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(74) Agent: **DILWORTH, Michael, P.**; Crompton Corpora-
tion, Benson Road, Middlebury, CT 06749 (US).

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(71) Applicant (for all designated States except US): **CHEM-
TURA CORPORATION** [US/US]; Benson Road, Mid-
dlebury, CT 06749 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ZHU, Zhenya**
[CN/US]; 3 Allison Lane, New Milford, CT 06776 (US).
ROSENBERG, Ronald, O. [US/US]; 781 Quarter Mile
Road, Orange, CT 06477 (US). **GAJEWSKI, Vincent,
J.** [US/US]; 44 Guinevere Ridge, Cheshire, CT 06410
(US). **NYBAKKEN, George** [US/US]; P.O. Box 1117,
Middlebury, CT 06762 (US).

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(54) Title: HIGH PERFORMANCE PARAPHENYLENE DIISOCYANATE BASED POLYURETHANES CURED WITH ALKY-
LATED 4,4'-METHYLENEDIANILINE

(57) Abstract: A polyurethane-urea is prepared by reacting a mixture of a p-phenylene diisocyanate terminated urethane prepoly-
mer, at least one plasticizer, and alkylated 4,4'-methylenedianiline chain extender.



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HIGH PERFORMANCE POLYURETHANES CURED WITH ALKYLATED 4,4'-METHYLENEDIANILINE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to castable polyurethane-urea compositions with high
5 temperature property retention and improved processing characteristics, including
reduced viscosity of prepolymers and longer pour life, as well as processes for the
production of such polyurethane-urea.

2. Background of the Art

Polyurethanes are well known as materials useful in highly demanding
10 applications. Typical advantages of polyurethanes include excellent load/bearing
properties and superior tear resistance. Property retention at elevated temperature is also
sought by users.

Segmented polyurethanes are two-phase polymers, consisting of alternating rigid
and flexible blocks, or so-called hard and soft segments. Soft segments are obtained by
15 reacting polyols with diisocyanates; the polyol moieties primarily contribute to the elastic
nature of the product. Hard segments, on the other hand, consist of the diisocyanate and
chain extender (usually an aromatic diamine or an aliphatic diol). They particularly
affect the modulus, hardness and tear strength, and determine the upper use temperature
by their ability to remain associated at elevated temperatures.

20 Aromatic diisocyanates are well known and are widely used in the preparation of
polyurethanes and polyurethane/ureas. These aromatic diisocyanates generally include

compositions such as 2,4-toluene diisocyanate and 2,6-toluene diisocyanate (TDI); 4,4'-methylene-bis-(phenyl isocyanate) (MDI); p-phenylene diisocyanate (PPDI); and the like.

In the preparation of polyurethanes and polyurethane-ureas, the aromatic diisocyanates are reacted with a long chain (high molecular weight) polyol to produce a prepolymer containing free isocyanate groups. This prepolymer may then be chain extended with a short chain (low molecular weight) polyol or an aromatic diamine to form a polyurethane or polyurethane-urea (known generically as polyurethane or urethane). Upon polymerization, a liquid mixture of prepolymer and chain extender (curative) increases steadily in viscosity until finally a high molecular weight solid is formed.

Among the aromatic diisocyanates, PPDI (p-phenylene diisocyanate) based polyurethanes have been well known as premium materials with superior properties [Advances in Urethane Science and Technology, Vol.13, p112, 1996]. High performance of PPDI material is attributed to the compact, regular and symmetric structure of PPDI, which forms well-defined hard segment domains after reacting with chain extenders. Typically, PPDI materials are good in dynamic properties and high temperature performance. They are particularly suitable for applications where load, speed, and extreme temperature requirements limit the use of other materials.

Numerous diamines, such as 4,4'-methylene bis (o-chloroaniline) (MOCA), are well known chain extenders for polyurethane elastomers. While diamines form good hard segments and provide good properties, they are usually associated with toxicity or processing difficulty. For example, MOCA is a suspect carcinogenic agent. Also, MOCA usually only works well with TDI based prepolymer. Further, MOCA cured TDI

material may not be good enough to meet challenging and demanding applications, such as applications in environments of 70°C or above. Load bearing and tear resistance properties of MOCA cured materials drop significantly as the temperature increases.

A different series of amine chain-extending agents for polyurethanes is alkylated methylenedianiline, either chlorinated or non-chlorinated. For example, 4,4'-methylene-
5 bis-(3-chloro-2, 6-diethylaniline) (MCDEA), is available as Lonzacure MCDEA (trademark of the Lonza Corporation). This curative is reportedly lower in toxicity but faster than MOCA to react with isocyanates [Th. Voelker et al. Journal Elastomers and Plastics, 20, 1988 and *ibid*, 30th Annual Polyurethane Technical/Marketing Conference,
10 October, 1986]. This curative reacts with isocyanate-terminated prepolymers to give materials with desirable properties, especially with PPDI to give exceptional performance at high temperature. However, the high reactivity of MCDEA with PPDI creates difficulty in cure processing.

Problems associated with the high reactivity of MCDEA with PPDI prepolymers
15 include the high viscosity and high melting point of the prepolymers. For example, the melting point of a representative PPDI/polycarbonate prepolymer is 70°C or above. The viscosity of this PPDI/polycarbonate prepolymer is 60 poise at 80°C. With such a high melting point and high viscosity, regular liquid casting has to be processed at $\geq 80^\circ\text{C}$. However, at that temperature, the high reactivity of MCDEA with the isocyanate groups
20 on the PPDI prepolymer makes pour life extremely short. Casting of many designed parts becomes impractical. There will be no time to mix the curative well with prepolymer, and no time to pour the mixture into molds properly.

In terms of applications, automotive and general industry sectors have been requiring materials performing at higher temperature. People have been developing materials, such as hydrogenated nitrile butadiene rubber (HNBR) and its derivatives to meet the demands, with improved heat resistance and mechanical strength. However, to further promote the mechanical properties and their retention at high temperature is always a challenge in modern needs of engineering materials [Rubber & Plastics News, October 20, 2003, p14]. Comparing PPDI urethane/urea materials cured with MCDEA to HNBR, the performance of the PPDI/MCDEA materials is much superior to that of HNBR. We have found that at 150°C, PPDI materials retain much higher tear strength, and much high elongation than HNBR does. PPDI materials are also more stable in hardness under heat and are higher in tensile strength.

A need exists for more easily processible PPDI urethane-urea materials that retain the excellent high-temperature properties.

15

SUMMARY OF THE INVENTION

20

A polyurethane-urea is provided herein. The polyurethane-urea is prepared by reacting a mixture of p-phenylene diisocyanate terminated urethane prepolymer and at least one plasticizer, and alkylated 4,4'-methylene dianiline chain extenders. The melting point and the viscosity of prepolymers are reduced significantly. Thereafter, the castings of the prepolymers with alkylated methylenedianiline become feasible at lower temperature. Materials become easier to mix together. The mixture becomes easier to fill into molds because of the prolonged pour life.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

Use of plasticizers in polyurethane prepolymers is known. However, the mechanical properties of the resulting elastomers are ordinarily impaired by incorporation of plasticizers. See, e.g.: Polyurethane Handbook, 2nd Ed., Gunter Oertel, editor, Hanser
5 Gardner Publications, Inc, p.250 (1994); and *VIBRATHANE® Castable Urethane Elastomers for Printing and Coating Rolls*, Product Bulletin, Uniroyal Chemical Company, page 17 (1979).

Surprisingly, it has been found that adding certain plasticizers into PPDI prepolymers not only improves the processability in curing with alkylated
10 methylenedianiline, but also retains the high performance of the resulting polymerized elastomers. Extent of the reduction of melting point and viscosity may vary depending on the nature and amount of the plasticizers added. Mechanical properties of MCDEA cured PPDI materials are exceptional even at temperatures as high as 150°C. In other words, plasticizers are used as effective processing aids to the PPDI prepolymers and
15 make the castings of PPDI urethane-urea feasible, resulting in heat resistant materials.

This invention relates to the use of certain plasticizers for PPDI urethane-urea materials. Processing temperature is lowered due to the reduction of viscosity and melting point of the prepolymers. Therefore, it becomes feasible for alkylated methylenedianiline type of amine curatives. For example, 4,4'-methylene-bis-(3-chloro-2, 6-diethylaniline)
20 (MCDEA) and 4,4'-methylene-bis-(2, 6-diethylaniline) (MDEA) were used as curing agents of polyurethane materials. Exceptional properties can be obtained from MCDEA cured plasticized prepolymers prepared from PPDI and polycarbonate and/or polyester

polyols; these properties are retained at high temperature after long term heat aging at high temperature.

Both relatively volatile plasticizer such as dibutyl phthalate (DBP) and non volatile ones such as polymeric plasticizers may be added into PPDI prepolymers at the level
5 from 5% to 40% by weight. Melting point of the plasticized prepolymers can be 20°C lower or more. The viscosity of the prepolymers can be reduced by half or more. Cast processing may be carried out at a temperature of 50 – 70°C, in order to get a longer pour life. The plasticizer is preferably inert, i.e., it preferably does not take part in the polymerization reaction.

10 The plasticized prepolymers cured with alkylated methylenedianiline, for example MCDEA, provide castable urethane articles with the desirable properties at high temperature and enhanced processing characteristics:

- 1) extended pour life (a slower rate of viscosity build-up after curative and prepolymer are mixed)
- 15 2) reduced viscosity of the prepolymer/curative mixture which facilitates the filling of the molds
- 3) high tensile strength of the elastomers at 150°C after aging at 150°C
- 4) high tear strength at 150°C after aging at 150°C
- 5) even higher elongation at 150°C after aging at 150°C vs. initial value
- 20 6) little change in hardness at 150°C

The urethane products described in this invention will find use in industrial applications that require toughness retention at very high temperature and extended

duration of time. Automobile parts, seal materials and down hole parts in oil fields are a few examples.

It has been surprisingly found that some plasticizers, for example, trimellitate type of plasticizers have a remarkable compatibility with PPDI urethane prepolymers. The boiling point of trimellitates can be high ($>500^{\circ}\text{C}$). They have a very low tendency of migrating from the urethane matrix to the surface, even when exposed at 150°C for long term. Plasticizers may serve as process aids and be retained in the cured materials. Depending on the amount of the plasticizer added, viscosity of PPDI prepolymers may be reduced to less than half with lowered melting point. These features are highly desirable to the liquid casting with alkylated methylenedianiline cures. Castings may be carried out at 60°C or lower to have manageable pour life. There will be no appreciable plasticizer evaporation during and after cure process. Therefore, they may also reduce the modulus and T_g of the cast elastomers and improve the performance at low temperature.

It has also been found that some plasticizers with relatively low boiling point, such as dibutyl phthalate (DBP), may serve as the processing aid. DBP has a boiling point of 192°C at 10 torr and 340°C at 1 atmosphere. DBP reduces the viscosity of PPDI prepolymers, and lets castings to be carried out at reduced temperature. DBP and other plasticizers with boiling point below 200°C at 10 torr may largely migrate out of the matrix and evaporate after post cure. In this way, the plasticizer will not alter the physical property of the cast materials.

Furthermore, it is surprisingly found that plasticized PPDI urethane-urea materials cured with alkylated methylenedianiline, e.g., MCDEA, retain remarkable properties at

elevated temperature, even after long term heat aging. Aged at 150°C for 6 weeks long, then tested at 150°C, parts retain > 50% tear strength, with little change in elongation and hardness compared to the original values tested at room temperature without aging. This is sharply distinguished from other urethane materials and rubber materials such as HNBR. This exceptional performance at high temperature is achieved by applying plasticizers to make the liquid casting process feasible.

PPDI is compact and symmetric in molecular structure. Alkylated methylenedianilines are the bulky and rigid compounds. Once these two compounds are incorporated with each other and into urethane materials, they form the hard segment that is hard to melt. Furthermore, the urea-containing hard segments with extra H-bonding sites facilitate aggregation and form well-defined hard domains, and promote phase separation. As is well known in the art, good urethane materials come from a good phase separation between hard and soft domains. Indeed, materials disclosed herein exhibit exceptional properties.

For applications at elevated temperature, polycarbonate (PC) and polyester backbone PPDI urethanes are used. In particular, the PPDI/PC has a unique combination of hydrolytic stability, solvent resistance and high temperature performance. Because of the tendency of thermal oxidation, urethanes with polyether backbone are not recommended for the use at high temperature.

To liquid cast the PPDI/carbonate or PPDI/ester prepolymers with alkylated methylenedianiline, up to 40% by weight of plasticizers are preferably added into the prepolymers first. Then the diamine curative is added with the molar ratio of isocyanate groups to amine groups generally at about 0.80 to 1.30, or expressing in another way,

80% to 130% of stoichiometry. The preferable ratio is 0.95 to 1.15, or 95% to 115% of stoichiometry.

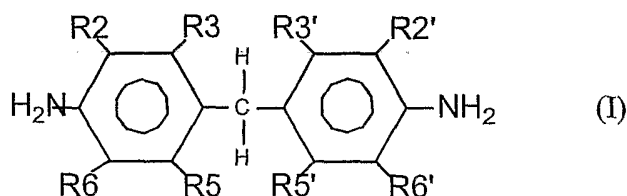
Processing of curing urethane prepolymers may be carried out at 20°C - 120 °C , preferably 40°C -100 °C , more preferably 50°C – 90°C, followed by cure/post cure at
5 100°C – 150°C for 16 – 24 hours.

Urethanes are tougher materials compared to other materials. However, property loss at elevated temperature is a common phenomenon. As indicated before, pursuing the property retention and the performance at high temperature is often the mission of the industry. Cured with alkylated methylenedianilines, PPDI based materials accomplish
10 this mission with surprising results, significantly outperforming the HNBR that is currently in the applications at elevated temperature. These novel urethane-ureas are expected to extend applications into new areas.

Suitable plasticizers may include aromatic esters such as phthalates, isophthalates, terephthalates, trimellitates, and benzoates; aliphatic esters such as dialkyl esters and
15 polymeric esters; hydrocarbons incorporating an aromatic moiety; and organic phosphates. Phthalates, trimellitates, and aliphatic esters are preferred. Plasticizers with boiling point at 10 torr above 250°C are preferred, as they will be slow to volatilize from the elastomer under sustained use at high temperature. More preferred are those with boiling point at 10 torr above 300°C.

20 Alternatively, plasticizers with boiling point below 200°C at 10 torr may be used and then deliberately volatilized from the elastomer before it is put into service. Suitable volatilization conditions include temperatures above 100°C, preferably under vacuum.

Suitable chain extenders (curatives) may include derivatives of 4,4'-methylene dianiline with one or more alkyl groups at the 2, 3, 5, or 6 ring positions, and optionally one or more halogen groups (fluorine, chlorine, bromine, iodine) at remaining 2, 3, 5, or 6 ring positions. Preferred are those derivatives with methyl, ethyl, propyl, or butyl groups at both the 2 and 6 position on each of the two rings (hence four alkyl groups total). More preferred are 4,4'-methylene-bis-(3-chloro-2, 6-diethylaniline) (MCDEA) and 4,4'-methylene-bis-(2, 6-diethylaniline) (MDEA). See Formula I below:



wherein R2, R2', R3, R3', R5, R5', R6, R6' are
H or alkyl groups or halogen groups

Optionally, in addition to the 4,4'-methylenedianiline chain extender, the reaction mixture can additionally include short or long chain diols, triols, or tetrols.

Suitable polyol soft segments for the prepolymer include those comprising carbonate and/or ester linkages, with molecular weight of 250 to 12,000. Examples include polycarbonate polyols derived from 1,6-hexanediol and dialkyl or diaryl carbonate monomers; polyester polyols derived from 1,4-butanediol and adipic acid monomers; and polycaprolactone polyols derived from diol and epsilon-caprolactone monomers.

The following non-limiting examples illustrate the preparation of the novel PPDI urethane/urea materials made from alkylated methylenedianiline, ex. MCDEA.

Properties of the samples will follow these examples.

5

EXAMPLE I

To 90 g of ADIPRENE® LFP 3940A (Crompton Corporation) was added 10g dibutyl phthalate (DBP) plasticizer (Eastman Chemicals). ADIPRENE® LFP 3940A is a PPDI terminated polycarbonate backbone prepolymer. This prepolymer/plasticizer mixture can be prepared in accordance with the procedure set forth in U.S. Patent No. 10 5,703,193, which is herein incorporated by reference, and which contains about 3.3% wt of available isocyanate groups and an unreacted PPDI monomer content of below about 0.1% by weight. The mixture was fully agitated and 13.5g molten MCDEA was added and mixed. This final mixture was poured into molds and cured/post cured at 127°C (260°F) for 16 hours. Tough parts were obtained after demolding after the curing cycle.

15

EXAMPLE II

To 90 g of ADIPRENE® LFP 3940A p-phenylene diisocyanate terminated polycarbonate backbone prepolymer was added 10g diisopropyl naphthalene, a plasticizer from RKS under the name Ruetasolv DI. This prepolymer/plasticizer contains about 20 3.0wt % of available isocyanate groups. The mixture was fully agitated and 13.5g molten MCDEA was added and mixed. This final mixture was poured into molds and cured/post cured at 127°C (260°F) for 16 hours. Tough parts were obtained after demolding after curing cycle.

EXAMPLE III

To 90 g of ADIPRENE® LFP 3940A p-phenylene diisocyanate terminated polycarbonate backbone prepolymer was added 10g triisononyl trimellitate (JAYFLEX-TINTM) that is a plasticizer from Exxon Mobil. This plasticizer has a boiling point higher than 300°C at 10 torr. This prepolymer/plasticizer contains about 3.0% by weight of available isocyanate groups. The mixture was fully agitated and 13.5g molten MCDEA was added and mixed. This final mixture was poured into molds and cured/post cured at 127°C (260°F) for 16 hours. Tough parts were obtained after demolding after curing cycle.

EXAMPLE IV

To 80 g of ADIPRENE® LFP 3940A was added 20g JAYFLEX TINTM. This prepolymer/plasticizer contains about 2.6% wt of available isocyanate groups. The mixture was fully agitated and 11.7g molten MCDEA was added and mixed. This final mixture was poured into molds and cured/post cured at 127°C (260°F) for 16 hours. Tough parts were obtained after demolding after curing cycle.

EXAMPLE V

To 80 g of ADIPRENE® LFP 3940A was added 20g Paraplex A-8200, a polymeric ester type plasticizer from C.P.HALL. This prepolymer/plasticizer contains about 2.6wt% of available isocyanate groups. The mixture was fully agitated and 11.7g molten MCDEA was added and mixed. This final mixture was poured into molds and

" cured/post cured at 127°C (260°F) for 16 hours. Tough parts were obtained after demolding after curing cycle.

EXAMPLE VI

5 To 90 g of ADIPRENE® LFP 1950A (a PPDI terminated polyester prepolymer having a low free PPDI content, available from Crompton Corporation) was added 10g dibutyl phthalate (DBP). This prepolymer/plasticizer contains about 2.9% wt of available isocyanate groups. The mixture was fully agitated and 13.0g molten MCDEA was added and mixed. This final mixture was poured into molds and cured/post cured at 127°C
10 (260°F) for 16 hours. Tough parts were obtained after demolding after curing cycle.

The following comparative examples do not demonstrate the invention.

COMPARATIVE EXAMPLE A

This is a demonstration of failed hot liquid casting of ADIPRENE® LFP 3940A,
15 using MCDEA without adding the plasticizer to reduce viscosity. Casting process has to be carried out at the temperature at least 80°C to have the prepolymer fully melted.

To 14.8 g of molten MCDEA was added 100 g of ADIPRENE® LFP 3940A at 80°C. Without using the plasticizer, this prepolymer contains about 3.3wt % of available isocyanate groups and is very viscous. The mixture was agitated. However, pour life
20 was too short to pour the mixture into molds. Casting was abandoned.

COMPARATIVE EXAMPLE B

This is a demonstration of a hot liquid casting of ADIPRENE® LFP 1950A, without adding plasticizer. The casting process is carried out at 65°C using MCDEA as the curative. Viscosity of the prepolymer is high at that temperature so that the casting is
5 difficult.

To 14.4 g of molten MCDEA was added 100 g of ADIPRENE® LFP 1950A at 65°C. Without using the plasticizer, this prepolymer contains about 3.2wt % of available isocyanate groups and is very viscous. The mixture was agitated and was poured into molds. Due to the high viscosity of the mixture during process, after demolding after
10 curing cycle, parts were not as even comparing to that from the castings with adding plasticizers.

COMPARATIVE EXAMPLE C

This sample is a typical hot liquid casting of a conventional MDI prepolymer with
15 diol. Parts made from this casting are used as the comparison to the amine cured PPDI materials as described in the previous examples for aging and testing.

To 8.0g of 1,4-butanediol was added 100 g of VIBRATHANE® 8522 prepolymer (a polyester based MDI terminated liquid urethane prepolymer, available from Crompton Corporation) at 90°C. This prepolymer contains about 7.7% wt of available isocyanate
20 groups and is prepared from polyester glycol and MDI. The mixture was fully agitated and then was poured into molds and cured/post cured at 100°C (212°F) for 16 hours. Cured parts were obtained after demolding after curing cycle. These parts were heat aged

and tested and compared to the alkylated methylenedianiline cured parts of PPDI prepolymers.

COMPARATIVE EXAMPLE D

5 This sample is a typical hot liquid casting of TDI prepolymer with MOCA. Parts made from this sample are used as the comparison to the amine cured PPDI materials described in the previous examples in aging and testing.

To 10.1g of MOCA was added 100 g of ADIPRENE® LF1800A (a TDI terminated polyester prepolymer having a low free TDI content and low viscosity,
10 available from Crompton Corporation) at 90°C. This prepolymer contains about 3.2% wt of available isocyanate groups and is prepared from polyester glycol and TDI. The mixture was fully agitated and then was poured into molds and cured/post cured at 100°C (212°F) for 16 hours. Cured parts were obtained after demolding after curing cycle. Cast parts were heat aged and tested and compared to the alkylated methylenedianiline cured
15 parts of PPDI prepolymers.

Representative data of the improvement of cast processing via plasticizer are given in Table 1.

TABLE 1
Processing characteristics of plasticized PPDI prepolymers with MCDEA

		<u>LFP3940A</u>		<u>LFP1950A</u>	
		no plast. 20% TINTM		no plast. 10% DBP	
25	Viscosity at 80°C, poise	60	22	18	10
	Pour life, minute (prepolymer 65°C, MCDEA 95°C)	---	1.5	1.3	1.5

The data above show that at 10-20% plasticizer level, viscosity of PPDI prepolymers has been significantly reduced. Especially for PPDI/polycarbonate prepolymer (LFP3940A), it is not feasible to do the regular liquid casting without process aid.

Representative data of the retention of plasticizers in the cast PPDI urethane/urea materials are listed in Table 2.

TABLE 2
Weight retention of cast PPDI urethane-ureas with low volatile and relatively high volatile plasticizers

	<u>150°C/1 wk</u>	<u>150°C/2 wk</u>	<u>150°C/3 wk</u>	<u>150°C/6 wk</u>
LFP3940A/10%TINTM/MCDEA	99.1%	98.1%	98.3%	96.9%
LFP3940A/10%DBP/MCDEA	91.2%	90.9%	---	---

Triisononyl trimellitate (TINTM) plasticizer has relatively low volatility (i.e., a boiling point of above about 250°C at 10 torr) and is highly compatible with PPDI urethane/urea. It serves as both a processing aid and also is well retained in the cast parts.

Dibutyl phthalate (DBP) plasticizer has a relatively high volatility (i.e., a boiling point of below about 200°C at 10 torr). It serves as a processing aid but will evaporate after the cast part is exposed to high temperature over a period of time. As shown in the table above, DBP basically left the elastomer after heated at 150°C for a week.

Physical property retention of novel PPDI urethane/urea materials after heat aging is demonstrated in Table 3.

TABLE 3

Property retention of novel PPDI urethane-urea materials and
the comparison with conventional urethane materials and HNBR

		<u>LFP3940A/MCDEA</u> 15%TINTM	<u>LFP1950A/MCDEA</u> 10% DBP	<u>8522/BDO</u>	<u>LF1800/MOCA</u>	<u>HNBR</u>
5	Tested at RT, un-aged					
	100% modulus, psi	1210	1060	1110	700	2030
10	300% modulus, psi	2500	1630	2920	1400	-----
	Tensile, psi	6200	7330	5900	7100	2830
	Elongation, %	460	550	390	600	210
	Break energy, 10 ³ psi (tensile X elongation)	2852	4032	2301	4260	594
15	Split tear, pli	155	160	95	125	25
	Tested at 150°C, after aged at 150°C/3 wks					
	100% modulus, psi	900	820	----	220	----
20	300% modulus, psi	1020	880	----	----	----
	Tensile, psi	1480	1230	130	240	1210
	Elongation, %	900	850	90	220	20
	Break energy, 10 ³ psi (tensile X elongation)	1332	1046	12	53	24
25	Split tear, pli	105	145	<5	<5	<5
	Tested at 150°C, after aged at 150°C/6 wks					
	100% modulus, psi	790	700	N/A	N/A	*
30	300% modulus, psi	930	800	N/A	N/A	*
	Tensile, psi	1040	890	N/A	N/A	*
	Elongation, %	560	540	N/A	N/A	*
	Break energy, 10 ³ psi (tensile X elongation)	582	481			
35	Split tear, pli	90	85	N/A	N/A	*

* HNBR sample is too brittle to run the test at 150°C after aged at 150°C for 6 weeks.

Table 3 above strongly evidences that novel plasticized PPDI urethane-urea
materials are much superior over the HNBR and conventional urethane materials in high
temperature performance:

1. Before heat aging, break energy (approximated as tensile times elongation) and tear strength of plasticized PPDI urethane/ureas are 3 - 6 times higher than that of HNBR.

2. After being aged at 150°C for 3 weeks and tested at 150°C, HNBR lost elasticity. While conventional MDI and TDI materials are tough and comparable to PPDI before the aging, they significantly lost tensile strength and modulus after heat aging. PPDI urethane/urea becomes more than 20 times higher than HNBR and others in break energy. The gap between tear strength is increased as well.

3. After aged at 150°C for 6 weeks, HNBR had become so brittle that no testing could be run at 150°C, while PPDI urethane/ureas still retain respectable physical strength.

Hardness retention of novel plasticized PPDI urethane/urea materials after heat aging is demonstrated in Table 4.

TABLE 4
Hardness retention of novel plasticized PPDI urethane-urea materials and the comparison with HNBR

	<u>LFP3940A/MCDEA</u> 10% DBP	<u>LFP1950A/MCDEA</u> 10% DBP	<u>HNBR</u>
At RT, initial hardness	93A	92A	90A
At RT, after 150°C/3 weeks	92A	91A	96A
At 150°C, after 150°C/3 weeks	92A	90A	93A

Novel plasticized PPDI urethane-ureas have little change in hardness after being aged at 150°C. HNBR is hardened and becomes brittle.

Effect of plasticizer on the toughness of PPDI urethane-urea vs. other urethane is compared in Table 5.

TABLE 5

Effect of plasticizer on toughness retention of novel PPDI urethane-
urea and the comparison with conventional TDI material

5		<u>LFP1950A/MCDEA</u>		<u>Vibrathane6007/TMP-TIPA*</u>	
		no plast.	10% DBP	no plast.	10% Benzoflex**
10	100% modulus, psi	1260	1060	310	220
	300% modulus, psi	2050	1630	830	560
	Tensile, psi	8210	7330	3800	2500
	Elongation, %	490	550	400	450
	Break energy, 10 ³ psi (tensile X elongation)	4023	4032	1520	1125
	Split tear, pli	165	160	14	11
15					

*VIBRATHANE® 6007 is a TDI terminated polyester prepolymer with 4.2% NCO. TMP is trimethylolpropane. TIPA is triisopropanolamine. TMP-TIPA is at 3/1 ratio. Data from *VIBRATHANE® Castable Urethane Elastomers for Printing and Coating Rolls*, Product Bulletin, Uniroyal Chemical Company, page 17 (1979).

20 ** Benzoflex 9-88 SG is a plasticizer named for dipropylene glycol dibenzoate.

Plasticized PPDI urethane-urea has little change in break energy and tear strength, while conventional TDI material retains only about 75% of the original strength after using 10% plasticizer.

25 While the above description includes many specifics, these specifics should not be construed as limitations on the scope of the inventions, but merely as exemplifications of preferred embodiments thereof. Those skilled in the art will envision many other possibilities within the scope and spirit of the invention as defined by the claims appended hereto.

30

WHAT IS CLAIMED IS:

1. A polyurethane-urea prepared by reacting a mixture of a p-phenylene diisocyanate-terminated urethane prepolymer, at least one plasticizer, and alkylated 4,4'-methylenedianiline chain extender.

5

2. The polyurethane-urea of Claim 1 in which the plasticizer is selected from the group consisting of phthalates, isophthalates, terephthalates, trimellitates, benzoates, dialkyl esters, polymeric esters, hydrocarbons incorporating an aromatic moiety, organic phosphates and combinations thereof.

10

3. The polyurethane-urea of Claim 2 in which the alkylated 4,4'-methylenedianiline chain extender is selected from the group consisting of 4,4'-methylenedianiline possessing methyl, ethyl, propyl, or butyl groups at the 2 and 6 positions on each of the two rings.

15

4. The polyurethane-urea of Claim 2 in which the alkylated 4,4'-methylenedianiline chain extender includes at least one compound selected from the group consisting of 4,4'-methylene-bis-(3-chloro-2, 6-diethylaniline) and 4,4'-methylene-bis-(2, 6-diethylaniline).

20

5. The polyurethane-urea of Claim 2 in which the alkylated 4,4'-methylenedianiline chain extender comprises 4,4'-methylene-bis-(3-chloro-2, 6-diethylaniline).

6. The polyurethane-urea of Claim 2 in which the p-phenylene diisocyanate terminated urethane prepolymer comprises p-phenylene diisocyanate and a polycarbonate moiety and/or a polyester moiety.

5

7. The polyurethane-urea of Claim 2 in which the plasticizer has a boiling point higher than 300°C at 10 torr.

8. The polyurethane-urea of Claim 2 in which the plasticizer has a boiling point lower than 200°C at 10 torr and in which more than half of the plasticizer has been evaporated from the elastomer at a temperature of 100°C or higher, subsequent to the formation of the elastomer.

9. The polyurethane-urea of Claim 1 wherein the polyurethane urea molecular structure includes one or more alkyl groups on chlorinated phenyl rings.

15

10. The polyurethane-urea of Claim 1 wherein the polyurethane urea molecular structure includes one or more alkyl groups on phenyl rings which are not chlorinated.

20

11. The polyurethane-urea of Claim 1 wherein the molar ratio of isocyanate groups on p-phenylene diisocyanate-terminated prepolymer to amine groups on alkylated 4,4'-methylenedianiline chain extender is from about 0.80 to about 1.30.

12. The polyurethane-urea of Claim 1 wherein the molar ratio of isocyanate groups on the p-phenylene diisocyanate to amine groups on the alkylated 4,4'-methylenedianiline chain extender is from about 0.95 to about 1.15.

5

13. The polyurethane-urea of Claim 1 wherein the plasticizer possesses a boiling point above 250°C at 10 torr.

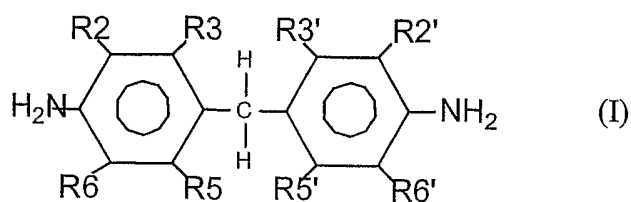
14. The polyurethane-urea of Claim 1 wherein the plasticizer possesses a
10 boiling point below 200°C at 10 torr.

15. The polyurethane-urea of Claim 1 wherein the plasticizer is used at the range of from about 5 % to about 40% by weight based on the cured polyurethane elastomer.

15

16. The polyurethane-urea of Claim 1 wherein the plasticizer is preferably used at the range of from about 10% to about 30% by weight based on the cured polyurethane elastomer.

20 17. The polyurethane urea of Claim 1 wherein the chain extender has the molecular formula (1) below:



wherein R2, R2', R3, R3', R5, R5', R6, R6' are
H or alkyl groups or halogen groups

wherein at least one of R2, R2', R3, R3', R5, R5', R6 and R6' is an alkyl group and the
remaining are independently hydrogen, alkyl or halogen.

5 18. The polyurethane-urea of Claim 17 wherein the alkyl group is methyl,
ethyl, propyl or butyl.

19. The polyurethane-urea of Claim 17 wherein at least one of R2, R2', R3,
R3', R5, R5', R6 and R6' is chlorine.

10

20. The polyurethane-urea of Claim 17 wherein all of said R2, R2', R3, R3',
R5, R5', R6 and R6' are alkyl groups.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2005/016511

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/10 C08G18/76 C08G18/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	GB 2 336 847 A (* SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V) 3 November 1999 (1999-11-03) page 2, line 30 - page 2, line 34 page 8, line 8 - page 8, line 33 page 11, line 12 - page 11, line 25 claims 1,11,12	1-20

A	US 5 907 014 A (QUINT ET AL) 25 May 1999 (1999-05-25) column 1, line 51 - column 1, line 65 column 3, line 16 - column 3, line 22 column 4, line 3 - column 4, line 35 column 4, line 48 - column 4, line 56 column 5, line 29 - column 5, line 36 figures 1-5 claims 1,5	1-20

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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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
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- *&* document member of the same patent family

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Heidenhain, R

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2005/016511

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 046 297 A (ROSENBERG ET AL) 4 April 2000 (2000-04-04) column 3, line 2 - column 3, line 28 column 3, line 57 - column 3, line 59 claim 1 -----	1-20
A	EP 0 387 894 A (LONZA AG) 19 September 1990 (1990-09-19) page 2, line 25 - page 2, line 50 tables 1-3 claim 1 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/016511

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2336847	A	03-11-1999	NONE
US 5907014	A	25-05-1999	NONE
US 6046297	A	04-04-2000	AT 153351 T 15-06-1997
		AU 5613494 A 04-07-1994	
		CA 2150386 A1 23-06-1994	
		DE 69310927 D1 26-06-1997	
		DE 69310927 T2 09-10-1997	
		EP 0672075 A1 20-09-1995	
		FI 952744 A 05-06-1995	
		FI 20011153 A 01-06-2001	
		JP 2689376 B2 10-12-1997	
		JP 7509274 T 12-10-1995	
		KR 275076 B1 15-12-2000	
		WO 9413722 A1 23-06-1994	
EP 0387894	A	19-09-1990	AT 106910 T 15-06-1994
		CA 2011712 A1 17-09-1990	
		CZ 9000656 A3 18-01-1995	
		DD 292005 A5 18-07-1991	
		DE 59005982 D1 14-07-1994	
		DK 387894 T3 04-07-1994	
		EP 0387894 A2 19-09-1990	
		ES 2055198 T3 16-08-1994	
		FI 95718 B 30-11-1995	
		HU 53382 A2 28-10-1990	
		IE 65289 B1 18-10-1995	
		JP 2281022 A 16-11-1990	
		MX 171741 B 11-11-1993	
		SK 65690 A3 04-02-1998	
		RU 2071484 C1 10-01-1997	
		US 5026815 A 25-06-1991	
		YU 32590 A1 31-10-1991	