



(51) International Patent Classification:

C08G 18/00 (2006.01) *C08G 18/58* (2006.01)
C08G 18/22 (2006.01) *C08G 18/79* (2006.01)
C08G 18/38 (2006.01) *C08L 75/00* (2006.01)
C08G 18/48 (2006.01) *C08G 59/40* (2006.01)

(21) International Application Number:

PCT/EP2012/074048

(22) International Filing Date:

30 November 2012 (30.11.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

11195897.1 28 December 2011 (28.12.2011) EP

(71) Applicant: HUNTSMAN INTERNATIONAL LLC
[US/US]; 500 Huntsman Way, Salt Lake City, Utah 84108
(US).

(72) Inventors: **ESBELIN, Christian**; Rue Artan 68, B-1030
Schaerbeek (BE). **VERBEKE, Hugo**; Leerlooierijstraat
17/210, B-3000 Leuven (BE). **VERBEKE, Hans Gode-
lieve Guido**; Langebeekstraat 24, B-3210 Lubbeek (BE).

(74) Agents: VAN DEN BROECK, Kristel et al; Everslaan
45, B-3078 Everberg (BE).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))



(54) Title: CURABLE COMPOSITION COMPRISING A POLYISOCYANATE COMPOSITION

(57) Abstract: Stable polyisocyanate composition comprising a compound comprising a group having the structure -CO-NH-CO- in such an amount that the ratio of the number of -CO-NH- CO- groups to the number of isocyanate groups is at most equal to 1. Curable composition comprising this polyisocyanate composition, lithium halide, urea and an epoxy resin.

CURABLE COMPOSITION COMPRISING A POLYISOCYANATE COMPOSITION

The present invention relates to a stable polyisocyanate composition, to a process for making such a composition, to a curable composition wherein the stable polyisocyanate composition according to the present invention is used, to a process for making such curable composition, to a polyisocyanurate material made or obtainable from such curable composition and to a process for making such polyisocyanurate materials.

Recently a curable composition has been proposed which comprises a polyisocyanate, a lithium halide, a urea compound and an epoxy resin; see PCT/EP2010/054492.

The use of lithium chloride and compounds comprising urea groups has been disclosed by Sheth, Aneja and Wilkes in Polymer 45 (2004) 5979-5984. They studied the influence of the extent of hydrogen bonding in mediating the long-range connectivity and percolation of the hard segment phase in model tri-segment oligomeric polyurethanes using LiCl as a molecular probe.

In US 5086150 an isocyanate-terminated prepolymer is reacted with a diamine in the presence of a rather high amount of LiCl to prepare an elastomer solution which is stable for at least two days. At the beginning of the reaction the number of moles of lithium chloride per isocyanate equivalent is rather high; the lithium chloride is used to act as a solubilizer. At the beginning of the reaction, the composition is not stable and does not contain urea and at the end of the reaction it is an elastomer and not an isocyanate composition anymore. The product obtained is an elastomer solution used for making threads and films.

The polyisocyanate composition according to the present invention is very suitable to make a curable composition together with epoxy compounds.

The use of isocyanates and epoxides together with LiCl has been disclosed in Russian Chemical Reviews 52(6) 1983, 576-593. The reaction is influenced by the nature of the

catalyst. In the presence of metal halides an activated complex is formed which ultimately gives an oxazolidone. One of the side reactions is the formation of isocyanurate rings which decompose to oxazolidone on treatment with epoxides. Further it has been disclosed therein that epoxides are capable of cleaving urea linkages with
5 formation of oxazolidones.

US 4658007 discloses a process for preparing oxazolidone containing polymer using organoantimony iodide catalyst by reacting a polyisocyanate and a polyepoxide.

US 5326833 discloses a composition comprising a polyisocyanate, an epoxide and a catalyst consisting of a solution of an alkali halide, like LiCl, in a polyoxyalkylenic
10 compound. These compositions are able to gel rapidly between 0 °C and 70 °C.

Juan et al discuss in the Journal of East China University of Science and Technology Vol. 32, No 11, 2006, 1293-1294 the influence of LiCl on the morphology structure and properties of polyurethane-urea. It shows that the viscosity of polyurethane urea solutions first decreases and subsequently increases. The polyurethane urea was made by reacting
15 polyepoxypropane glycol and isophorone diisocyanate with excess polyisocyanate.

In US 3517039 acylated urea polyisocyanates are made by reacting an organic diisocyanate with an organic monocarboxylic acid. These polyisocyanates are used in the preparation of polyurethanes, especially when small amounts of branching are desirable.
20

In US 3970600 stable solutions of isocyanurate-polyisocyanates containing amide and/or acylurea groups have been described. They avoid deposition of fine or coarse crystalline solids in polyisocyanates comprising isocyanurate groups. First a polyisocyanate is reacted with polybasic carboxylic acid to prepare a polyisocyanate with amide and/or
25 - substituted - acylurea groups. Then this polyisocyanate is trimerized to form an isocyanurate-polyisocyanate and this conversion is stopped by adding acid.

In JP 2-1 10123 an aliphatic diisocyanate is trimerized to prepare polyisocyanates which have an isocyanurate structure using a catalyst and a deactivating agent once the desired
30 degree of conversion has been attained. The deactivating agent has the structure -CO-NH₂ or -SO-NH₂ and may be urea, methyl urea, 1,1-dimethyl urea, phenyl

carbamate, ethylcarbamate or butylcarbamate. Subsequently deactivated catalyst, excess diisocyanate and solvent, if used, are eliminated. By using this deactivating agent the polyisocyanate comprising polyisocyanurate structure shows a lower degree of discolouration.

5

WO 2008/068198 and US 2010/0022707 disclose a process for preparing an oligomerized polyisocyanate using a catalyst wherein a deactivator is used once the desired conversion has been obtained followed by removal of the polyisocyanate which was not converted. The deactivator may be selected from urea and urea containing
10 compounds, amongst others.

15

EP 585835 discloses a process for preparing isocyanurate and urethane group containing polyisocyanate mixtures by partially cyclizing diisocyanates in the presence of a trimerization catalyst, deactivating the trimerization catalyst when the desired conversion
15 is achieved, and subsequently reacting the resulting isocyanurate group containing polyisocyanate with hydroxyl compounds and then separating off the monomeric diisocyanate.

20

Further disclosures related to partially trimerized polyisocyanate compositions using
20 different methods to stop the trimerization are: EP 447093, US 4284730, US 4537961, US 4697014, US 4743627, US 5124370, US 5221743 and US 7553963. None of these disclosures reveal the present invention or point into its direction.

25

In US 7071353 reaction products of isocyanates and carboxylic acids are disclosed. First
25 amides are formed which then form acylureas by reaction with further isocyanate groups. US 4371544 discloses the reaction product of phenylisocyanate and 1-ethyl, 1-methyl urea.

30

Thermally activated PIR catalysis has been disclosed in US 6127308.

Urea and amides have been disclosed as blocking agents in US 5817732.

US 4302351 discloses isocyanurates and acid hydrogen containing blocking agents.

In GB 1463809 mono-substituted ureas and in US 4330656 N-methylurea have been used
5 as catalyst.

Choline type catalysts have been disclosed in EP 1085030, US 6613863 and US 6875243.

Surprisingly we have found a polyisocyanate composition comprising a compound
10 having a -CO-NH-CO- group and which is stable and liquid at 20 °C and ambient
pressure and which may be used in making a curable composition which is useful to
make a polyisocyanurate material at elevated temperature and which has a long pot-life at
20 °C and ambient pressure.

Therefore the present invention is concerned with a stable polyisocyanate composition
15 comprising a compound having a -CO-NH-CO- group which is suitable for making a
curable composition. The compound having a -CO-NH-CO- group is an "imide-like"
structure comprising 2 carbonyl groups attached to a -NH- group.

The compound having a -CO-NH-CO- group is present in such an amount that the ratio
of -CO-NH-CO- groups over the number of isocyanate groups is at most 1, preferably at
20 most 0.01, more preferably at most 0.0015.

According to an embodiment the compound having a -CO-NH-CO- group may be added
to a polyisocyanate composition in order to create the stable polyisocyanate composition
according to the invention.

According to an embodiment the compound having a -CO-NH-CO- group may be a
25 compound having an acylurea group having the structure -CO-NH-CO-NH-. Said
compound having an acylurea group may be the reaction product of a polyisocyanate and
a compound comprising a carboxamide group having the structure -CO-NH₂. However
the compounds having an acylurea group according to the invention are not limited to
reaction products of a compound comprising a carboxamide and a polyisocyanate.

30 Further the present invention is concerned with a process for preparing the above stable
polyisocyanate composition which process comprises adding and mixing a compound

comprising a -CO-NH-CO- group to a polyisocyanate composition. The final concentration of the compound comprising a -CO-NH-CO- group in the stable polyisocyanate composition is such that the ratio of -CO-NH-CO- groups over the number of isocyanate groups is at most 1, preferably at most 0.01, more preferably at most 0.0015.

In case the compound having a -CO-NH-CO- group is a compound having an acylurea group having the structure -CO-NH-CO-NH- and which is also a reaction product of a polyisocyanate and a compound comprising a carboxamide group having the structure -CO-NH₂, the compound having the carboxamide group having the structure -CO-NH₂ may be added (mixed) to the polyisocyanate composition and allowing the mixture to react, wherein the amount of the compound comprising the carboxamide group is such that after the reaction has been conducted the ratio of acylurea groups over the number of isocyanate groups is at most 1, preferably at most 0.01, more preferably at most 0.0015.

Still further the present invention is related to the use of the stable polyisocyanate composition according to the present invention for improving the pot-life of a curable polyisocyanate composition, to such curable polyisocyanate composition, to a process to make such curable polyisocyanate composition, to a polyisocyanurate material made from such curable polyisocyanate composition and to a process to make such polyisocyanurate material.

In the context of the present invention the following terms have the following meaning:

1) isocyanate index or NCO index or index:
the ratio of NCO-groups over isocyanate-reactive hydrogen atoms present in a formulation, given as a percentage :

$$\frac{[\text{NCOI} \times 100]}{[\text{active hydrogen}]} \quad (\%).$$

[active hydrogen]

In other words the NCO-index expresses the percentage of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically

required for reacting with the amount of isocyanate-reactive hydrogen used in a formulation.

5 It should be observed that the isocyanate index as used herein is considered from the point of view of the actual polymerisation process preparing the material involving the isocyanate ingredient and the isocyanate-reactive ingredients. Any isocyanate groups consumed in a preliminary step to produce modified polyisocyanates (including such isocyanate-derivatives referred to in the art as prepolymers) or any active hydrogens consumed in a preliminary step (e.g. 10 reacted with isocyanate to produce modified polyols or polyamines) are not taken into account in the calculation of the isocyanate index. Only the free isocyanate groups and the free isocyanate-reactive hydrogens (including those of water, if used) present at the actual polymerisation stage are taken into account.

15 2) The expression "isocyanate-reactive hydrogen atoms" as used herein for the purpose of calculating the isocyanate index refers to the total of active hydrogen atoms in hydroxyl and amine groups present in the reactive compositions; this means that for the purpose of calculating the isocyanate index at the actual polymerisation process one hydroxyl group is considered to comprise one reactive 20 hydrogen, one primary amine group is considered to comprise one reactive hydrogen and one water molecule is considered to comprise two active hydrogens.

25 3) Reaction system : a combination of components wherein the polyisocyanates are kept in one or more containers separate from the isocyanate-reactive components.

30 4) The term "average nominal hydroxyl functionality" (or in short "functionality") is used herein to indicate the number average functionality (number of hydroxyl groups per molecule) of the polyol or polyol composition on the assumption that this is the number average functionality (number of active hydrogen atoms per molecule) of the initiator(s) used in their preparation although in practice it will often be somewhat less because of some terminal unsaturation.

- 5) The word "average" refers to number average unless indicated otherwise.
- 6) "Liquid" means having a viscosity of less than 10 Pa.s measured according to
5 ASTM D445-1 1a at 20 °C.
- 7) "Stable polyisocyanate composition" is a polyisocyanate composition according
to the present invention which does not change more than 10 % from its initial
NCO value when kept at 80 °C and ambient pressure for 10 minutes, the NCO
10 value being determined at ambient conditions. As an example: a polyisocyanate
composition having an NCO value of 25 % by weight should have an NCO value
within the range 22.5-27.5 % by weight after having been kept at 80 °C for 10
minutes in order to be regarded as stable, both NCO values being determined at
ambient conditions

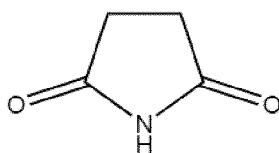
15

The compounds having a -CO-NH-CO- group according to the invention corresponds to
the formula $R_1\text{-CO-NH-CO-R}_2$ wherein R_1 and R_2 each independently from each other
are selected from 1) hydrogen (-H), 2) $\text{-NR}_3\text{R}_4$, 3) hydrocarbyl having 1-100 carbon
atoms and optionally comprising hydroxy, ether, halogen, carboxyl, oxygen, isocyanate
20 and/or amine groups, wherein R_3 and R_4 independently from each other, are selected
from hydrogen, hydroxy, halogen and hydrocarbyl groups which hydrocarbyl groups
have 1-20 carbon atoms and optionally comprise hydroxy, ether, halogen, carboxyl,
isocyanate and/or amine groups, wherein R_1 and R_2 may be linked to each other
essentially forming a ring structure including the -CO-NH-CO- group, and wherein the
25 hydrocarbyl groups in the compounds corresponding to the formula $R_1\text{-CO-NH-CO-R}_2$
may be a combination of linear, branched, saturated, unsaturated, cyclic and/or non-
cyclic aliphatic, aromatic or araliphatic hydrocarbyls and mixtures of such compounds. .
Preferably the compound having a -CO-NH-CO- group according to the invention has a
molecular weight of at most 1500.

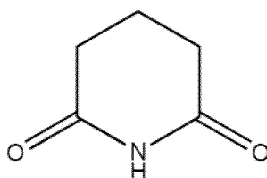
30

In case R_1 and R_2 are linked to the $-\text{CO}-\text{NH}-\text{CO}-$ group such that a ring structure is formed in the compound $R_1-\text{CO}-\text{NH}-\text{CO}-R_2$ then R_1 and R_2 together with the $-\text{CO}-\text{NH}-\text{CO}-$ group may form a 4 to 12 membered ringstructure (in case of a 4 membered ring structure there is no R_2 involved). Examples of suitable compounds

5 $R_1-\text{CO}-\text{NH}-\text{CO}-R_2$ having a ringstructure are:

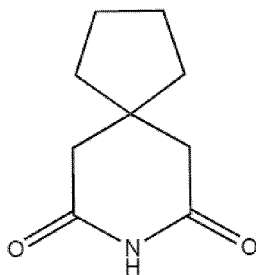


Pyrrolidine-2,5-dione (succinimide) (1)



10

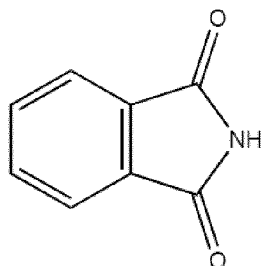
Piperidine-2,6-dione (glutarimide) (2)



15 8-azaspiro[4.5]decane-7,9-dione (3)
(Tetramethylene glutarimide)

The ringstructure may comprise 1 or more unsaturations and/or optionally 1 or more aromatic rings and/or optionally rings with heteroatoms. Examples of suitable compounds $R_1-\text{CO}-\text{NH}-\text{CO}-R_2$ wherein R_1 and R_2 together with the $-\text{CO}-\text{NH}-\text{CO}-$ group

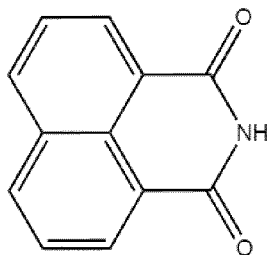
may form a 4 to 12 membered ring structure and comprise unsaturations, aromatic rings and/or heteroatoms are given below.



5

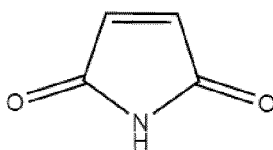
Iso indoline-1,3-dione(Phthalimide)

(4)



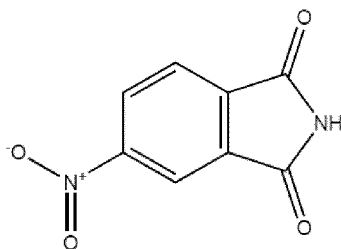
1 *H*-benzo[ife]isoquinoline-1,3(2*H*)-dione (5)
(Naphthalimide)

10

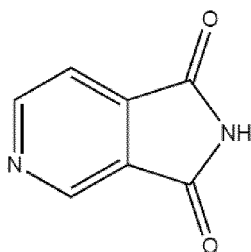


2,5 pyrrole dione (Maleimide)

(6)



5-nitro isoindoline-1,3-dione (7)
(4 nitro phthalimide)



1H-pyrrolo[3,4-c]pyridine-1,3(2 H)-dione (8)
(3,4 pyridine dicarboxamide)

5

According to an embodiment, the compound having a -CO-NH-CO- group may be a
 10 compound having an acylurea group having the structure -CO-NH-CO-NH-. Said
 compound having an acylurea group according to the invention corresponds to the
 formula $R_6\text{-CO-NH-CO-NH-R}_7$ and may be the reaction product of a polyisocyanate
 comprising reactive NCO groups and corresponding to the formula $R_7\text{-NCO}$ and a
 15 compound comprising a carboxamide group having the structure -CO-NH₂ and
 corresponding to the formula NH₂-CO-R₆.

The polyisocyanate compound comprising reactive NCO groups is corresponding to the
 formula $R_7\text{-NCO}$ wherein R₇ may be selected from hydrogen and hydrocarbyl groups
 which hydrocarbyl groups have 1-20 carbon atoms and optionally comprise hydroxy,
 20 ether, halogen, carboxyl, isocyanate and/or amine groups and wherein said hydrocarbyl
 groups may be a combination of linear, branched, saturated, unsaturated, cyclic and/or

non-cyclic aliphatic, aromatic or araliphatic hydrocarbyls and mixtures of such compounds.

The compound comprising the carboxamide, which compound may be used to make the compound comprising an acylurea group having the structure -CO-NH-CO-NH- according to the present invention, preferably is selected from a compound according to the formula $\text{NH}_2\text{-CO-R}_6$ wherein R_6 is 1) hydrogen (-H), 2) $\text{-NR}_8\text{R}_9$, 3) hydrocarbyl having 1-20 carbon atoms and optionally comprising hydroxy, ether, halogen and/or amine groups, or 4) -Rio-CO-NH_2 , wherein R_8 and R_9 , independently from each other, are selected from hydrogen, hydroxy, halogen and hydrocarbyl groups which hydrocarbyl groups have 1-10 carbon atoms and optionally comprise hydroxy, ether, halogen and/or amine groups and wherein Rio is a bivalent hydrocarbon radical having up to 8 carbon atoms. Mixtures of these carboxamides may be used as well. Preferably such carboxamides have a molecular weight of at most 499.


The hydrocarbyl groups in these carboxamides may be linear or branched, saturated or unsaturated and cyclic or non-cyclic; they may be aliphatic, aromatic or araliphatic.

More preferred carboxamides are those wherein R_6 is 1) $\text{-NR}_8\text{R}_9$, 2) alkyl having 1-10 carbon atoms and optionally comprising 1-3 hydroxy and/or ether groups, 3) phenyl or 4) tolyl, wherein R_8 and R_9 , independently from each other, are selected from hydrogen, hydroxy, phenyl, tolyl and alkyl having 1-6 carbon atoms and optionally comprising an hydroxy and/or an ether group. Mixtures of such more preferred compounds are also more preferred.

Examples of very useful carboxamides ($\text{NH}_2\text{-CO-Re}$) are the following ones:

25

Re	Name
-NH_2	Carbamide (urea)
-NHOH	Hydroxycarbamide (Hydroxy urea)
$\text{-NH(CH}_3)$	N-Methyl carbamide (N-Methyl urea)
$\text{-N(CH}_3)_2$	1,1 - dimethyl carbamide (1,1 - dimethyl urea)
$\text{-N(C}_2\text{H}_5)_2$	1,1 - diethyl carbamide (1,1 - diethyl urea)
$\text{-NH-C}_6\text{H}_5$	Phenyl carbamide (Phenyl urea)

-NH-C ₆ H ₄ -CH ₃	Tolylcarbamide (Tolyl urea)
-H	Formamide
-CH ₃	Ethanamide
-C ₂ H ₅	Propionamide
-OC ₂ H ₅	Ethyl carbamate
-OC ₄ H ₉	Butyl carbamate
-OC ₆ H ₅	Phenyl carbamate
-OCH ₂ -CH ₂ OH	Hydroxyethyl carbamate
-OCH(CH ₃)-CH ₂ OH	Hydroxypropyl carbamate
-CH(CH ₃)-OH	Lactamide
-C ₆ H ₅	Benzamide
	Nicotinamide

Most preferably carbamide (urea) is used. It is to be noted that in calculating the number of carboxamide equivalents carbamide (urea) is regarded as containing 2 carboxamide groups.

5

The compound comprising an acylurea group having the structure -CO-NH-CO-NH- may be provided and/or prepared beforehand and after preparation added to a polyisocyanate composition in order to form the stable polyisocyanate composition according to the invention. The polyisocyanate used for making the acylurea compound may be identical or different from the polyisocyanate being present in the stable polyisocyanate composition.

Alternatively, the compound comprising an acylurea group having the structure -CO-NH-CO-NH- may be prepared by combining and mixing the compound comprising the carboxamide group having the structure -CO-NH₂ to a polyisocyanate composition and allowing them to react to form the compound having an acylurea group and to form the stable polyisocyanate composition according to the invention.

If desirable, the compound comprising the carboxamide may be dissolved in a solvent before being reacted with the polyisocyanate. The solvent may be selected from a solvent which is not reactive with NCO groups or from solvents which are reactive with NCO

20

groups like monools, polyols. One or more solvents may be used. Examples of solvents have been given further in this specification.

5 According to the invention, the reaction (the carboxamide with the polyisocyanate compound) is preferably conducted under stirring and nitrogen atmosphere. The reaction is preferably conducted at a temperature of 15 to 90 °C and preferably of 20-85 °C. In general the reaction is conducted for 1 minute to 5 hours and preferably for 1 minute to 1 hour.

10 The polyisocyanate corresponding to the formula $R_7\text{-NCO}$ used for making the acylurea compound corresponding to the formula $R_6\text{-CO-NH-CO-NH-R}_7$ may be identical or different to the polyisocyanate compound being present in the stable polyisocyanate composition which is used to make the curable polyisocyanate composition according to the invention.

15 In general, the polyisocyanate compound(s) according to the present invention may be selected from aliphatic and, preferably, aromatic polyisocyanates. Preferred aliphatic polyisocyanates are hexamethylene diisocyanate, isophorone diisocyanate, methylene dicyclohexyl diisocyanate and cyclohexane diisocyanate and preferred aromatic polyisocyanates are toluene diisocyanate, naphthalene diisocyanate, tetramethylxylene diisocyanate, phenylene diisocyanate, tolidine diisocyanate and, in particular, methylene
20 diphenyl diisocyanate (MDI) and polyisocyanate compositions comprising methylene diphenyl diisocyanate (like so-called polymeric MDI, crude MDI, uretonimine modified MDI and prepolymers having free isocyanate groups made from MDI and polyisocyanates comprising MDI) and mixtures of such polyisocyanates. MDI and
25 polyisocyanate compositions comprising MDI are most preferred and especially those selected from 1) a diphenylmethane diisocyanate comprising at least 35%, preferably at least 60% by weight of 4,4'-diphenylmethane diisocyanate (4,4'-MDI); 2) a carbodiimide and/or uretonimine modified variant of polyisocyanate 1), the variant having an NCO value of 20% by weight or more; 3) a urethane modified variant of polyisocyanate 1) and/or 2), the variant having an NCO value of 20% by weight or more and being the
30 reaction product of an excess of polyisocyanate 1) and/or 2) and of a polyol having an

average nominal hydroxyl functionality of 2-4 and an average molecular weight of at most 1000; 4) a diphenylmethane diisocyanate comprising a homologue comprising 3 or more isocyanate groups; 5) prepolymers having an NCO value of 5-30 % by weight and being the reaction product of any one or more of polyisocyanates 1)-4) and of a polyol
5 having an average nominal hydroxyl functionality of 2-4 and an average molecular weight of more than 1000 and up to 8000; and 6) mixtures of any of the aforementioned polyisocyanates.

Polyisocyanate 1) comprises at least 35% by weight of 4,4'-MDI. Such polyisocyanates
10 are known in the art and include pure 4,4'-MDI and isomeric mixtures of 4,4'-MDI, 2,4'-MDI and 2,2'-MDI. It is to be noted that the amount of 2,2'-MDI in the isomeric mixtures is rather at an impurity level and in general will not exceed 2% by weight, the remainder being 4,4'-MDI and 2,4'-MDI. Polyisocyanates as these are known in the art and commercially available; for example Suprasec^R MPR and 1306 ex Huntsman
15 (Suprasec is a trademark of the Huntsman Corporation or an affiliate thereof which has been registered in one or more but not all countries).

The carbodiimide and/or uretonimine modified variants of the above polyisocyanate 1) are also known in the art and commercially available; e.g. Suprasec^R 2020, ex Huntsman. Urethane modified variants of the above polyisocyanate 1) are also known in the art, see
20 e.g. The ICI Polyurethanes Book by G. Woods 1990, 2nd edition, pages 32-35.

Polyisocyanate 4) is also widely known and commercially available. These polyisocyanates are often called crude MDI or polymeric MDI. Examples are Suprasec^R 2185, Suprasec^R 5025 and Suprasec^R DNR ex Huntsman.

The prepolymers (polyisocyanate 5)) are also widely known and commercially available.
25 Examples are Suprasec^R 2054 and Suprasec^R 2061, both ex Huntsman.

Mixtures of the aforementioned polyisocyanates may be used as well, see e.g. The ICI Polyurethanes Book by G. Woods 1990, 2nd edition pages 32-35. An example of such a commercially available polyisocyanate is Suprasec^R 2021 ex Huntsman.

The NCO value of the stable polyisocyanate composition after addition and/or (in-situ) formation of the compound having a -CO-NH-CO- group according to the present invention may range from 10 to 48 % by weight and preferably ranges from 20 to 33 % by weight.

5

The polyisocyanate composition according to the present invention obtained after addition and/or (in-situ) formation of the compound having a -CO-NH-CO- group is stable and liquid and may be used to improve the pot-life of a curable polyisocyanate composition. Such a curable polyisocyanate composition is obtained by combining a
10 lithium halide, a urea compound (not being an acylurea as described above) and an epoxy resin with the stable polyisocyanate composition according to the present invention.

The lithium halide used in the curable polyisocyanate composition used according to the present invention is used in an amount of 0.0001-0.04 and preferably of 0.00015-0.025
15 and most preferably of 0.0005-0.02 moles per isocyanate equivalent and preferably is selected from lithium chloride and lithium bromide. Lithium chloride is most preferred.

The urea compound used in the curable polyisocyanate composition used according to the present invention is used in such an amount that the number of urea + biuret equivalents
20 is 0.0001-0.4 and preferably 0.001-0.2 and most preferably 0.001-0.05 per isocyanate equivalent. Most preferably the number of urea + biuret equivalents in the urea compound in the polyisocyanate composition per mole of lithium halide ranges of from 0.5-60 and most preferably of from 0.5-30. The urea compound should not comprise other isocyanate-reactive groups (i.e. other than urea groups). In calculating the number
25 of urea equivalents, the urea groups in the carboxamides are not taken into account.

The urea compound used in the curable polyisocyanate composition used according to the present invention has an average molecular weight of 500-15000 and preferably of 600-
10000 and most preferably of 800-8000. Such urea compounds are prepared by reacting
30 polyisocyanates and amines (not being carboxamides having the structure R-CO-NH₂).

The polyisocyanates used to prepare such urea compound may be selected from the polyisocyanates mentioned above. The preferences mentioned above apply here as well. Most preferably polyisocyanates 1) and 2) and mixtures thereof are used. The polyisocyanate used to make the stable polyisocyanate composition according to the present invention and the polyisocyanate used to make the urea compound may be the same or different.

The amines used to prepare the urea compounds may be monoamines or polyamines. Preferably monoamines, optionally comprising a small amount of polyamines, are used. The average amine functionality of such mixtures preferably is at most 1.2. Most preferably only monoamines are used. Such amines preferably are primary amines.

The molecular weight of the amines is selected in such a way that once reacted with the selected polyisocyanate the molecular weight of the urea compound obtained falls within the above ranges. In general the molecular weight of the amines ranges of from 200-7500 and preferably of from 200-4500 and most preferably of from 200-3000.

The amines may be selected from those known in the art like amine-terminated hydrocarbons, polyesters, polyethers, polycaprolactones, polycarbonates, polyamides and mixtures thereof. Most preferred are amine-terminated polyoxyalkylene monoamines and more in particular polyoxyethylene polyoxypropylene monoamines. Preferably the oxypropylene content in these polyoxyalkylene monoamines is at least 50 and preferably at least 75 % by weight calculated on the total weight of the monoamine molecule. Preferably the polyoxyalkylene monoamines have a monoalkyl group at the other end of the polymer chain, the alkyl group having 1-8 and preferably 1-4 carbon atoms. Such monoamines are known in the art. They are made by alkoxyating an alkylmonoalcohol having 1-8 carbon atoms and by subsequently converting the polyoxyalkylene monool into the monoamine. Such monoamines are commercially available. Examples are Jeffamine^R M-600 and M-2005, both ex Huntsman (Jeffamine is a trademark of the Huntsman Corporation or an affiliate thereof which has been registered in one or more but not all countries). Mixtures of monoamines may be used as well.

In view of the above, a most preferred urea compound used in the polyisocyanate composition used according to the present invention is a urea compound obtained by reacting a methylene diphenyl diisocyanate or a polyisocyanate comprising a methylene diphenyl diisocyanate or a mixture of these polyisocyanates and a polyoxyalkylene monoamine, comprising oxypropylene groups in an amount of at least 75 % by weight calculated on the total weight of the monoamine molecule and having an average molecular weight of 200-3000 and wherein the amine is a primary amine.

10 The polyisocyanate and the monoamine are combined and mixed and allowed to react. The reaction is exothermic and therefore does not require heating and/or catalysis, although heat and/or catalysis may be applied if this is regarded as convenient. For instance it may be convenient to pre-heat the polyisocyanate and/or the monoamine to 40-60 °C and to mix them then. After mixing, the temperature of the reacting mixture preferably is kept below 90 °C in order to avoid side reactions, like e.g. biuret formation. In order to ensure that all the amine reacts, a slight excess of polyisocyanate may be used; conducting the reaction at an index of 101-110 is preferred therefore. After at most 1 hour the reaction may be regarded as complete and the urea compound is ready for use to make the polyisocyanate composition used according to the present invention.

20 Since a small excess of polyisocyanate is used in preparing the urea compound and since the urea compound in a next step is added to a relatively large amount of polyisocyanate, some of the urea groups might be converted to biuret groups. By controlling the reaction temperature and the temperature of the subsequent mixing steps, such biuret formation is avoided as much as possible. In general, the number of urea groups which are converted into biuret groups is less than 25 % and preferably less than 10 %.

The epoxy resin used preferably is selected from any epoxy resin which is liquid at 20 °C.

30

Examples of epoxy resins are:

I) Polyglycidyl and poly(β -methylglycidyl) esters, obtainable by reacting a compound having at least two carboxyl groups in the molecule and, respectively, epichlorohydrin and β -methylepichlorohydrin. The reaction is expediently effected in the presence of bases.

Aliphatic polycarboxylic acids can be used as the compound having at least two carboxyl groups in the molecule. Examples of such polycarboxylic acids are oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and dimerized or trimerized linoleic acid.

However, cycloaliphatic polycarboxylic acids, such as, for example, tetrahydrophthalic acid, 4-methyltetrahydrophthalic acid, hexahydrophthalic acid or 4-methylhexahydrophthalic acid, may also be used.

Furthermore, aromatic polycarboxylic acids, such as, for example, phthalic acid, isophthalic acid or terephthalic acid, may be used.

II) Polyglycidyl or poly(β -methylglycidyl) ethers, obtainable by reacting a compound having at least two free alcoholic hydroxyl groups and/or phenolic hydroxyl groups with epichlorohydrin or β -methylepichlorohydrin under alkaline conditions or in the presence of an acidic catalyst with subsequent treatment with alkali.

The glycidyl ethers of this type are derived, for example, from acyclic alcohols, for example from ethylene glycol, diethylene glycol or higher poly(oxyethylene) glycols, propane-1,2-diol or poly(oxypropylene) glycols, propane-1,3-diol, butane-1,4-diol, poly(oxytetramethylene) glycols, pentane-1,5-diol, hexane-1,6-diol, hexane-2,4,6-triol, glycerol, 1,1,1-trimethylolpropane, pentaerythritol or sorbitol, and from polyepichlorohydrins. Further glycidyl ethers of this type are derived from cycloaliphatic alcohols, such as 1,4-cyclohexanedimethanol, bis(4-hydroxycyclohexyl)methane or 2,2-bis(4-hydroxycyclohexyl)propane, or from alcohols which contain aromatic groups and/or further functional groups, such as N,N-bis(2-hydroxyethyl)aniline or p,p'-bis(2-hydroxyethylamino)-diphenylmethane .

The glycidyl ethers may also be based on mononuclear phenols, such as, for example, p-tert-butylphenol, resorcinol or hydroquinone, or on polynuclear phenols, such as, for example, bis(4-hydroxyphenyl)methane, 4,4'-dihydroxybiphenyl, bis(4-hydroxyphenyl) sulphone, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane or
5 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane.

Further suitable hydroxy compounds for the preparation of glycidyl ethers are novolaks, obtainable by condensation of aldehydes, such as formaldehyde, acetaldehyde, chloral or furfuraldehyde, with phenols or bisphenols which are unsubstituted or substituted by chlorine atoms or Ci-C9-alkyl groups, such as, for example, phenol, 4-chlorophenol, 2-
10 methylphenol or 4-tert-butylphenol.

III) Poly(N-glycidyl) compounds, obtainable by dehydrochlorination of the reaction products of epichlorohydrin with amines which contain at least two amine hydrogen atoms. These amines are, for example, aniline, n-butylamine, bis(4-aminophenyl)methane,
15 m-xylylenediamine or bis(4-methylaminophenyl)methane.

The poly(N-glycidyl) compounds also include triglycidyl isocyanurate, N,N'-diglycidyl derivatives of cycloalkyleneureas, such as ethyleneurea or 1,3-propyleneurea, and diglycidyl derivatives of hydantoins, such as of 5,5-dimethylhydantoin.

20 IV) Poly(S-glycidyl) compounds, for example di-S-glycidyl derivatives, which are derived from dithiols, such as, for example, ethane-1,2-dithiol or bis(4-mercaptomethylphenyl) ether.

V) Cycloaliphatic epoxy resins, such as, for example, bis(2,3-epoxycyclopentyl) ether,
25 2,3-epoxycyclopentyl glycidyl ether, 1,2-bis(2,3-epoxycyclopentyl)ethane or 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate.

It is also possible to use epoxy resins in which the 1,2-epoxy groups are bonded to different hetero atoms or functional groups; these compounds include, for example, the N,N,O-triglycidyl derivative of 4-aminophenol, the glycidyl ether-glycidyl ester of
30 salicylic acid, N-glycidyl-N'-(2-glycidylloxypropyl)-5,5-dimethylhydantoin or 2-glycidylloxy-1,3-bis(5,5-dimethyl-1-glycidylhydantoin-3-yl)propane.

Particularly preferred are those mentioned in I and II and most preferred are those mentioned in II.

If an epoxy resin is used which contains hydroxyl groups or other isocyanate-reactive hydrogens then these hydroxyl groups and hydrogens are not taken into account in calculating the index or the number of hydroxyl equivalents.

The curable polyisocyanate composition according to the present invention is made by mixing the stable polyisocyanate composition according to the present invention, the urea compound, the lithium halide, the epoxy resin and optionally further polyisocyanate in any order under ambient conditions or at elevated temperature, e.g. at 40-70 °C. Preferably the lithium halide is premixed with the urea compound and optional further polyisocyanate and this mixture is subsequently added to the stable polyisocyanate and mixed. Before mixing the lithium halide and the urea compound, it may be convenient to dissolve the lithium halide in a solvent, like in an organic solvent like an alcohol, e.g. methanol or ethanol. The dissolved lithium halide is then added to the urea compound. Subsequently the solvent may be stripped off if desired. Premixing and mixing is conducted under ambient conditions or at elevated temperature, e.g. at 40-70 °C and is done by means of normal stirring. The relative amounts of the polyisocyanate, the urea compound and the lithium halide are chosen in such a way that the final polyisocyanate composition used according to the invention has the relative amounts of isocyanate groups, urea groups and lithium halide as has been described before. Without wishing to be bound to any theory, the lithium halide is believed to be present in dissociated form, complexed with the urea group as a so-called bidentate complex. Finally the epoxy resin is added and mixed in such relative amounts that the number of epoxy equivalents per isocyanate equivalent ranges from 0.003-1 and preferably from 0.003-0.5 and most preferably from 0.005-0.25 and under the same conditions as mentioned above.

The curable composition so obtained has a good pot-life under ambient conditions. It is used to make a polyisocyanurate material preferably having a Tg (measured according to ASTM D4065) of at least 120 °C by allowing it to react at elevated temperature,

preferably above 50 °C and most preferably above 80 °C. Therefore the invention is further concerned with a polyisocyanurate material made by allowing a curable composition according to the present invention to react at elevated temperature and with a polyisocyanurate material obtainable by allowing a curable composition according to the present invention to react at elevated temperature and with a process for making these polyisocyanurate materials by allowing a curable composition according to the present invention to react at elevated temperature. Preferably the reaction is conducted at an index higher than 100, preferably at least 300 (e.g. in range of 300-100000) and most preferably at least 500. Preferably heat is applied in order to bring the curable composition to a temperature above 50 °C and most preferably above 80 °C. Then the curable composition may cure fast (so-called snap-cure) while the temperature increases further (the reaction is exothermic).

The curable compositions according to the present invention may be used in a wide variety of composite processing methods to make a wide variety of composite materials. For example, they may be used to repair an object and in particular a pipe by applying them onto the interior and / or the exterior surface of such an object or such a pipe according to the so-called cured in place method. The curable compositions according to the present invention may be used in resin transfer moulding to produce door panels or honeycomb like structures, in vacuum assisted resin infusion to make structural automotive parts such as car bonnets or chassis rails, in filament winding to produce pressure vessels or gas tanks and in pultrusion to make glass fibre reinforced composite ladders or to produce prepregs used in printed circuit boards and in sheet and bulk moulding compounding processes. The polyisocyanurate composite materials according to the present invention may further be used in sporting goods, in high volume production of automotive parts, in train parts, aerospace, marine applications, wind power devices, window lineals, structural parts, adhesives, packaging, encapsulants and insulators.

Before curing it, the curable composition may be fed into a mould in order to give it a certain shape or into a cavity of an object in order to provide the object with a polyisocyanurate interior or onto a surface to provide such a surface with a

polyisocyanurate cover or it may be used to repair an object and in particular a pipe by applying it onto the interior and/or the exterior surface of such an object or such a pipe (examples of such pipe repair have been described in US 4009063, 4366012 and 4622196) or it may be used to bind materials as has been disclosed in WO 2007/096216.

5

Before the curable composition is cured, additives may be added to it or to its constituents. Examples of additives are further non-isocyanate-reactive solvents, polyols and monools, other catalysts, blowing agents, surfactants, water scavengers, like alkylorthoformate and in particular tri-isopropylorthoformate, antimicrobial agents, fire
10 retardants, smoke suppressants, UV-stabilizers, colorants, plasticizers, internal mould release agents, rheology modifiers, wetting agents, dispersing agents and fillers.

The monool and/or polyol optionally used in the present invention preferably has an average nominal hydroxy functionality of 1-8 and an average molecular weight of 32-
15 8000. Mixtures of monools and/or polyols may be used as well.

Examples of such monools are methanol, ethanol, propanol, butanol, phenol, cyclohexanol and hydrocarbon monools having an average molecular weight of 200-5000 like aliphatic and polyether monools. Examples of polyols are ethylene glycol, diethylene
20 glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, trimethylol propane, sorbitol, sucrose, glycerol, ethanediol, propanediol, butanediol, pentanediol, hexanediol, aromatic and/or aliphatic polyols having more carbon atoms than these compounds and having a molecular weight of up to 8000, polyester polyols having an average molecular weight of 200-8000, polyether polyester polyols having an
25 average molecular weight of 200-8000 and polyether polyols having an average molecular weight of 200-8000. Such monools and polyols are commercially available. Useful examples are Daltocel F555 and Daltocel F442, which are all polyether triols from Huntsman, Voranol P400 and Alcupol R1610, which are polyether polyols from DOW and Repsol, respectively, and Priplast 1838 and 3196 which are high molecular weight
30 polyester polyols from Croda, and Capa 2043 polyol, a linear polyesterdiol of average MW of about 400 from Perstorp, and K-flex polyols 188 and A308 which are polyester

polyols from King Industries having a MW of about 500 and 430 respectively, and aromatic polyester polyols like Stepanpol PH56 and BC180 having average molecular weights of about 2000 and 600 respectively, and Neodol 23E which is an aliphatic monool from Shell.

- 5 Most preferred are polyester and polyether polyols having an average molecular weight of 200-6000 and an average nominal functionality of 2-4.

The solvent having no isocyanate-reactive groups, which optionally may be used, preferably is an organic solvent which is liquid at 20 °C. Solvents having a viscosity at
10 20°C of 3000 mPa.s or less as measured according to ASTM D445-1 1a are regarded as liquid solvents. Most preferred are organic, liquid solvents which are able to dissolve more than 1mg of a certain compound comprising the -CO-NH-CO- group per litre solvent at 20 °C.

Those skilled in the art can easily determine whether or not an organic liquid is suitable
15 for use as solvent in the present invention, certainly with the above guidance. Examples of suitable solvents are esters (such as ethyl acetate, propyl acetate, propylene carbonate, phthalate esters), ketones (such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone), aliphatic hydrocarbons (such as cyclohexane, heptane), chlorinated hydrocarbons (such as chloroform, dichloromethane), aromatic solvents (such as benzene,
20 toluene), ethers (such as dimethyl ether, diethyl ether, dioxane, tetrahydrofuran) and mixtures thereof. Most preferably solvents are selected which have a low boiling point at ambient pressure or under vacuum (then they may be stripped off from the curable composition easily). They should preferably be able to dissolve at least 10g of carboxamide per kg of solvent. The amount of solvent may vary between wide ranges.
25 The lower limit is determined by the desired type and amount of compound comprising the carboxamide and its solubility in the selected solvent. The upper limit is determined by considerations of convenience and cost: the less the better. Preferred amounts range of from 0 to 50 and more preferably of from 0 to 25 and most preferably of from 0 to 10 % by weight on the weight of the epoxy resin composition.

If desired the polyisocyanurate material according to the present invention may be subjected to post-curing.

The invention is illustrated with the following examples.

5

EXAMPLES

Chemicals used:

10 Jeffamine M-600 ex Huntsman: a monofunctional polyoxyethylene polyoxypropylene primary amine having a molecular weight of about 560 and an oxypropylene/oxyethylene ratio of about 9/1. In these examples referred to as M-600.

Suprasec 1306 polyisocyanate ex Huntsman: 4,4'-MDI, in these examples referred to as S1306.

15 Suprasec 2020 polyisocyanate ex Huntsman : a uretonimine modified polyisocyanate, in these examples indicated as S2020

Polyol 3380 ex Perstorp.: TMP initiated polyoxyethylene polyol with an OH-value of 380 mg KOH/g,

Succinimide ex Sigma

Carbamide (urea) 99%+ ex Acros Organics

20 1,1-diethyl carbamide (diethyl urea) 97% ex Aldrich

Polyglycol DME500 ex Clariant : PEG 500 dimethylether, in these examples indicated as DME 500

Araldite DY-T, ex Huntsman, triglycidylether of trimethylolpropane, indicated herein as DY-T.

25 Alcupol R1610, ex Repsol glycerol initiated polyoxypropylene polyol with an OH-value of 160 mg KOH/g

Lithium chloride, anhydrous ex Acros Organics

Ethanol 96%, ex Commercial Alcohols INC.

30 Araldite®, Suprasec® and Jeffamine® are trademarks of the Huntsman Corporation or an Affiliate thereof and are registered in one or more but not all countries.

In none of the following examples biuret formation was observed.

Examples 1-2 : Preparation of compounds comprising a -CO-NH-CO- group

5 Examples 1-2 describe the preparation of compounds having a -CO-NH-CO- group according to the invention wherein the compound having a -CO-NH-CO- group is a compound having an acylurea group having the structure -CO-NH-CO-NH- and wherein said compound is the reaction product of a polyisocyanate and a compound comprising a carboxamide group having the structure -CO-NH₂.

10

Example 1

To 90 pbw of Suprasec 2020 at 85°C (0.64 isocyanate equivalents), 10 pbw of a solution containing 10 wt% carbamide[^] (0.033 carboxamide equivalents) in polyol 3380 was added dropwise, under stirring and nitrogen atmosphere. After 20 minutes of reaction, a clear liquid reaction product was obtained comprising the compound having an acylurea group.

15

[^]carbamide = urea = NH₂-CO-NH₂

20 Example 2

To 80 pbw of Suprasec 2020 at 85°C (0.56 isocyanate equivalents), 20 pbw of a solution containing 10 wt% 1,1-dimethyl carbamide^(*) 500 (0.017 carboxamide equivalents) in DME 500 was added dropwise, under stirring and nitrogen atmosphere. After 20 minutes of reaction, a clear liquid reaction product was obtained comprising the compound having an acylurea group.

25

^(*) 1,1 dimethyl carbamide = 1,1 dimethyl urea = NH₂-CO-N(CH₃)₂

30

Examples 3-11 : Preparation of stable polyisocyanate compositions according to the invention

The compound having a -CO-NH-CO- group is added to a polyisocyanate composition in order to create the stable polyisocyanate composition according to the invention.

In examples 3-8, said compound is the reaction product of a polyisocyanate and a compound comprising a carboxamide group having the structure -CO-NH₂ as described in examples 1-2.

In examples 9-11, said compound corresponds to succinimide.

10

Table 1

example	S2020 amount in pbw	compound from example 1 amount in pbw	Compound from example 2 amount in pbw	5 wt % solution of succinimide in DME 500 amount in pbw	CO-NH-CO / isocyanate ratio
3	94	1			0.0005
4	93	2			0.001
5	92	3			0.0015
6	94		1		0.00026
7	93		2		0.00052
8	92		3		0.00078
9	95			0.66	0.0005
10	95			1.32	0.001
11	95			1.98	0.0015

Example 12 : Preparation of the urea/salt mixture

15

1123.7 g Jeffamine M600, which was kept at 50 °C, and 260 g S1306, which was also kept at 50 °C, were mixed and allowed to react for 1 hour at 80°C under stirring, so as to form a urea compound.

23.9 g of lithium chloride was dissolved in 125.3 g ethanol while stirring.

20 This lithium chloride solution was added to the above prepared urea compound which

was still kept at 80 °C. Stirring was continued for about 15 minutes. A substantial amount of ethanol was afterwards stripped off by distillation at 85-95 °C.

5 Examples 13-22 :Preparation of curable compositions and polyisocyanurate materials according to the present invention.

The compositions of Table 1 (example 3-1 1) were mixed with 5 pbw of the urea/salt mixture prepared in example 12, 4 pbw of an epoxy resin Araldite DY-T and 15 pbw of polyol Alcupol R1610 for 5 minutes. 100 g of these curable composition was poured in a
10 glass jar of 120 ml and closed with a screw lid and placed at room temperature in order to determine the pot-life by following the temperature profile with a thermocouple placed in the liquid resin till the onset (30°C) of the temperature rise. 100 g of these curable compositions were allowed to cure in an 4 mm thick aluminium closed mould for 1 hour at 120°C, so as to prepare polyurethane polyisocyanurate materials according to the
15 present invention.

The glass transition temperature (T_g) from the obtained materials was determined by Differential Mechanical Thermo Analysis (DMTA) on a TA Q800 apparatus with a heating rate of 3°C/min and a frequency of 1 Hz (measured according to ASTM D 4065). The T_g was defined as the first inflection point on the E' (storage modulus) curve
20 determined by the TA Universal analysis software.

A reference material not according to the invention without the presence of a compound having the -CO-NH-CO- group was prepared with the same procedure (example 13).

The ingredients used, the amounts in parts by weight, the pot-lives, T_g of the cured materials, the equivalent ratio of -CO-NH-CO- group per isocyanate, equivalent ratio
25 Urea + biuret per isocyanate, equivalent ratio LiCl per isocyanate, equivalent ratio epoxy per isocyanate, equivalent ratio urea + biuret per lithium chloride of the compositions are given in Table 2.

The ingredients used, the amounts in parts by weight, the pot-lives, T_g of the cured materials, the equivalent ratio of -CO-NH-CO- group per isocyanate, equivalent ratio
30 Urea + biuret per isocyanate, equivalent ratio LiCl per isocyanate, equivalent ratio epoxy

per isocyanate, equivalent ratio urea + biuret per lithium chloride of the compositions are given in Table 2.

Figures 1-3 illustrate the pot-life measurements of the cured material according to the invention (examples 14-22) with significantly improved pot-lives compared to the comparative example 13.

Table 2

example	S2020 amount in pbw	compositions from Table 1 example / amount in pbw	Pot-life of the curable composition (hours)	Tg cured material (°C)	Equivalent ratio -CO-NH-CO- / isocyanate	Equivalent ratio Urea + biuret / Isocyanate	Equivalent ratio LICI / isocyanate	Equivalent ratio Epoxy / isocyanate	Equivalent ratio Urea + biuret / LICI
13	95	0	2.7	145	0	0.0109	0.003	0.0480	3.65
14	0	3 / 95	24.7	152	0.0005	0.01 10	0.003	0.0481	3.65
15	0	4 / 95	55	156	0.001	0.01 10	0.003	0.0482	3.65
16	0	5 / 95	94	152	0.0015	0.01 10	0.003	0.0484	3.65
17	0	6 / 95	9.7	151	0.00026	0.01 10	0.003	0.0481	3.65
18	0	7 / 95	18	167	0.00052	0.01 10	0.003	0.0482	3.65
19	0	8 / 95	25.9	161	0.00078	0.01 10	0.003	0.0483	3.65
20	0	9 / 95,66	16.7	154	0.0005	0.0109	0.003	0.0480	3.65
21	0	10 / 96,32	40	149	0.001	0.0109	0.003	0.0480	3.65
22	0	11 / 96,98	69.7	150	0.0015	0.0109	0.003	0.0480	3.65

CLAIMS

1. A curable composition obtained by a process comprising, combining and mixing
 - a polyisocyanate composition comprising a compound comprising a group having the structure -CO-NH-CO- in such an amount that the ratio of the number of -CO-NH-CO- groups to the number of isocyanate groups is at most 1, preferably at most 0.01, more preferably at most 0.0015, and
 - a lithium halide, and
 - an urea compound, having an average molecular weight of 500-15000 and optionally comprising biuret groups, and
 - an epoxy resin,wherein the number of moles of lithium halide per isocyanate equivalent ranges of from 0.0001-0.04 and the number of urea + biuret equivalents per isocyanate equivalent ranges of from 0.0001-0.4 and the number of epoxy equivalents per isocyanate equivalent ranges of from 0.003-1 .
2. Curable composition according to claim 1 wherein the polyisocyanate composition has an isocyanate value of 10 to 48 % by weight and preferably from 20 to 33 % by weight .
3. Curable composition according to any of claims 1-2 wherein the compound comprising a group having the structure -CO-NH-CO- corresponds to the structure $R_1\text{-CO-NH-CO-R}_2$ wherein R_1 and R_2 each independently from each other are selected from 1) hydrogen (-H), 2) $\text{-NR}_3\text{R}_4$, 3) hydrocarbyl having 1-100 carbon atoms and optionally comprising hydroxy, ether, halogen, carboxyl, oxygen, isocyanate and/or amine groups wherein R_3 and R_4 independently from each other, are selected from hydrogen, hydroxy, halogen and hydrocarbyl groups which hydrocarbyl groups have 1-20 carbon atoms and optionally comprise hydroxy, ether, halogen, carboxyl, isocyanate and/or amine groups, wherein R_1 and R_2 may be linked to each other essentially forming a ring structure including the -CO-NH-CO- group, and wherein the hydrocarbyl groups in the compounds

corresponding to the formula $R_1\text{-CO-NH-CO-R}_2$ may be a combination of linear, branched, saturated, unsaturated, cyclic and/or non-cyclic aliphatic, aromatic or araliphatic hydrocarbyls and mixtures of such compounds.

4. Curable composition according to foregoing claims wherein the compound comprising a group having the structure -CO-NH-CO- corresponds to a compound comprising a -CO-NH-CO-NH- group which is a reaction product of a compound comprising a carboxamide group having the structure -CO-NH_2 and a polyisocyanate compound comprising a reactive NCO group.
5. Curable composition according to foregoing claims wherein the compound comprising a group having the structure -CO-NH-CO- corresponds to $R_6\text{-CO-NH-CO-NH-R}_7$ and wherein
 - the compound comprising a carboxamide group corresponds to $\text{NH}_2\text{-CO-}R_6$ and wherein R_6 is 1) hydrogen (-H), 2) -NR_8R_9 , 3) hydrocarbyl having 1-20 carbon atoms and optionally comprising hydroxy, ether, halogen and/or amine groups, or 4) $\text{-R}_{10}\text{-CO-NH}_2$, wherein R_8 and R_9 , independently from each other, are selected from hydrogen, hydroxy, halogen and hydrocarbyl groups which hydrocarbyl groups have 1-10 carbon atoms and optionally comprise hydroxy, ether, halogen and/or amine groups and wherein R_{10} is a bivalent hydrocarbon radical having up to 8 carbon atoms and mixtures of these carboxamides, and
 - the compound comprising a reactive NCO group corresponds to $R_7\text{-NCO}$ and wherein R_7 is selected from hydrogen and hydrocarbyl groups which hydrocarbyl groups have 1-20 carbon atoms and optionally comprise hydroxy, ether, halogen, carboxyl, isocyanate and/or amine groups and wherein said hydrocarbyl groups may be a combination of linear, branched, saturated, unsaturated, cyclic and/or non-cyclic aliphatic, aromatic or araliphatic hydrocarbyls and mixtures of such compounds.
6. Curable composition according to foregoing claims wherein the compound comprising a -CO-NH-CO- group corresponds to $R_6\text{-CO-NH-CO-NH-R}_7$ which is made by adding a compound comprising a carboxamide group having the structure -CO-NH_2 to a polyisocyanate composition and allowing the mixture to

react in order to form the compound corresponding to R_6 -CO-NH-CO-NH- R_7 in the polyisocyanate composition.

7. Curable composition according to claim 6 wherein R_6 is selected from 1) -NR₈R₉, 2) alkyl having 1-10 carbon atoms and optionally comprising 1-3 hydroxy and/or ether groups, 3) phenyl or 4) tolyl wherein R_8 and R_9 , independently from each other, are selected from hydrogen, hydroxy, phenyl, tolyl and alkyl having 1-6 carbon atoms and optionally comprising an hydroxy and/or an ether and mixtures of such compounds.
8. Curable composition according to claims 1-3 wherein R_1 and R_2 together with the -CO-NH-CO- group form a 4 to 12 membered ring structure including the -CO-NH-CO- group.
9. Curable composition according to any of foregoing claims, wherein the urea compound does not comprise other isocyanate-reactive groups than urea groups and wherein the number of urea + biuret equivalents per isocyanate equivalent is 0.001-0.2 and wherein the urea compound has been prepared by reacting a methylene diphenyl diisocyanate or a polyisocyanate comprising a methylene diphenyl diisocyanate or a mixture of these polyisocyanates with a polyoxyalkylene monoamine comprising oxypropylene groups in an amount of at least 50 % by weight calculated on the total weight of the monoamine molecule and having an average molecular weight of 200-3000 and wherein the amine is a primary amine and wherein the number of urea + biuret equivalents per mole of lithium halide is 0.5-60.
10. Curable composition according to any of foregoing claims, wherein the composition comprises a toluene diisocyanate, a methylene diphenyl diisocyanate or a polyisocyanate composition comprising a methylene diphenyl diisocyanate or a mixture of such polyisocyanates.
11. Curable composition according to any of foregoing claims, wherein the amount of lithium halide is 0.00015-0.025 moles per isocyanate equivalent.
12. Curable composition according to any of foregoing claims, wherein the lithium halide is lithium chloride.

13. Use of a polyisocyanate composition comprising a compound comprising a group having the structure -CO-NH-CO- in such an amount that the ratio of the number of -CO-NH-CO- groups to the number of isocyanate groups is at most 1, preferably at most 0.01, more preferably at most 0.0015 for improving the pot-life of a curable polyisocyanate composition.
14. Process for making a curable composition according to claims 1-12, by combining and mixing a polyisocyanate composition comprising a compound comprising a group having the structure -CO-NH-CO- in such an amount that the ratio of the number of -CO-NH-CO- groups to the number of isocyanate groups is at most 1, preferably at most 0.01, more preferably at most 0.0015, and a lithium halide, and a urea compound, having an average molecular weight of 500-15000 and optionally comprising biuret groups, and an epoxy resin, wherein the number of moles of lithium halide per isocyanate equivalent ranges of from 0.0001-0.04 and the number of urea + biuret equivalents per isocyanate equivalent ranges of from 0.0001-0.4 and the number of epoxy equivalents per isocyanate equivalent ranges of from 0.003-1 .
15. Polyisocyanurate comprising material made by allowing a curable composition according to claims 1-12 to react at elevated temperature.
16. Polyisocyanurate comprising material obtainable by allowing a curable composition according to claims 1-12 to react at elevated temperature.
17. Process for making a polyisocyanurate comprising material according to claims 15-16 by allowing the curable composition according to claims 1-12 to react at elevated temperature.

FIGURE 1

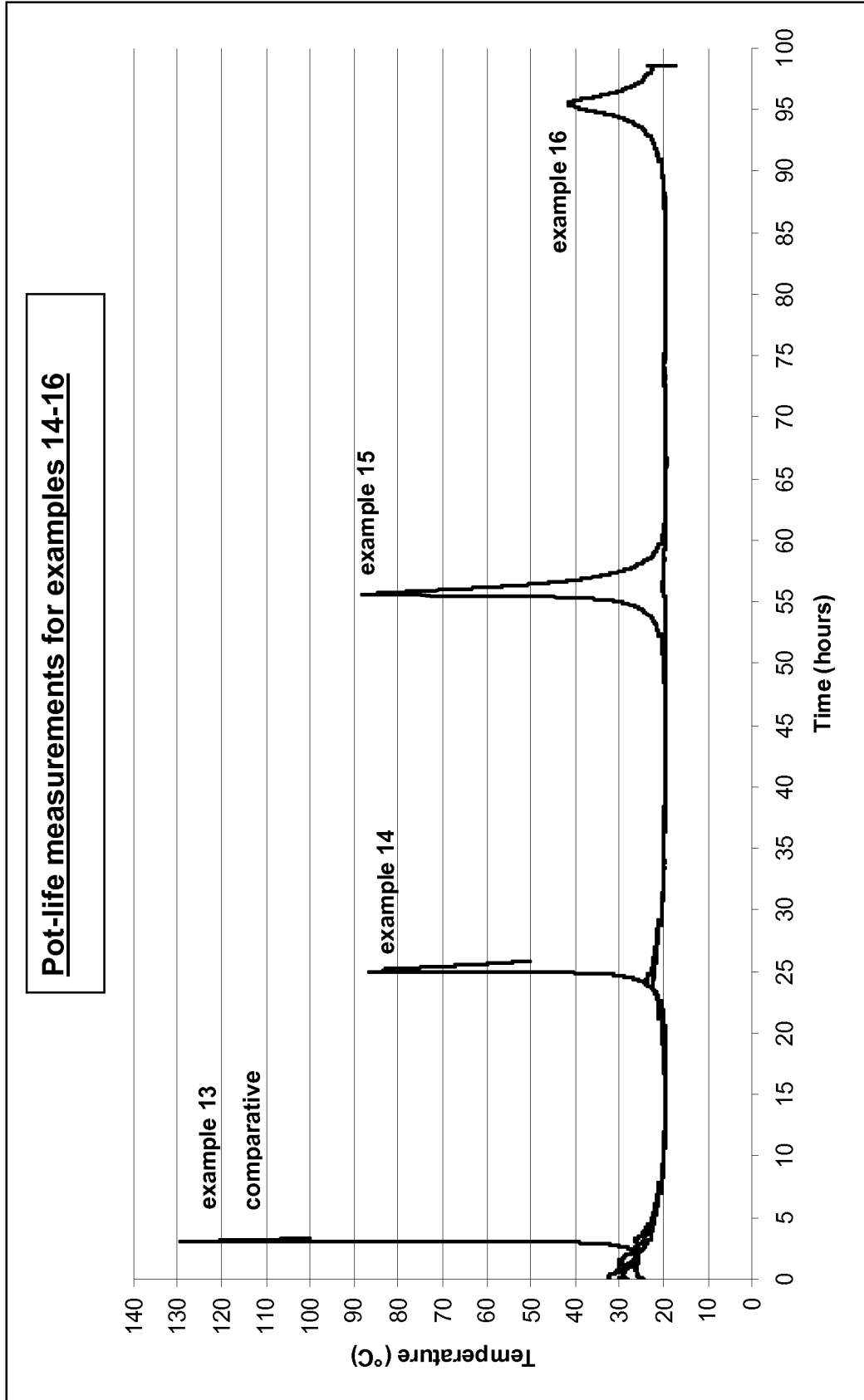


FIGURE 2

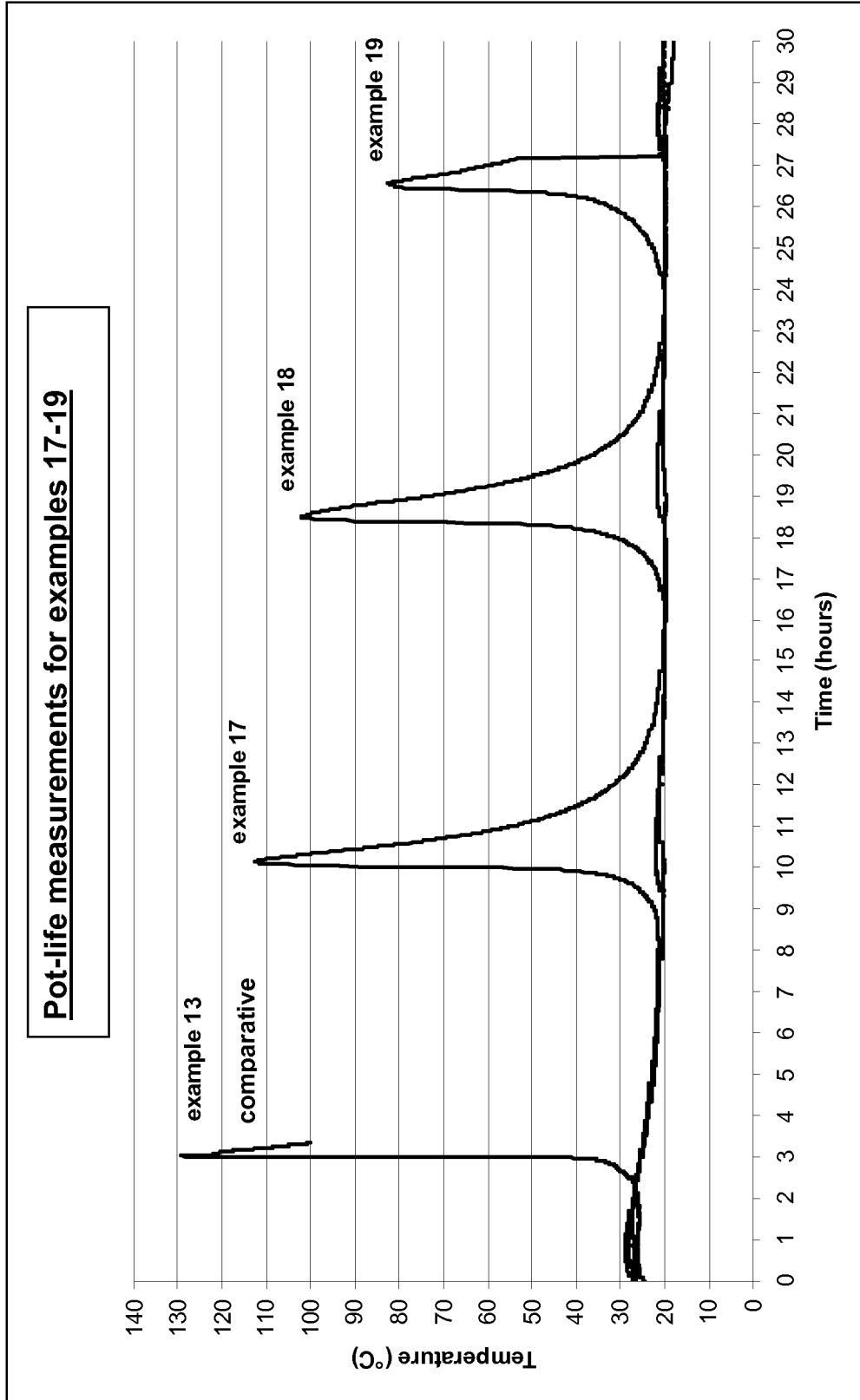
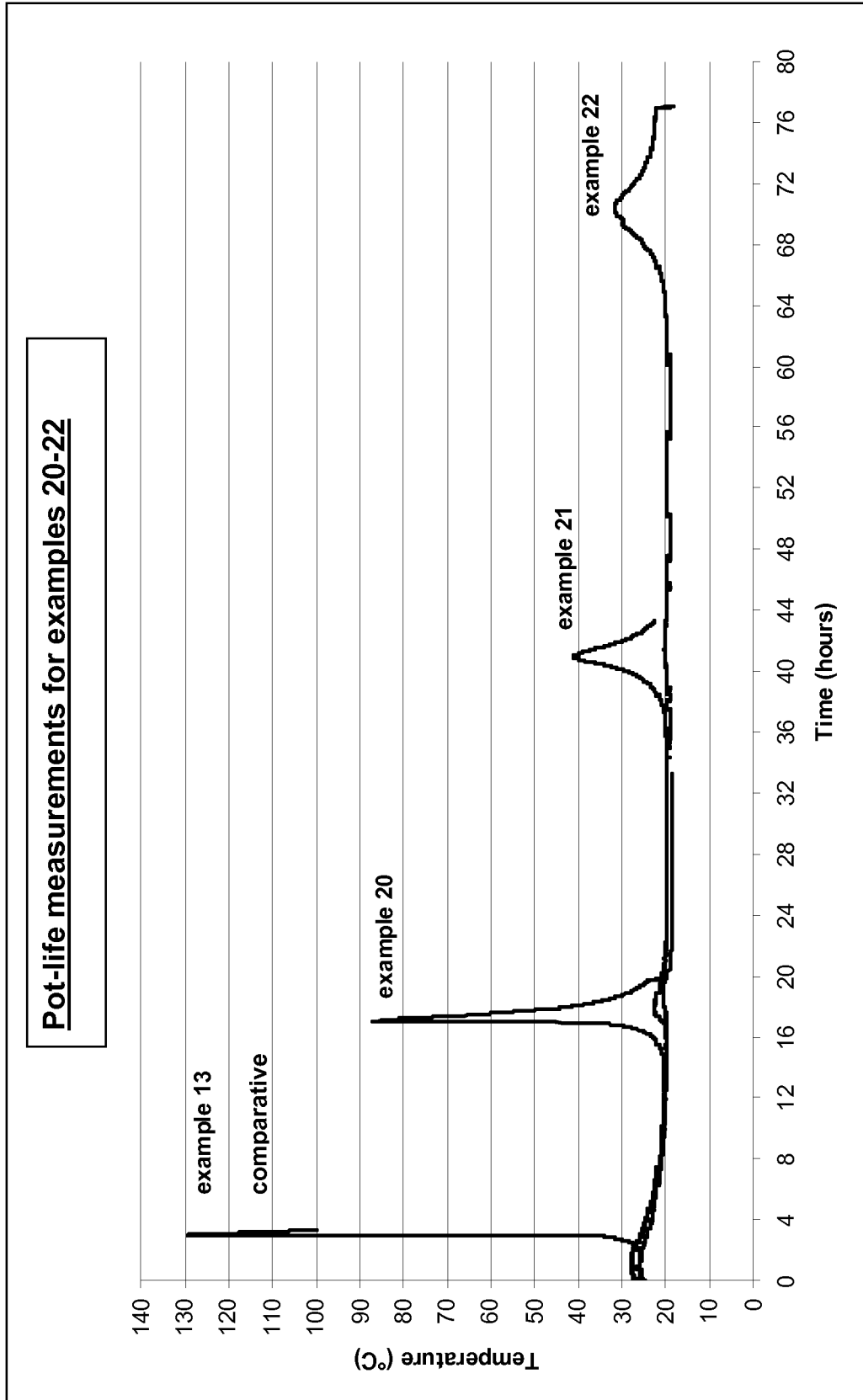


FIGURE 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/074048

A. CLASSIFICATION OF SUBJECT MATTER	INV. C08G18/00	C08G18/22	C08G18/38	C08G18/48	C08G18/58
	C08G18/79	C08L75/00	C08G59/40		
ADD.					
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) C08G C08L

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 practicable, search terms used)
EPO-Internal , WPI Data, COMPENDEX, INSPEC, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 660 456 A (NAITO KENJI ET AL) 2 May 1972 (1972-05-02)	13
Y	claims; examples 1-4	1-12 , 14-17
Y	----- US 3 799 963 A (ADAMS P) 26 March 1974 (1974-03-26) column 2, line 44 - line 49 column 3, line 13 - line 19; claims	1-12 , 14-17
Y	----- wo 2008/060454 A2 (BAYER MATERIALSCIENCE LLC [US]; ADKINS RICK L [US]; SLACK WILLIAM E [U]) 22 May 2008 (2008-05-22) page 8, line 3 - line 5 claims 1,5,7,11,12,18,22 ----- -/-- .	1-12 , 14-17

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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 when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

14 January 2013

Date of mailing of the international search report

22/01/2013

Name and mailing address of the ISA/

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

Authorized officer

Hein, Friedrich

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/074048

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 331 810 A (CHRISTMAN DONALD L ET AL) 25 May 1982 (1982-05-25) column 6, line 13 - line 22; claims ; examples 3-5 , 10, 11, 14,21 ,22 -----	1-12 , 14-17
Y	US 2003/134971 AI (BLOUNT DAVID H [US]) 17 July 2003 (2003-07-17) claims 1,4, 16; example 2a) -----	1-12 , 14-17
Y	JP 2 110123 A (ASAHI CHEMICAL IND) 23 April 1990 (1990-04-23) abstract -----	1-12 , 14-17
Y	GB 1 463 809 A (ICI LTD) 9 February 1977 (1977-02-09) cited in the application claims ; example -----	1-12 , 14-17
Y	US 4 330 656 A (GROEGLER GERHARD ET AL) 18 May 1982 (1982-05-18) cited in the application claims 1,5; examples 3,5 -----	1-12 , 14-17
L	GB 701 549 A (WINGFOOT CORP) 30 December 1953 (1953-12-30) the whole document -----	1-17
Y	WO 2010/121898 AI (HUNTSMAN INT LLC [US] ; DEBIEN CHRISTIAAN [BE] ; ESBELIN CHRISTIAN [BE] ;) 28 October 2010 (2010-10-28) the whole document -----	1-12 , 14-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/074048

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3660456	A	02-05-1972	DE 1817017 AI 14-08-1969
			FR 1604179 A 26-07-1971
			GB 1192859 A 20-05-1970
			NL 6818810 A 01-07-1969
			US 3660456 A 02-05-1972

US 3799963	A	26-03-1974	AU 463658 B2 31-07-1975
			AU 5197373 A 08-08-1974
			CA 1002063 AI 21-12-1976
			DE 2316028 AI 22-11-1973
			FR 2184592 AI 28-12-1973
			GB 1350374 A 18-04-1974
			IT 977208 B 10-09-1974
			JP 49024916 A 05-03-1974
			JP 51000102 B 05-01-1976
			US 3799963 A 26-03-1974
ZA 7300520 A 31-10-1973			

wo 2008060454	A2	22-05-2008	US 2008139777 AI 12-06-2008
			wo 2008060454 A2 22-05-2008

US 4331810	A	25-05-1982	NONE

US 2003134971	AI	17-07-2003	NONE

JP 2110123	A	23-04-1990	NONE

GB 1463809	A	09-02-1977	NONE

US 4330656	A	18-05-1982	DE 2843739 AI 10-04-1980
			EP 0009756 AI 16-04-1980
			JP 1085212 A 30-03-1989
			JP 3014847 B 27-02-1991
			JP 55050016 A 11-04-1980
			JP 64006218 B 02-02-1989
US 4330656 A 18-05-1982			

GB 701549	A	30-12-1953	NONE

wo 2010121898	AI	28-10-2010	CA 2755856 AI 28-10-2010
			CN 102405244 A 04-04-2012
			EP 2421906 AI 29-02-2012
			JP 2012524824 A 18-10-2012
			KR 20120017023 A 27-02-2012
			US 2012046436 AI 23-02-2012
			wo 2010121898 AI 28-10-2010
