabco	0.24
Water	0.38
TOTAL	100.00

EXAMPLE 20

An M.E.P., with specific gravity greater than 1, very resilient, particularly suitable for producing antislip surfaces exposed to climatically critical environments (temperatures between -20 and -50°C)

DOSAGE OF THE COMPONENTS :

	flow rate (g/s)
SOLUTION 1 - Catalyst	0.14
SOLUTION 3 - Foaming Agent	0.00
SOLUTION 2 - Chain Lengthener	0.72
Total additives	0.86
BASE 1	13.65
BASE 2	14.74
TOTAL BASES	28.39
TOTAL FLOW RATE	29.25

This M.E.P. has the following chemical composition:

MDI	20.75
Polyester 1	28.90
Polyester 2	47.43
MEG (*)	2.78
Dabco	0.14
Water	0.00
TOTAL	100.00

EXAMPLE 21

An M.E.P., with specific gravity greater than 1, very stiff, particularly suitable for being worked with machine tools and cut into slabs, cylinders, and so forth.

DOSAGE OF THE COMPONENTS :

	flow rate (g/s)
SOLUTION 1 - Catalyst	0.28
SOLUTION 3 - Foaming Agent	0.00
SOLUTION 2 - Chain Lengthener	3.23
Total additives	3.51
BASE 1	45.50
BASE 2	0.00
TOTAL BASES	45.50
TOTAL FLOW RATE	49.01

This P.E.M. has the following chemical composition:

MDI	35.37
Polyester 1	57.47
Polyester 2	0.00
MEG (*)	6.99
Dabco	0.17
Water	0.00
TOTAL	100.00

EXAMPLE 22

An M.E.P., specifically produced for making the soles of sport shoes that require particular stress resistance properties.

DOSAGE OF THE COMPONENTS :

	flow rate (g/s)
SOLUTION 1 - Catalyst	0.23
SOLUTION 3 - Foaming Agent	0.19
SOLUTION 2 - Chain Lengthener	1.64
Total additives	2.06
BASE 1	29.57
BASE 2	7.37
TOTAL BASES	36.94
TOTAL FLOW RATE	39.00

This M.E.P. has the following chemical composition :

MDI	30.01
Polyester 1	46.95
Polyester 2	17.78
MEG (*)	4.95
Dabco	0.18
Water	0.14
TOTAL	100.00

MEG (*) = monoethylene glycol.

The M.E.P.'s that can be made with the process of the instant invention can be used in the widest range of fields such as e.g. shoe manufacturing in order to produce: polyurethane bottoms for any kind of shoe, innersoles, leggings, footwear and sandals; in the marine sector for producing :

the inner sheels of ships, buoys, antislip carpets, handles and handrails; in road works to produce: expansion joints, obstacles for reducing the speed of vehicles, removable buffers; in the car industry to produce: bumpers, steering wheels, protective sumps, panellings; in the sector of technical articles to produce: joints, suckers, gears,shock absorbers, protection gloves; in the furniture sector to produce: furniture, frames, paving tiles, decorations.

C L A I M S

1. A process for molding microcellular elastomeric polyurethane articles characterized by the fact that in a mixing head are reacted, according to per se known methods, a quasi-polyurethane having a molecular weight of from 600 to 2200 and a free isocyanate group percent content of from 14 to 3.8,with :

a) an other quasi-polyurethane having a molecular weight of from 3000 to 8000 and a free hydroxyl group percent content of from 1.13 to 0.48, and water;

or

b) an other quasi-polyurethane having a molecular weight of from 3000 to 8000 and a free hydroxyl group percent content of from 1.13 to 0.48, a glycol and water;

or

c) an other quasi-polyurethane having a molecular weight of from 3000 to 8000 and a free hydroxyl group percent content of from 1.13 to 0.48, and a glycol;

or

d) an other quasi-polyurethane having a molecular weight of from 3000 to 8000 and a free hydroxyl group percent content of from 1.13 to 0.48,

or

e) a glycol and water;

or

f) a glycol.

2. A molding process according to claim 1, characterized by the fact that said microcellular elastomeric polyurethane is made by reacting a quasi-polyurethane,having a molecular weight of from 700 to 1100 and a free isocyanate group percent content of from 12 to 7.6, with an other quasi-polyurethane having a molecular weight of from 3750 to 4500 and a free hydroxyl group percent content of from 0.9 to 0.75, and water.

3. A molding process according to claim 1, characterized by the fact that said microcellular elastomeric polyurethane is made by reacting a quasi-polyurethane,having a molecular weight of from 700 to 1100 and a free isocyanate group percent content of from 12 to 7.6, with an other quasi-polyurethane having a molecular weight of from 3750 to 4500 and a free hydroxyl group percent content of from 0.9 to 0.75, and a glycol and water.

4. A molding process according to claim 1, characterized by the fact that said microcellular elastomeric polyurethane is made by reacting a quasi-polyurethane, having a molecular weight of from 700 to 1100 and a free isocyanate group percent content of from 12 to 7.6, with an other quasi-poly-

urethane having a molecular weight of from 3750 to 4500 and a free hydroxyl group percent content of from 0.9 to 0.75, with a glycol.

5. A molding process according to claim 1, characterized by the fact that said microcellular elastomeric polyurethane is made by reacting a quasi-polyurethane, having a molecular weight of from 700 to 1100 and a free isocyanate group percent content of from 12 to 7.6, with an other quasi-polyurethane having a molecular weight of from 3750 to 4500 and a free hydroxyl group percent content of from 0.9 to 0.75.

6. A molding process according to claim 1, characterized by the fact that said microcellular elastomeric polyurethane is made by reacting a quasi-polyurethane, having a molecular weight of from 700 to 1100 and a free isocyanate group percent content of from 12 to 7.6, with a glycol and water.

7. A molding process according to claim 1, characterized by the fact that said microcellular elastomeric polyurethane is made by reacting a quasi-polyurethane, having a molecular weight of from 700 to 1100 and a free isocyanate group percent content of from 12 to 7.6, with a glycol.

8. A molding process according to any one of claims 1 to 7, characterized by the fact that the quasi-polyurethane, having a moleculare weight of from 600 to 2200 and a free isocyanate group percent content of from 14 to

3.8, is made by reacting, according to per se known methods, a diphenylmethane diisocyanate with a saturated polyester having a molecular weight of from 1500 to 2500, in a molar ratio of 1 : 2.

9. A molding process according to any one of claims 1 to 7, characterized by the fact that the quasi-polyurethane,having a molecular weight of from 600 to 2200 and a free isocyanate group percent content of from 14 to 3.8, is made by reacting, according to per se known methods, a diphenylmethane diisocyanate with a polyether having a molecular weight of from 1500 to 2500, in a molar ratio of 1 : 2.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 91/01803

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 G 18/10, 18/42, 18/48, 18/64, 18/76

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 08 G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	US, A, 4190711 (ZDRAHALA ET AL) 26 February 1980, see the whole document --	1-9
A	US, A, 4334032 (PATTON, JR. ET AL) 8 June 1982, see the whole document --	1-9
A	US, A, 4559366 (FRITZ HOSTETTLER) 17 December 1985, see the whole document --	1-9
A	US, A, 4686242 (TURNER ET AL) 11 August 1987, see the whole document --	1-9

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
4th December 1991	09. 01. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Daniella van der Haas

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4791148 (RILEY ET AL) 13 December 1988, see the whole document	1-9

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/EP 91/01803

SA 51190

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 31/10/91
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For more details about this annex : see Official Journal of the European patent Office, No. 12/82

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