

(12) PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. **AU 200138763 B2**
(10) Patent No. **776569**

(54) Title
Aliphatic thermoplastic polyurethanes and use thereof

(51) ⁶ International Patent Classification(s)
C08G 018/73 C08G 018/66
C08G 018/48

(21) Application No: 200138763 (22) Application Date: 2001.04.20

(30) Priority Data

(31) Number (32) Date (33) Country
10020163 2000.04.25 DE

(43) Publication Date : 2001.11.01
(43) Publication Journal Date : 2001.11.01
(44) Accepted Journal Date : 2004.09.16

(71) Applicant(s)
Bayer Aktiengesellschaft

(72) Inventor(s)
Wolfgang Kaufhold; Henricus Peerlings; Hans-Gorg Hoppe

(74) Agent/Attorney
Davies Collison Cave,GPO Box 3876,SYDNEY NSW 2001

(56) Related Art
US 5541277
EP 0922719

Aliphatic Thermoplastic Polyurethanes and Use Thereof

Abstract of the Disclosure

A thermoplastic moulding composition that contains an aliphatic thermoplastic polyurethane (TPU) resin is disclosed. The TPU is the product of a reaction of A) a diisocyanate reactant that contains predominantly hexamethylene diisocyanate, and B) a polyol reactant that contains polytetramethylene glycol and C) a chain extending reactant that contains primarily 1,6-hexanediol. The TPU that is further characterized in the equivalence ratio of A to B and NCO index exhibits improved properties.

Our Ref:7594120

P/00/011
Regulation 3:2

AUSTRALIA

Patents Act 1990

**ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT**

Applicant(s):

Bayer Aktiengesellschaft
Germany

D-51368 Leverkusen

Address for Service:

DAVIES COLLISON CAVE
Patent & Trade Mark Attorneys
Level 10, 10 Barrack Street
SYDNEY NSW 2000

Invention Title:

Aliphatic thermoplastic polyurethanes and use thereof

The following statement is a full description of this invention, including the best method of performing it known to me:-

5020

Aliphatic thermoplastic polyurethanes and use thereof

5 This invention relates to aliphatic thermoplastic polyurethanes (TPU) prepared from hexamethylene diisocyanate, polytetramethylene glycol and hexanediol with improved properties.

10 Aromatic thermoplastic polyurethanes (aromatic TPUs) are not light-stable because they are synthesised from aromatic diisocyanates. In coloured mouldings, exposure to light brings about severe yellowing and changes in colour and degree of gloss occur even in black mouldings.

15 DE-C 42 03 307 describes a thermoplastic polyurethane moulding composition processable in the form of a sinterable powder for the production of grained sintered films, wherein the powder is produced exclusively from linear, aliphatic components. The polyol component is composed of 60 to 80 parts by weight of an aliphatic polycarbonate diol having a molecular weight $\overline{M}_n$ of 2000 and 40 to 20 parts by weight of a polydiol based on adipic acid, hexanediol and neopentyl glycol having a molecular weight $\overline{M}_n$ of 2000. Preferably, 1,6-hexamethylene diisocyanate is used in an equivalence ratio of 2.8:1.0 to 4.2:1.0, relative to the polyol mixture, and 20 1,4-butanediol is used as the chain extender, wherein the equivalence ratio of 1,4-butanediol relative to the polydiol is 1.3:1.0 to 3.3:1.0.

25 This moulding composition has the disadvantage (especially for optically demanding applications) that it has a tendency to form a white deposit after storage (at room temperature and in particular during accelerated ageing tests, such as the alternating climate test, Arizona test and at elevated temperatures (60-95°C)). The resultant deposit has the further disadvantage that it cannot readily be wiped off with a cloth.

30 While formation of the stated deposit is indeed reduced when 1,6-hexanediol is used as chain extender, the deposit reforms on storage at room temperature. However, this deposit may be removed by wiping with a cloth.

The present invention seeks to provide light-stable thermoplastic polyurethanes to meet demanding optical requirements, which polyurethanes, after storage at room temperature and after accelerated ageing testing (for example after storage at 60°C), yield mouldings which exhibit only very slight or no formation of deposits.

Accordingly, the present invention provides aliphatic, thermoplastic polyurethanes prepared by reacting

- A) 100 to 60 mol%, preferably 100 to 70 mol%, particularly preferably 100 to 80 mol% of hexamethylene diisocyanate (HDI) and 0 to 40 mol%, preferably 0 to 30 mol%, particularly preferably 0 to 20 mol% of other aliphatic diisocyanates differing from HDI,
- B) 40 to 100 wt.% of polytetramethylene glycol having a number average molecular weight of 600 to 1600 g/mol and 0 to 60 wt.% of a polyol or polyol mixture differing from polytetramethylene glycol and having a number average molecular weight of 600 to 5000 g/mol and
- C) 80 to 100 wt.% of 1,6-hexanediol and 0 to 20 wt.% of a chain extender differing from 1,6-hexanediol and having a number average molecular weight of 60 to 500 g/mol.

The inventive thermoplastic polyurethane may be prepared in the presence of

- D) optional catalysts and may contain

CAJOC 40JOC

E) optional further conventional auxiliary substances and additives.

The equivalence ratio of diisocyanate A) to polyol B) is between 1.5:1.0 and 10.0:1.0 and the NCO index (formed from the quotients, multiplied by 100, of the equivalence ratios of isocyanate groups and the sum of the hydroxyl groups of polyol and chain extending agent) characterizing the TPU is 95 to 105.

The present invention furthermore provides aliphatic thermoplastic polyurethanes prepared by reacting

A) 100 to 60 mol%, preferably 100 to 70 mol%, particularly preferably 100 to 80 mol% of hexamethylene diisocyanate (HDI) and 0 to 40 mol%, preferably 0 to 30 mol%, particularly preferably 0 to 20 mol% of other aliphatic diisocyanates differing from HDI,

B) 70 to 30 wt.% of at least one polyol differing from polytetramethylene glycol and having a number average molecular weight of 600 to 5000 g/mol and 30-70 wt.% of polytetramethylene glycol having a number average molecular weight of 200 to 590 g/mol and

C) 80 to 100 wt.% of 1,6-hexanediol and 0 to 20 wt.% of a chain extender having a number average molecular weight of 60 to 500 g/mol, which differs from polytetramethylene glycol having a number average molecular weight of 200 to 590 g/mol and differs from 1,6-hexanediol,

wherein the equivalence ratio of diisocyanate A) to polyol B) is between 1.5:1.0 and 10.0:1.0 and wherein the NCO index (formed from the quotients, multiplied by 100, of the equivalence ratios of isocyanate groups and the sum of the hydroxyl groups of polyol and chain extending agent) is 95 to 105.

The preparation of the inventive TPU may be in the presence of D) catalysts and the composition may contain E) conventional additives.

5 The above sequence of components A to E is no indication of the method by which the TPUs according to the invention are produced. The TPUs according to the invention may be produced by various process variants, wherein these variants are mutually equivalent.

10 The TPUs according to the invention based on two different aliphatic diisocyanates "A1" (HDI) and "A2" (aliphatic diisocyanate differing from HDI) may, for example, be produced in a reaction process to yield TPU "A1-2". It is, however, also possible in known manner initially to produce TPU "A1" based on the aliphatic diisocyanate "A1" and to produce separately therefrom TPU "A2" based on the aliphatic diisocyanate "A2", wherein the other components B to E are identical. TPU "A1" and
15 TPU "A2" are then mixed in known manner in the desired ratio to yield TPU "A1-2" (for example using extruders or kneaders).

20 The TPUs according to the invention based on polyol mixtures may likewise be produced by using polyol mixtures (polyol B1 and polyol B2) (for example in mixers) in a reaction process to yield TPU "B1-2". Alternatively, it is also possible in known manner initially to produce TPU "B1" based on polyol "B1" and to produce separately therefrom TPU "B2" based on polyol "B2", wherein the remaining components A and C to E are identical. TPUs "B1" and "B2" are then mixed in known manner in the desired ratio to yield TPU "B1-2" (for example using extruders
25 or kneaders).

Depending upon the requirements placed upon the moulding which is produced from the TPU according to the invention, the hexamethylene diisocyanate (HDI) may be replaced in part by one or more other aliphatic diisocyanates, in particular isophorone
30 diisocyanate (IPDI), 1,4-cyclohexane diisocyanate, 1-methyl-2,4-cyclohexane

diisocyanate, 1-methyl-2,6-cyclohexane diisocyanate and isomer mixtures thereof, 4,4'-, 2,4'- and 2,2'-dicyclohexylmethane diisocyanate and isomer mixtures thereof.

5 In applications having low requirements with regard to light stability, for example dark coloured moulding compositions, proportions (0 to 20 wt.%) of the aliphatic diisocyanate may even be replaced by aromatic diisocyanates. Aromatic diisocyanates are described in *Justus Liebigs Annalen der Chemie*, 562, pp. 75-136. Examples are 2,4-tolylene diisocyanate, mixtures of 2,4- and 2,6-tolylene diisocyanate, 4,4'-, 2,2'- and 2,4'-diphenylmethane diisocyanate, mixtures of 2,4- and 4,4'-diphenylmethane diisocyanate, urethane-modified, liquid 2,4- and/or 4,4'-diphenylmethane diisocyanates, 4,4'-diisocyanato-1,2-diphenylethane and 1,5-naphthylene diisocyanate.

15 Linear hydroxyl-terminated polyols for instance polyester diol and polyether diol, having an average molecular weight of 600 to 5000 g/mol, preferably of 700 to 4200 g/mol, are used as component B2). As a result of the production process, these frequently contain small amounts of non-linear compounds. For this reason, they are often also referred to as "substantially linear polyols".

20 Suitable polyester diols may be produced for example from dicarboxylic acids having 2 to 12 carbon atoms, preferably 4 to 6 carbon atoms, and polyhydric alcohols. Dicarboxylic acids which may be considered are, for example: aliphatic dicarboxylic acids, such as succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid and sebacic acid and aromatic dicarboxylic acids, such as phthalic acid, isophthalic acid and terephthalic acid. The dicarboxylic acids may be used individually or as mixtures, for example in the form of a succinic, glutaric and adipic acid mixture. To produce the polyester diols, it may optionally be advantageous to use, instead of the dicarboxylic acids, the corresponding dicarboxylic acid derivatives, such as carboxylic acid diesters with 1 to 4 carbon atoms in the alcohol residue, carboxylic acid anhydrides or carboxylic acid chlorides. Examples of polyhydric alcohols are glycols having 2 to 10, preferably 2 to 6 carbon atoms, such as ethylene glycol,

25

30

diethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, 2,2-dimethyl-1,3-propanediol, 1,3-propanediol and dipropylene glycol. Depending on the desired properties, the polyhydric alcohols may be used alone or as mixtures. Esters of carbonic acid with the stated diols are also suitable, in particular those
 5 having 4 to 6 carbon atoms, such as 1,4-butanediol or 1,6-hexanediol, condensation products of hydroxycarboxylic acids, for example hydroxycaproic acid and polymerisation products of lactones, for example optionally substituted caprolactones. Preferred polyester diols are ethanediol polyadipates, 1,4-butanediol polyadipates, ethanediol/1,4-butanediol polyadipates, 1,6-hexanediol/neopentyl glycol poly-
 10 adipates, 1,6-hexanediol/1,4-butanediol polyadipates and polycaprolactones. The polyester diols have average molecular weights of from 600 to 5000, preferably 700 to 4200, and may be used individually or mixed together.

Suitable polyether diols may be produced in that one or more alkylene oxides having
 15 2 to 4 carbon atoms in the alkylene residue are reacted with a starter molecule, which contains two attached active hydrogen atoms. Examples of alkylene oxides which may be mentioned are: ethylene oxide, 1,2-propylene oxide, epichlorohydrin and 1,2-butylene oxide and 2,3-butylene oxide. Ethylene oxide, propylene oxide and mixtures of 1,2-propylene oxide and ethylene oxide are preferably used. The alkylene
 20 oxides may be used individually, alternately one after the other or as mixtures. Starter molecules which may be considered are, for example: water, amino alcohols, such as N-alkyldiethanolamines, for example N-methyldiethanolamine, and diols, such as ethylene glycol, 1,3-propylene glycol, 1,4-butanediol and 1,6-hexanediol. Mixtures of starter molecules may optionally also be used. Suitable polyether diols are
 25 additionally the hydroxyl group-containing polymerisation products of tetrahydrofuran. Trifunctional polyethers in proportions of from 0 to 30 wt.%, relative to the difunctional polyethers, may also be used, but at most only in such an amount that a melt-processable product is obtained. The substantially linear polyether diols have molecular weights of 600 to 5000, preferably 700 to 4200. They may be used both
 30 individually and mixed together.

1,6-Hexanediol is used as the chain extending agent C), optionally blended with up to 20 wt.% of chain extenders having a number average molecular weight of 60 to 500 g/mol and differing from 1,6-hexanediol and from polytetramethylene glycol having a number average molecular weight of 200 to 590 g/mol, preferably aliphatic diols having 2 to 14 carbon atoms, such as for example ethanediol, diethylene glycol, dipropylene glycol and in particular 1,4-butanediol, or (cyclo)aliphatic diamines, such as for example isophoronediamine, ethylenediamine, 1,2-propylenediamine, 1,3-propylenediamine, N-methylpropylene-1,3-diamine, N,N'-dimethylethylenediamine. In addition, relatively small amounts of triols may also be added.

10

In applications having low requirements with regard to light stability, for example in dark coloured mouldings, proportions of the aliphatic diols and diamines (up to 20 wt.% relative to chain extender) may be replaced by aromatic diols and diamines. Examples of suitable aromatic diols are diesters of terephthalic acid with glycols having 2 to 4 carbon atoms, such as for example terephthalic acid bis-ethylene glycol or terephthalic acid bis-1,4-butanediol, hydroxyalkylene ethers of hydroquinone, such as for example 1,4-di(hydroxyethyl)hydroquinone, and ethoxylated bisphenols. Examples of suitable aromatic diamines are 2,4-tolylenediamine and 2,6-tolylenediamine, 3,5-diethyl-2,4-tolylenediamine and 3,5-diethyl-2,6-tolylenediamine and primary mono-, di-, tri- or tetraalkyl-substituted 4,4-diaminodiphenylmethane.

20

In addition, conventional monofunctional compounds may also be used in small quantities, for example as chain terminators or mould-release auxiliaries. Examples which may be mentioned are alcohols such as octanol and stearyl alcohol or amines such as butylamine and stearylamine.

25

The TPUs according to the invention may be produced using known procedures, including belt or extruder processes (GB-A 1,057,018 and DE-A 2,059,570). The process according to PCT/EP 98/07753 is preferred.

30

A catalyst is preferably used in the continuous production of thermoplastic polyurethanes by the extruder or belt processes. Suitable catalysts are conventional tertiary amines known according to the prior art, such as for example triethylamine, dimethylcyclohexylamine, N-methylmorpholine, N,N'-dimethylpiperazine, 2-(dimethylaminoethoxy)ethanol, diazabicyclo[2,2,2]octane and the like together with in particular organic metal compounds such as titanate acid esters, iron compounds, tin compounds, for example tin diacetate, tin dioctoate, tin dilaurate or the dialkyltin salts of aliphatic carboxylic acids such as dibutyltin diacetate, dibutyltin dilaurate or the like. Preferred catalysts are organic metal compounds, in particular titanate acid esters, iron or tin compounds. Dibutyltin dilaurate is very particularly preferred.

The TPU may optionally contain UV stabilisers, auxiliary substances and additives. Examples which may be mentioned are lubricants, such as fatty acid esters, the metal soaps thereof, fatty acid amides and silicone compounds, antiblocking agents, inhibitors, stabilisers acting with regard to hydrolysis, heat and discolouration, flame retardants, dyes, pigments, inorganic and organic fillers and reinforcing agents, which may be coated with a size. Further details about the above-mentioned auxiliary substances and additives may be found in the specialist literature, for example J.H. Saunders, K.C. Frisch: "High Polymers", Vol. XVI, Polyurethane, parts 1 and 2, Interscience Publishers 1962 and 1964, R. Gächter, H. Müller (eds.): Taschenbuch der Kunststoff-Additive, 3rd edition, Hanser Verlag, Munich 1989 or DE-A-29 01 774.

Additives may be added after polymerisation by compounding or during polymerisation. Antioxidants and UV stabilisers may, for example, be dissolved in the polyol during polymerisation. Lubricants and stabilisers may, however, also be added in the extruder process, for example in the second section of the screw.

The TPUs according to the invention may be used to produce mouldings, in particular to produce extrudates (for example films) and injection moulded articles. Moreover, the TPUs according to the invention may be used as sinterable powder for

producing the mouldings according to the invention in the form of sheet products and hollow articles.

The following Examples are intended to illustrate the invention in greater detail.

5

Examples

Production of TPUs and injection moulded sheets

10

The TPUs were produced continuously as follows:

15

Component B), which additionally also contains auxiliary substances (see table), chain extender C) and dibutyltin dilaurate were heated with stirring in a boiler to approx. 110°C and mixed intensively together with component A), which had been heated to approx. 110°C by means of heat exchangers, by a static mixer made by Sulzer (DN6 with 10 mixing elements and a shear rate of 500 s⁻¹) and then conveyed into the feed zone of a screw (ZSK 32). The complete mixture reacted in the extruder until conversion was complete and was then pelletised.

20

The resultant pellets were dried and several injection moulded sheets were then produced therefrom. Some of the injection moulded sheets were stored in a circulating air drying cabinet at 60°C and tested for the formation of a surface deposit. Others of the injection moulded sheets were stored at room temperature.

25

Formation of deposits is particularly recognisable from finger prints formed on the moulding. The samples were assessed qualitatively as no measurement method is known.

Test conditions

Rectangular injection moulded sheets (125 mm x 50 mm x 2 mm) were produced from the TPUs.

5

Qualitative assessment (increasing levels of deposits):
none<very slight<slight<distinct<severe<very severe.

	DBTL:	dibutyltin dilaurate
10	DE2020:	1,6-hexanediol-based polycarbonate diol with average molecular weight $\overline{M}_n = 2000$ g/mol
	PE 225B:	Polybutanediol adipate with average molecular weight $\overline{M}_n = 2250$ g/mol
	Therathane 2000®:	Polytetrahydrofuran diol with $\overline{M}_n = 2000$ g/mol (DuPont)
15	Therathane 1000®:	Polytetrahydrofuran diol with $\overline{M}_n = 1000$ g/mol (DuPont)
	Therathane 650®:	Polytetrahydrofuran diol with $\overline{M}_n = 650$ g/mol (DuPont)
	Therathane 250®:	Polytetrahydrofuran diol with $\overline{M}_n = 250$ g/mol (DuPont)
	Acclaim® 2220:	Polyether polyol with polyoxypropylene/polyoxyethylene units (with approx. 85% primary hydroxyl groups and an average molecular weight $\overline{M}_n$ of approx. 2000 g/mol, Lyondell)
20	HDI:	Hexamethylene diisocyanate
	Irganox® 1010:	Tetrakis[methylene-(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]methane (Ciba Geigy)
25	Stabaxol® P200:	Aromatic polycarbodiimide (Rhein-Chemie)
	1,4BDO:	1,4-butanediol
	1,6 HDO:	1,6-hexanediol.

Composition of TPUs

TPU	HDI moles / g	Polyol 1		Polyol 2		1,4BDO moles / g	1,6HDO moles / g
		moles / g		moles / g			
Comparison 1 ¹⁾	5.09 / 856	1.0 / 2000	DE 2020	0.43 / 967	PE 225 B	3.76 / 339	-
Comparison 2 ¹⁾	5.09 / 856	1.0 / 2000	DE 2020	0.43 / 967	PE 225 B	-	3.76 / 445
Comparison 3 ¹⁾	3.78 / 636	1.0 / 2250	PE 225B	-	-	-	2.85 / 337
Comparison 4 ¹⁾	5.39 / 908	1.0 / 2250	PE 225 B	0.43 / 964	Acclaim 2220	-	4.08 / 482
Comparison 5 ¹⁾	3.38 / 569	1.0 / 2000	Terathane 2000			-	2.45 / 290
Example 1 ¹⁾	3.25 / 545	1.0 / 1000	Terathane 1000	-	-	-	2.31 / 273
Example 2 ¹⁾	5.61 / 941	1.0 / 1000	Terathane 1000	-	-	-	4.72 / 557
Example 3 ²⁾	8.77 / 820	1.0 / 1250	PE 225 B	2.25 / 1250	Terathane 1000	-	5.71 / 375
Example 4 ²⁾	7.9 / 739	1.0 / 1250	PE 225 B	2.31 / 833	Terathane 650	-	4.76 / 312
Example 5 ²⁾	11.52 / 1077	1.0 / 1250	PE 225 B	6.0/833	Terathane 250	-	4.76 / 312

All TPUs were produced with addition of 40 ppm DBTL, relative to the introduced polyols.

1) These TPUs additionally contain 0.5 wt.% Irganox 1010, relative to TPU.

2) These TPUs additionally contain 0.5 wt.% Irganox 1010, relative to TPU, and 1 wt.% Stabaxol P 200, relative to PE 225 B.

Results

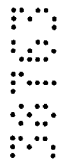
TPU	Formation of deposit on storage at 60°C after			
	7 days	14 days	28 days	28 days: removable by wiping with a dry cloth
Comparison 1	very severe	very severe	very severe	no
Comparison 2	none	none	none	-
Comparison 3	none	none	none	-
Comparison 4	none	none	none	-
Comparison 5	none	none	none	-
Example 1	none	none	none	-
Example 2	none	none	none	-
Example 3	none	none	none	-
Example 4	none	none	none	-
Example 5	none	none	none	-

TPU	Formation of deposit on storage at room temperature (20-25°C) after			
	1 month	2 months	3 months	3 months: removable by wiping with a dry cloth
Comparison 1	very severe	very severe	very severe	no
Comparison 2	severe	severe	severe	yes
Comparison 3	distinct	severe	severe	yes
Comparison 4	distinct	distinct	distinct	yes
Comparison 5	distinct	distinct	distinct	yes
Example 1	none	none	none	-
Example 2	none	none	none	-
Example 3	none	none	very slight	yes
Example 4	none	none	very slight	yes
Example 5	none	none	very slight	yes

- 12a -

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or step or group
5 of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgement or any form of suggestion that that prior art forms part of the
10 common general knowledge in Australia.



The claims defining the invention are as follows:

1. A thermoplastic moulding composition comprising thermoplastic polyurethane that is the product of a reaction of
- 5
- A) a diisocyanate reactant that contains
- A1) 100 to 60% of hexamethylene diisocyanate, and optionally
- 10 A2) 0 to 40% of at least one other aliphatic diisocyanate, the % being relative to the molar amount of A), and
- B) a polyol reactant that contains
- 15 B1) 100 to 30 percent relative to the weight of B) polytetramethylene glycol and
- B2) 0 to 70 percent relative to the weight of B) of at least one polyol having a number average molecular weight of 600 to 5000 g/mol that differs from said B1, and
- 20
- C) a chain extending reactant that contains
- C1) 80 to 100% relative to the weight of C, of 1,6-hexanediol,
- 25 C2) 0 to 20% relative to the weight of C, of at least one chain extender that differ from C1, said chain extender having a number average molecular weight of 60 to 500,
- 30 wherein the equivalence ratio of A to B is 1.5:1.0 to 10.0:1.0, and wherein NCO index is 95 to 105

with the provisos that (i) in the embodiments where the number average molecular weight of B1) is 600 to 1600 g/mol B1) is present in an amount of 40 to 100% relative to the weight of B), and B2) is present in an amount of 0 to 60 % relative to the weight of B), and that (ii) in the embodiments where the number average molecular weight of B1) is 200 to 590 g/mol, B1) is present in an amount of 30 to 70% relative to the weight of B), and B2) is present in an amount of 70 to 30 percent relative to the weight of B), and C2) is different from B1).

2. The composition of Claim 1 wherein reaction is catalyzed.
3. The composition of Claim 1 further comprising at least one additive selected from the group consisting of UV stabilizer, lubricant, antiblocking agent, inhibitor, hydrolytic stabilizer, heat stabilizer, discoloration stabilizer, flame retardant, dye, pigment, filler and reinforcing agent.
4. A moulded article comprising the composition of Claim 1.
5. A process for making a hollow article comprising sintering a powder comprising the composition of Claim 1.
6. Thermoplastic polyurethanes, molding compositions containing the same, and uses thereof substantially as hereinbefore described with reference to the Examples (excluding the Comparative Examples).

DATED this 7th day of July 2004

BAYER AKTIENGESELLSCHAFT

By its Patent Attorneys

DAVIES COLLISON CAVE

DAVIES COLLISON CAVE