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(54) **Polyoxyalkylene polyether polyols and polyurethane foams prepared therefrom.**

(57) The invention relates to polyols prepared by reacting ethylene oxide with an initiator followed by additional alkylene oxide. The ethylene oxide blocks at the initiator ranges from 1 to 30 weight percent based on the weight of the polyol. Polyurethane foams prepared from these polyols exhibit good air flow and improved load bearing properties.

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POLYOXYALKYLENE POLYETHER POLYOLS
AND POLYURETHANE FOAMS PREPARED THEREFROM

The invention relates to a process for the preparation of polyoxyalkylene polyether polyols, the products of the process and the polyurethane foams prepared
5 therefrom. More particularly, the invention relates to the preparation of polyoxyalkylene polyether polyols by reacting an initiator compound or mixtures thereof with ethylene oxide in the presence of an alkaline catalyst and subsequently reacting the intermediate product with propylene
10 oxide, butylene oxide or a heteric mixture selected from the group consisting of ethylene oxide, propylene oxide and butylene oxide, optionally followed by capping with either propylene oxide or butylene oxide.

The preparation of polyoxyalkylene polyether
15 polyols is well known to those skilled in the art. It is also well known that a high oxyethylene content can have an effect on the physical properties of polyurethane foams. Generally the foams have closed cells. The prior art, however, is silent on the fact that a block of ethylene
20 oxide constituting as much as 30 percent of the total molecule may be added to the initiator molecule without creating excessive amounts of closed cells in the poly-

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urethane foam and, furthermore, can result in improved load bearing properties.

The polyoxyalkylene polyether polyol having a hydroxyl number of about 20 to 200 and functionality of 2.5 to 8 comprises (a) an organic initiator compound or mixtures thereof having from 2 to 12 carbon atoms and 2 to 8 active hydrogen groups, and an equivalent weight ranging from about 30 to about 50, (b) an ethylene oxide adduct adjacent to the initiator comprising from 1 to 30 weight percent based on the total weight of the polyol, and (c) a subsequent alkylene oxide adduct selected from the group consisting of propylene oxide, butylene oxide and a heteric mixture of ethylene oxide and propylene oxide or ethylene oxide and butylene oxide provided that the total ethylene oxide content does not exceed 30 weight percent based on the weight of the polyol and optionally further provided that when a heteric mixture is employed, a further addition of propylene oxide is made to cap the product.

Preferably the concentration of ethylene oxide adduct at the initiation ranges from about 5 to about 20 weight percent based on the weight of the polyol.

Suitable alkylene oxides which may be employed have 2 to 4 carbon atoms in the alkylene chain and weights of 44 to 120, preferably 44 to 72, include ethylene oxide,

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1,2- and 2,3-butylene oxide and 1,2-propylene oxide. Other oxides which may be employed include styrene oxide and cyclohexene oxide.

Possible initiator compounds include those with equivalent weights of 30 to 50, and which contain 2 to 8 Zerewitinoff-active hydrogen atoms. These include di- to pentafunctional polyamines and di- to octafunctional, preferably trifunctional, polyols. These include the following: ammonia, hydrazine, aliphatic and aromatic, possibly N-monoalkyl, N,N- and N,N'-dialkyl substituted diamines having 1 to 4 carbon atoms in the alkyl radical such as mono- and dialkyl-substituted ethylene diamine, diethylenetriamine, triethylenetetramine, 1,3-propylenediamine, 1,3- or 1,4-butylenediamine, 1,2-, 1,3-, 1,4-, 1,5- and 1,6-hexamethylenediamine, phenylenediamine, 2,4- and 2,6-toluenediamine, and 4,4'-, 2,4'- and 2,2'-diaminodiphenylmethane; monoamines such as methylamine, ethylamine, isopropylamine, butylamine, benzylamine, aniline, the toluidines and naphthylamines; alkanolamines such as ethanalamine, diethanalamine, N-methyl- and N-ethyl-diethanalamine, N-methyl- and N-ethyl-diethanalamine and triethanalamine; water, glycerine, trimethylolpropane, triethylolethane, propylene glycol, dipropylene glycol, ethylene glycol, diethylene glycol, pentaerythritol, sorbitol, α -methylglucoside and sucrose.

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Difunctional initiators are employed in mixture with higher functionality products to achieve a polyoxyalkylene polyether polyol functionality of 2.5 or greater. Preferred initiators are propylene glycol, glycerine and trimethylolpropane.

5 Commonly used catalysts include the alkali metal alkoxides having 1 to 4 carbon atoms in the alkyl radical such as sodium methylate, sodium and potassium ethylate, potassium isopropylate and sodium butylate, alkaline earth metal hydroxides such as calcium hydroxide and preferably
10 alkali metal hydroxides such as lithium hydroxide and most preferably, sodium and potassium hydroxide.

The hydroxyl-group-containing polyoxyalkylene polyether polyols produced according to this invention have hydroxyl numbers of 20 to 200, preferably 25 to 80, and
15 functionalities of 2.5 to 8.

The resulting crude product is treated to remove the residual catalyst by methods well known to those skilled in the art. These include neutralization with acids, filtration employing adsorbents such as magnesium silicate,
20 water washing or ion exchange.

The polyurethane foams employed in the present invention are generally prepared by the reaction of the polyol of the invention with an organic polyisocyanate in the presence of a blowing agent and optionally in the

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presence of additional polyhydroxyl-containing components, chain-extending agents, catalysts, surface-active agents, stabilizers, dyes, fillers and pigments. Suitable processes for the preparation of cellular polyurethane plastics are disclosed in U.S. Reissue Patent 24,514 together with suitable machinery to be used in conjunction therewith. When water is added as the blowing agent, corresponding quantities of excess isocyanate to react with the water and produce carbon dioxide may be used. It is possible to proceed with the preparation of the polyurethane plastics by a prepolymer technique wherein an excess of organic polyisocyanate is reacted in a first step with the polyol of the present invention to prepare a prepolymer having free isocyanate groups which is then reacted in a second step with water and/or additional polyol to prepare a foam. Alternatively, the components may be reacted in a single working step commonly known as the "one-shot" technique of preparing polyurethanes. Furthermore, instead of water, low boiling hydrocarbons such as pentane, hexane, heptane, pentene, and heptene; azo compounds such as azohexahydrobenzodinitrile; halogenated hydrocarbons such as dichlorodifluoromethane, trichlorofluoromethane, dichlorodifluoroethane, vinylidene chloride, and methylene chloride may be used as blowing agents.

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Organic polyisocyanates which may be employed include aromatic, aliphatic, and cycloaliphatic polyisocyanates and combinations thereof. Representative of these types are the diisocyanates such as m-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, mixtures of 2,4- and 2,6-toluene diisocyanate, hexamethylene diisocyanate, tetramethylene diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene diisocyanate (and isomers), naphthalene-1,5-diisocyanate, 1-methoxyphenyl-2,4-diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate and 3,3'-dimethyl-diphenylmethane-4,4'-diisocyanate; the triisocyanates such as 4,4',4"-triphenylmethane triisocyanate, and toluene 2,4,6-triisocyanate; and the tetraisocyanates such as 4,4'-dimethyldiphenylmethane-2,2'-5,5'-tetraisocyanate and polymeric polyisocyanates such as polymethylene polyphenylene polyisocyanate. Especially useful due to their availability and properties are toluene diisocyanate, 4,4'-diphenylmethane diisocyanate and polymethylene polyphenylene polyisocyanate.

Crude polyisocyanates may also be used in the compositions of the present invention, such as crude toluene diisocyanate obtained by the phosgenation of a mixture of toluene diamines or crude diphenylmethane isocyanate

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obtained by the phosgenation of crude diphenylmethane diamine. The preferred or crude isocyanates are disclosed in U.S. Patent No. 3,215,652.

Chain-extending agents which may be employed in the preparation of the polyurethane foams include those compounds having at least two functional groups bearing active hydrogen atoms such as water, hydrazine, primary and secondary diamines, amino alcohols, amino acids, hydroxy acids, glycols, or mixtures thereof. A preferred group of chain-extending agents includes water, ethylene glycol, 1,4-butanediol and primary and secondary diamines which react more readily with the prepolymer than does water such as phenylene diamine, 1,4-cyclohexane-bis-(methylamine), ethylenediamine, diethylenetriamine, N-(2-hydroxypropyl)-ethylenediamine, N,N'-di(2-hydroxypropyl)ethylenediamine, piperazine, and 2-methylpiperazine.

Any suitable catalyst may be used including tertiary amines such as, for example, triethylenediamine, N-methylmorpholine, N-ethylmorpholine, diethylethanolamine, N-cocomorpholine, 1-methyl-4-dimethylaminoethylpiperazine, 3-methoxypropyldimethylamine, N,N,N'-trimethylisopropylpropylenediamine, 3-diethylaminopropyldiethylamine, dimethylbenzylamine, and the like. Other suitable catalysts are, for example, stannous chloride, dibutyltin di-2-ethylhexanoate, stannous oxide, as well as other organometallic

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compounds such as are disclosed in U.S. Patent No.
2,846,408.

A surface-active agent is generally necessary for
production of high grade polyurethane foam according to the
5 present invention, since in the absence of same, the foams
collapse or contain very large uneven cells. Numerous
surface-active agents have been found satisfactory.
Nonionic surface active agents are preferred. Of these, the
nonionic surface-active agents such as the well-known
10 silicones have been found particularly desirable. Other
surface-active agents which are operative, although not
preferred, include polyethylene glycol ethers of long chain
alcohols, tertiary amine or alkanolamine salts of long chain
alkyl acid sulfate esters, alkyl sulfonic esters, and alkyl
15 arylsulfonic acids.

In the preparation of the flame retardant poly-
urethane foam products the flame retardants which may be
employed are: pentabromodiphenyl oxide, dibromopropanol,
tris(β -chloropropyl)phosphate, 2,2-bis(bromoethyl) 1,3-
20 propanediol, tetrakis(2-chloroethyl)ethylene diphosphate,
tris(2,3-dibromopropyl)phosphate, tris(β -chloroethyl)-
phosphate, tris(1,2-dichloropropyl)phosphate, bis-(2-chloro-
ethyl) 2-chloroethylphosphonate, molybdenum trioxide,
ammonium molybdate, ammonium phosphate, pentabromodiphenyl-
25 oxide, tricresyl phosphate, hexabromocyclododecane and

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dibromoethyl- dibromocyclohexane. The concentrations of flame retardant compounds which may be employed range from 5 to 25 parts per 100 parts of polyol mixture.

The following examples illustrate the nature of the invention. All parts are by weight unless otherwise stated. In the examples, the physical properties of the polyurethane foam were determined by the following ASTM tests:

Density - D1622-63
Tensile Strength - D1623-72
Elongation - D412
Split Tear - D470
Compression Set - D395
Compression Load - D1564
Humid Aging - D1564

The following abbreviations are employed in the examples below:

Dabco 33 LV[™] - 33 percent solution of triethylenediamine in dipropylene glycol
Silicone L-520[™] - a silicone surfactant
Catalyst T-9[™] - stannous octoate
E.O. - ethylene oxide
P.O. - propylene oxide
TDI - toluene diisocyanate, 80/20, 2,4- 2,6-isomers

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Examples 1-10

Procedure

The indicated amounts in the tables below of glycerine and 45 percent potassium hydroxide were charged to
5 a reactor equipped with a stirrer, heating means, and nitrogen inlet and the water was stripped off. This was followed by the addition of ethylene oxide, propylene oxide or propylene glycol as indicated, and the mixture was allowed to react at about 105°C over a total time period of
10 7 to 8 hours under nitrogen pressure. The reaction mixture was vented and additional charges of potassium hydroxide were made followed by stripping off the water. Ethylene oxide and propylene oxide additions were then made and the mixture allowed to react at 105°C for an additional 7 to 8
15 hours. This procedure was repeated with additional oxide charges. After the reaction was completed, the product was filtered to remove the catalyst, stripped at 105°C for 1 hour and discharged from the reactor.

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TABLE I

Example	1	2	3	4
Charge, pbw				
Glycerine	915	1657	244	221
45% KOH	5.5	4.0	95	67
Propylene Glycol	-	-	-	27
E.O.	1500	3000	-	-
P.O.			356	352
2nd Charge, pbw				
45% KOH	350	500		
Propylene Glycol	-	202		
E.O.			480*	-
P.O.			7000*	7480
3rd Charge, pbw				
P.O.			-	-
Hydroxyl No.	722	664	57.6	57.6

TABLE II

Example	5	6	7
Charge, pbw			
Polyol of Example 1	252	252	252
E.O.	-	150	300
2nd Charge, pbw*			
E.O.	171	162	152
PO.	2618	2477	2337
Hydroxyl No.	57.6	58.4	56.7
Unsaturation	0.025	0.021	0.019
Acid No.	0.003	0	0.04
Alkalinity, as ppm K	7.0	10	7
% E.O. at Initiator	5	10	15
Total % E.O.	11	16	21

*This charge was a mixture of E.O. and P.O.

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TABLE III

Example	8	9	10
Charge, pbw			
Polyol of Example 2	502	502	502
E.O.	-	300	600
2nd Charge, pbw			
P.O.	5574	5274	4974
Hydroxyl No.	58.6	58.8	57.4
Unsaturation	0.032	0.032	0.031
Acid No.	0.002	0.002	0
Alkalinity, as ppm K	2	4	5
% E.O. at Initiator	5	10	15

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Examples 11-19

The indicated amounts of polyol, water, Dabco 33LV and Silicone L-520 were added in a suitable container and mixed for about 30 seconds. Catalyst T-9 was added and the mixture was stirred for 15 seconds. TDI was then added, the mixture was stirred for 5 to 10 seconds and poured into suitable containers. After the foam had formed, it was cured in an oven at 115°C for 5 to 10 minutes. Physical properties were then determined.

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TABLE IV

Example	11	12	13	14	15
Polyol of Example	3	5	6	6	7
Percent Oxyethylene at Initiator	0	5	10	10	5
Charge, pbw					
Polyol	250	250	250	250	250
Water	10	10	10	10	10
DABCO 33 LV	0.75	0.75	0.75	0.75	0.75
Silicone L-520	2.5	2.5	2.5	2.5	2.5
Catalyst T-9	0.26	0.26	0.26	0.22	0.22
TDI Index	110	110	110	110	110
	115	115	95	80	110
Rise time, sec.					
Physical Properties					
Density, pcf	1.63	1.63	1.64	1.64	1.60
Tensile Strength, psi	11.8	11.3	11.5	11.7	10.5
Percent Elongation	150	133	150	117	150
Tear, PI	2.2	1.8	2.0	2.0	1.7
I.L.D. (lb/in ²)	4.04	4.04	4.04	4.04	4.04
Sample thickness (in.)	32.0	34.0	36.4	35.4	39.6
Load at 25% deflection	62.0	62.8	68.4	68.0	70.6
Load at 65% deflection	22.0	22.2	24.4	24.2	25.0
Load at 25% return	1.94	1.85	1.88	1.92	1.78
Sag Factor	19.6	20.9	22.2	21.6	24.7
Guide Factor	68.8	65.3	67.0	68.4	63.1
Percent Recovery					
C.L.D., psi	0.50	0.55	0.59	0.55	0.53
Load at 25% deflection					
Load at 50% deflection					
Load at 65% deflection					
Compression Sets					
% set at 50% compression	7.6	8.6	6.5	6.2	5.8
% set at 90% compression	6.3	8.0	7.4	7.7	7.5
Air flow, CFM at 0.5" H ₂ O	5.60	5.50	3.30	4.20	5.10

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TABLE V

Example	16	17	18	19
Polyol of Example	4	8	9	10
Percent Oxyethylene at initiator	0	5	10	15
Charge, pbw				
Polyol	250	250	250	250
Water	10	10	10	10
DABCO 33 LV	0.75	0.75	0.75	0.75
Silicone L-520	2.5	2.5	2.5	2.5
Catalyst T-9	0.26	0.26	0.26	0.26
TDI Index	110	110	110	110
Rise time, sec.	130	118	110	108
Physical Properties				
Density, pcf	1.58	1.60	1.59	1.60
Tensile Strength, psi	13.7	11.9	11.3	10.3
Percent Elongation	160	150	143	123
Tear, PI	1.7	1.8	1.8	1.9
I.L.D. (lb/in ²)				
Sample thickness (in.)	4.12	4.06	4.07	4.07
Load at 25% deflection	29.4	35.6	38.0	37.8
Load at 65% deflection	62.8	71.0	72.0	69.8
Load at 25% return	20.2	24.0	25.4	24.8
Sag Factor	2.14	1.99	1.89	1.85
Guide Factor	18.6	22.2	24.0	23.7
Percent Recovery	68.7	67.4	66.8	65.6
C.L.D., psi				
Load at 25% deflection	0.51	0.51	0.54	0.54
Load at 50% deflection				
Load at 65% deflection				
Compression Sets				
% set at 50% compression	9.2	8.6	7.2	8.5
% set at 90% compression	10.3	8.7	8.2	8.9
Air flow, CFM at 0.5" H ₂ O	4.80	5.00	4.50	3.30

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Examples 20-29

The procedure employed for the preparation of the polyols of Examples 20-29 was similar to that of Examples 1-10.

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TABLE VI

Example	20	21
Charge, pbw		
Glycerine	906	—
TMP	—	1235
45% KOH	27	27
Ethylene Oxide	4969	4648
2nd Charge, g.		
45% KOH	382	356
E.O. addition time, hr.	9.9	11.5
Reaction time, hr.	1.0	1.0
Hydroxyl No.	277	258

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TABLE VII

Example	22	23	24	25	26	27	28	29
Charge, pbw	1048	1048	1048	1048	-	-	-	-
Polyol of Example 20	-	-	-	-	1120	1120	1120	1120
Polyol of Example 21	-	333	633	933	-	.332	632	932
E.O.	-	-	-	-	4959	-	-	-
P.O.	5031	-	-	-	8.0	1.0	.9	2.9
Oxide addition time, hr.	8.2	0.8	2.0	3.2	-	-	-	-
2nd Charge, pbw	-	4698	4398	4098	-	4627	4327	4027
P.O.	-	-	-	-	-	-	-	-
P.O. addition time, hr.	-	8.2	7.2	6.0	-	8.1	7.1	6.4

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Examples 30-37

The procedure and formulation employed in Examples 11-19 were employed for the preparation of the foams of Examples 30-37 with the exception of the polyols as indicated in Tables VIII and XI. The foam properties indicate that employing polyols having an oxyethylene structure located as a block at the initiator resulted in a faster rise time, higher ILD without excessive closed cells as indicated air flow.

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TABLE VIII

Example	30	31	32	33
Polyol of Example	22	23	24	25
Density, pcf	1.57	1.64	1.59	1.62
Tensile Strength, psi	12.5	11.1	13.5	14.5
% Elongation	140	107	132	140
Tear (PI)	2.4	2.5	2.2	1.9
I.L.D. (lb/ 50 sq.in.)				
Sample thickness (inches)	4.00	4.00	4.00	4.00
Load at 25% deflection	36.0	38.5	45.2	43.8
Load at 65% deflection	70.5	74.5	80.8	80.0
Load at 25% return	25.0	27.0	32.5	30.6
Sag Factor	1.96	1.94	1.79	1.83
Guide Factor	22.9	23.5	28.3	27.1
% Recovery	69.4	70.1	71.9	69.9
C.L.D. (psi)				
Load at 50% deflection	.56	.56	.65	.64
Compression Sets				
% set at 50% compression	4.4	4.7	5.6	6.6
% set at 90% compression	4.7	4.3	4.8	8.0
Air Flow, cfm at .5 inch water	6.00	5.40	2.30	.30

TABLE IX

Example	34	35	36	37
Polyol of Example	26	27	28	29
Density, pcf	1.73	1.74	1.75	1.76
I.L.D. (lb/ 50 sq.in.)	4.00	4.00	4.00	4.00
Sample thickness (inches)	37.0	38.8	40.6	41.3
Load at 25% deflection	71.2	71.2	76.9	79.9
Load at 65% deflection	25.5	26.0	27.4	29.7
Load at 25% return	1.92	1.84	1.89	1.93
Sag Factor	21.4	22.3	23.2	23.5
Guide Factor	68.9	67.0	67.5	71.9
% Recovery	.63	.60	.62	.65
C.L.D. (psi)	2.7	3.1	3.3	5.7
Load at 50% deflection	4.2	3.9	4.7	5.3
Compression Sets	5.40	6.00	5.30	2.69
% set at 50% compression				
% set at 90% compression				
Air Flow, cfm at .5 inch water				

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The embodiments of the invention in which an exclusive privilege or property is claimed are defined as follows:

1. A polyoxyalkylene polyether polyol having a
5 hydroxyl number of about 20 to 200 and functionality of 2.5 to 8 comprising
 - (a) an organic initiator compound having from
2 to 8 active hydrogen groups and 2 to 12
carbon atoms and an equivalent weight
10 ranging from about 30 to about 50.
 - (b) an ethylene oxide adduct adjacent to the
initiator comprising from 1 to 30 weight
percent based on the total weight of the
polyol, and
 - 15 (c) a subsequent alkylene oxide adduct
selected from the group consisting of
propylene oxide, butylene oxide and a
heteric mixture of ethylene oxide and
propylene oxide provided that the
20 ethylene oxide content does not exceed 30
weight percent based on the weight of the
polyol and further provided that when the
heteric mixture is employed a further
addition of propylene oxide is made.

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2. The polyol of claim 1 wherein the initiator is selected from the group consisting of propylene glycol, glycerine, and trimethylolpropane.

5 3. The polyol of claim 1 wherein the concentration of ethylene oxide at the initiator ranges from about 5 to about 15 weight percent based on the weight of the polyol.

10 4. A process for the preparation of a polyoxy-alkylene polyether polyol having a hydroxyl number of about 20 to 200 and functionalities of 2.5 to 8 comprising the steps of reacting

- 15 (a) an organic initiator compound having from 2 to 8 active hydrogen groups, 2 to 12 carbon atoms and an equivalent weight ranging from 30 to 50,
- (b) ethylene oxide in an amount from 1 to 20 weight percent based on the total weight of the polyol, and
- 20 (c) alkylene oxide selected from the group consisting of propylene oxide, butylene oxide and a mixture of ethylene oxide and propylene oxide provided that the total ethylene oxide content does not exceed 30 weight percent based on the weight of the
- 25 polyol, in the presence of a catalyst.

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5. The process of claim 4 wherein the initiator is selected from the group consisting of propylene glycol, glycerine, and trimethylolpropane.

6. The process of claim 4 wherein the concentration of ethylene oxide at the initiator ranges from about 5 to about 15 weight percent based on the weight of the polyol.

7. A flexible polyurethane foam prepared by reacting an organic polyisocyanate with the polyoxyalkylene polyether polyol of claim 1.

8. A flexible polyurethane foam prepared by reacting an organic polyisocyanate with the polyoxyalkylene polyether polyol of claim 2.

9. A flexible polyurethane foam prepared by reacting an organic polyisocyanate with the polyoxyalkylene polyether polyol of claim 3.



European Patent
Office

EUROPEAN SEARCH REPORT

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Application number

EP 84 11 5324

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 457 203 (S.I. COHEN et al.) * Column 2, line 17 - column 3, line 3; claim 1 *	1,2,4, 5,7,8	C 08 G 18/48 C 08 G 18/14
X	EP-A-0 017 928 (BAYER) * Page 13, paragraph 2; examples 6,7,10,13; claims 1-6 *	1-9	
X	GB-A-1 025 242 (IMPERIAL CHEMICAL INDUSTRIES) * Column 2, lines 39-50; claims 1,2 *	1-9	
X	US-A-4 008 189 (B.G. VAN LEUWEN et al.) * Column 2, line 60 - column 3, line 37; claim 1 *	1,2,4, 5,7,8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
X	DD-A- 67 582 (SANYO CHEMICAL INDUSTRIE) * Column 2, line 28 - column 3, line 27; claims 1-3 *	1-9	C 08 G 18/48
A	DE-A-1 569 109 (LANKRO CHEMICALS) * Page 5, paragraph 4 - page 7, paragraph 1; example 10; claims 1-3,6-10 *	1-9	
<div style="text-align: center;"> <div>---</div> <div>---</div> </div>			
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 22-03-1985	Examiner BOURGONJE A.F.
<div> <div> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> </div> <div> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p> </div> </div>			



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-4 239 907 (W.C. BEDOIT) * Column 5, lines 54-60; claims 1-8,16-19 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 22-03-1985	Examiner BOURGONJE A.F.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	