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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C07C 269/02, C07B 43/00, C07C 271/20,</b> <b>C08F 8/30, C08G 63/685, C09D 5/03,</b> <b>C08G 18/22, 18/75, C09D 175/04</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/46517</b> <b>(43) International Publication Date:</b> 11 December 1997 (11.12.97)
<b>(21) International Application Number:</b> PCT/NL97/00300 <b>(22) International Filing Date:</b> 28 May 1997 (28.05.97) <b>(30) Priority Data:</b> 1003263                      4 June 1996 (04.06.96)                      NL <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VAN BENTHEM, Rudolfus, Antonius, Theodorus, Maria [NL/NL]; Sportlaan 9, NL-6141 BR Sittard (NL). JANSEN, Johan, Franz, Gradus, Antonius [NL/NL]; Marisstraat 11, NL-6165 AP Geleen (NL). STANSSENS, Dirk, Armand, Wim [BE/BE]; De Huttestraat 93, B-3530 Houthalen (BE). <b>(74) Agent:</b> SCHMEETZ, Marcel, Max, Hubertina, Johanna; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CATALYST FOR THE REACTION BETWEEN A COMPOUND THAT CAN REACT WITH ISOCYANATE GROUPS AND AN ALIPHATIC DIISOCYANATE WITH ONE ISOCYANATE GROUP BOUND TO A PRIMARY CARBON ATOM AND ONE ISOCYANATE GROUP BOUND TO A TERTIARY CARBON ATOM  <b>(57) Abstract</b>  The invention relates to a catalyst for the reaction between a compound that can react with isocyanate groups and an aliphatic diisocyanate with one isocyanate group bound to a primary carbon atom and one isocyanate group bound to a tertiary carbon atom. The catalyst is an ionogenic metal complex based on a metallic element from one of the groups III, IV or VII of the Periodic System, with at least one exchangeable counterion. Preferably the metallic element is titanium, zirconium, manganese or tin.		

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5     CATALYST FOR THE REACTION BETWEEN A COMPOUND THAT  
      CAN REACT WITH ISOCYANATE GROUPS AND AN ALIPHATIC  
      DIISOCYANATE WITH ONE ISOCYANATE GROUP BOUND TO A  
          PRIMARY CARBON ATOM  
      AND ONE ISOCYANATE GROUP BOUND TO A TERTIARY CARBON  
          ATOM

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      The invention relates to a catalyst for a  
reaction between a compound that can react with  
isocyanate groups and an aliphatic diisocyanate with  
15 one isocyanate group bound to a primary carbon atom and  
one isocyanate group bound to a tertiary carbon atom.

      Such a reaction is, for example, described on  
p. 42 of the "Proceedings of the XIX International  
Conference in Organic Coatings Science and Technology"  
20 (12-16 July 1993 in Athens). Said publication describes  
3(4)-isocyanatomethyl-1-methylcyclohexylisocyanate  
(IMCI) as a crosslinker in powder paint formulations.

      An aliphatic diisocyanate with one isocyanate  
group bound to a primary carbon atom and one isocyanate  
25 group bound to a tertiary carbon atom is a compound  
containing two or more isocyanate groups having  
different reactivities. The two isocyanate groups in  
3(4)-isocyanatomethyl-1-methylcyclohexylisocyanate  
(IMCI) differ in reactivity. In general, this  
30 difference in reactivity can be used in the case of a  
compound containing two or more isocyanate groups with  
different reactivities to cause certain isocyanate  
groups to react selectively with a compound that can  
react with isocyanate groups, while the other  
35 isocyanate groups remain unchanged and will be  
available for use at a later stage in a similar or a  
different chemical reaction. Such reactions in which  
the selectivity is complete or almost complete under

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industrially applicable conditions are not yet known. With an incomplete selectivity, for example in the reaction of a diisocyanate with an equimolar amount of alcohol, or with a compound containing alcohol groups, a more or less statistically determined mixture of unreacted diisocyanate units and diisocyanate units that have reacted once and twice is always obtained. Drawbacks of such a distribution are, on the one hand, that unreacted diisocyanate remains in the product and, on the other, that many isocyanate groups are lost as a result of the uncontrolled form of reaction. Moreover, substantial chain lengthening takes place when use is made of with bi- or multivalent compounds reacting with isocyanates, for example OH-functional polymers, which results in undesired product. Processes that result in such a distribution are described for example in "Angewandte Makromoleculaire Chemie 1984" (122), 83-99, and in "Journal of Polymer Science (Polymer Letters Edition)" 1985 (23), 509-515, while DE-A-4405054 describes an application of such a distribution for processing in polymers. For a successful use of said difference in reactivity, hereinafter to be referred to as "selectivity", it is very important that this selectivity is as great as possible under the usual and applicable industrial conditions.

The uncatalysed reactions between a compound containing two or more isocyanate groups with different reactivities and the compound that can react with isocyanate groups show substantially decreasing selectivities at higher temperatures. At room temperature the selectivity of the reaction is sufficient, but the reaction rate is too low. Moreover, the processing of some compounds that can react with isocyanate groups at this temperature is troublesome.

It is the object of the invention to obtain a very high selectivity in the reaction between an aliphatic diisocyanate with one isocyanate group bound

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to a primary carbon atom and one isocyanate group bound to a tertiary carbon atom and a compound that can react with isocyanate groups, under the usual industrial conditions, with the reaction also taking place at a sufficiently high rate. The reaction temperature may vary from room temperature in the case of liquid media, to above 100°C in the case of highly viscous media, such as polymers with high glass transition temperatures.

10           The invention is characterised in that the catalyst is an ionogenic metal complex based on a metallic element from one of the groups III, IV or VII of the Periodic System, with at least one exchangeable counterion.

15           This invention ensures that the reaction takes place at a high rate and that moreover a very high selectivity is obtained.

          The use of the catalyst according to the invention ensures that the coupling of the diisocyanate to for example a hydroxyl-functional polymer takes place exclusively or almost exclusively via the most reactive isocyanate group. Advantages of this selective coupling are for example that the product polymer for example a coating contains no free diisocyanate and that no chain lengthening takes place.

20           Suitable metallic elements in the suitable valency are aluminium(III), tin(IV), manganese(III), titanium(III), titanium(IV) and zirconium(IV).

          The preferred metallic element is tin(IV), titanium(IV), manganese(III) and zirconium(IV).

30           The number of counterions lies between 1 and 4.

          In the case of four-valent metals it is possible to use for example 4 monovalent counterions, 2 bivalent counterions or 1 trivalent combined with 1 monovalent counterion. Preferably use is made of 4 monovalent counterions.

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In the case of trivalent metals, the number of counterions lies between 1 and 3 and use is preferably made of 3 monovalent counterions.

Examples of suitable counterions are

- 5 halogenides, preferably chloride, (C<sub>1</sub>-C<sub>20</sub>) alkoxides, preferably (C<sub>1</sub>-C<sub>8</sub>) alkoxide, (C<sub>2</sub>-C<sub>20</sub>) carboxylates, preferably (C<sub>2</sub>-C<sub>8</sub>) carboxylates, enolates, preferably of 2,4-pentanedione (acetoacetonates), and alkyl esters of malonic acid and acetoacetic acid, phenolates,  
10 naphthenates, cresylates and mixtures of said counterions.

Examples of suitable catalysts are

- aluminium(III) acetate, aluminium(III) acetoacetate,  
aluminium(III) 2,2,6,6-tetramethyl-3,5-heptanedionate,  
15 aluminium(III) ethoxide, aluminium(III) isopropoxide, aluminium(III) sec-butoxide, aluminium(III) tert-butoxide, tin(IV) chloride, tin(IV) bromide, tin(IV) iodide, tin(IV) acetate, tin(IV) bis(acetoacetate) dichloride, tin(IV) bis(acetoacetate) dibromide, manganese(III) acetate,  
20 manganese(III) acetoacetate, manganese(III) fluoride, titanium(IV) chloride, titanium(IV) bromide, titanium(IV) methoxide, titanium(IV) ethoxide, titanium(IV) isopropoxide (TYZOR TPT™), titanium(IV) propoxide, titanium(IV) butoxide (TYZOR TBT™),  
25 titanium(IV) 2-ethylhexoxide (TYZOR TOT™), titanium(IV) acetoacetate, titanium(IV) bis(acetoacetate) diisopropoxide (TYZOR AA™), titanium(IV) bis(ethylacetoacetate) diisopropoxide, titanium(IV) (triethanolaminate) isopropoxide (TYZOR TE™),  
30 zirconium(IV) chloride, zirconium(IV) bromide, zirconium(IV) acetate, zirconium(IV) 2-ethylhexanoate, zirconium(IV) ethoxide, zirconium(IV) butoxide, zirconium(IV) tert-butoxide, zirconium(IV) citrate  
35 ammonium complex, zirconium(IV) isopropoxide, zirconium(IV) propoxide, zirconium(IV) acetoacetate and zirconium(IV) trifluoroacetoacetate.

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Preferred catalysts are titanium(IV) butoxide, zirconium(IV) acetoacetate, zirconium(IV) butoxide, tin(IV) acetate, manganese(III) acetoacetate, titanium(IV) isopropoxide, zirconium (IV) 2-ethylhexanoate and tin(IV) chloride.

The catalyst complex may also contain one or more neutral elements such as alkylcyanide, crown ether, (poly)ether, such as polytetrahydrofuran, polyethylene glycol or tetrahydrofuran, dialkylsulphide or tertiary amine.

The amount of catalyst is usually between 0.01 and 3 wt.% (relative to the compound that can react with isocyanate groups and the compound containing isocyanate groups).

One of the additional advantages of the catalysts according to the invention in the case of use in coatings is that colourless catalysts can be chosen.

Monomers, oligomers and polymers may all be used as the compounds that can react with isocyanate groups. Such compounds contain reactive groups that can form a chemical bond with isocyanate groups.

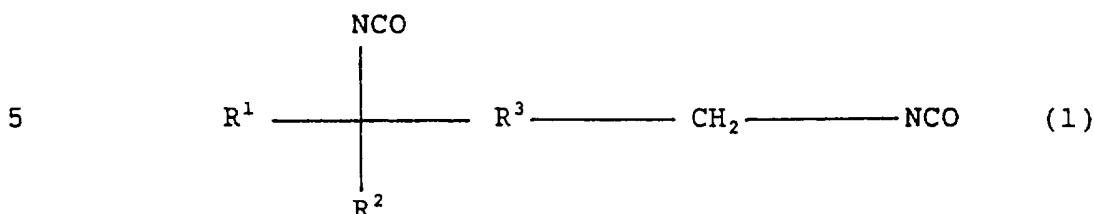
Examples of suitable reactive groups are alcohols, N-hydroxyl compounds such as oximes and N-hydroxyimides, amines, amides, for example N-alkoxyamides, lactams, imides, thiols, enolates such as 1,3-dicarbonyl compounds, carboxylates, epoxides and aromatic compounds containing heterocyclic nitrogen groups, such as pyrimidines, indoles, imidazoles, oxazoles, thiazoles, triazoles, pyrazoles and their derivatives.

Preferably use is made of alcohols, lactams, amines, N-hydroxyl compounds and aromatic compounds containing heterocyclic nitrogen.

Generally, the aliphatic diisocyanate having one sterically more accessible isocyanate group bound to a primary carbon atom and one sterically less accessible isocyanate group bound to a tertiary carbon

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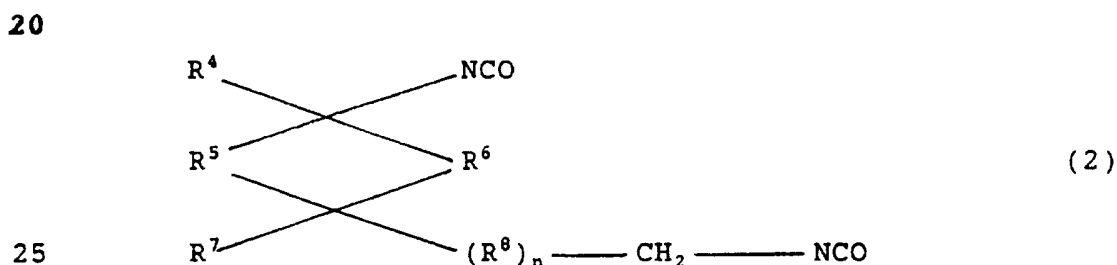
atom can be represented as follows by Formula (1):



10 where  $\text{R}^1$  and  $\text{R}^2$  contain the same or different ( $\text{C}_1\text{-C}_4$ ) alkyl groups and  $\text{R}^3$  contains a bivalent, optionally branched, saturated aliphatic ( $\text{C}_1\text{-C}_{10}$ ) hydrocarbon radical.

Preferably the diisocyanate is a cycloaliphatic diisocyanates containing one sterically more accessible isocyanate group bound to a primary carbon atom and one sterically less accessible isocyanate group bound to a tertiary carbon atom.

These compounds can be represented by Formula (2):



where:

- $\text{R}^4 = (\text{C}_1\text{-C}_4)$  alkyl group,
- $\text{R}^5$  and  $\text{R}^6 =$  the same or different bivalent, optionally branched, saturated, aliphatic ( $\text{C}_1\text{-C}_3$ ) hydrocarbon radicals,
- $\text{R}^7 =$  hydrogen or ( $\text{C}_1\text{-C}_4$ ) alkyl group,
- $\text{R}^8 =$  bivalent, optionally branched, saturated, aliphatic ( $\text{C}_1\text{-C}_6$ ) hydrocarbon radical and
- 35 -  $n=0$  or  $n=1$

Examples of suitable diisocyanates are 1,4-diisocyanato-4-methyl-pentane, 1,5-diisocyanato-5-



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methylhexane, 3(4)-isocyanatomethyl-1-methylcyclohexylisocyanate, 1,6-diisocyanato-6-methylheptane, 1,5-diisocyanato-2,2,5-trimethylhexane and 1,7-diisocyanato-3,7-dimethyloctane or 1-isocyanato-1-methyl-4-(4-isocyanatobut-2-yl)-cyclohexane, 1-isocyanato-1,2,2-trimethyl-3-(2-isocyanato-ethyl)-cyclopentane, 1-isocyanato-1,4-dimethyl-4-isocyanatomethyl-cyclohexane, 1-isocyanato-1,3-dimethyl-3-isocyanatomethyl-cyclohexane, 1-isocyanato-1-n-butyl-3-(4-isocyanatobut-1-yl)-cyclopentane, 1-isocyanato-1,2-dimethyl-3-ethyl-3-isocyanatomethyl-cyclopentane. The process for preparing such diisocyanates is described in for example DE-A-3608354, DE-A-3620821 and EP-A-153561.

Preferably use is made of 3(4)-isocyanotomethyl-1-methylcyclohexylisocyanate (IMCI) and 1,4-diisocyanate-4-methylpentane (DIMP).

The reaction according to the invention can be applied in a wide diversity of technical fields. A preferred field of application is the coating industry (in both powder paint systems and solvent- or water-based systems). Other suitable fields of application are, for example, construction resins, polyurethanes foams or compounds, lenses, materials based on acrylates, the preparation of resins for adhesives, sealants, compatibilisers, coupling agents and printing inks and also as chain extenders in engineering plastics.

In the preparation of both powder paint and solvent- and water-based coating compositions, the compounds that can react with isocyanate groups can be chosen from polymers such as, for example amorphous and crystalline polyesters, polyurethanes, unsaturated polyesters, polyethers, polycarbonates, polybutadienes, styrene-maleic anhydride copolymers and fluorine-containing polymers.

Preferably amorphous polyesters or

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polyacrylates are used as the polymer.

Polyesters are generally based on units of aliphatic polyalcohols and polycarboxylic acids. As the polycarboxylic acid, the polyester may contain for  
5 example isophthalic acid, terephthalic acid, hexahydroterephthalic acid, 2,6-naphthalene dicarboxylic acid and 4,4-oxybisbenzoic acid, 3,6-dichlorophthalic acid, tetrachlorophthalic acid, itaconic acid, tetrahydrophthalic acid,  
10 hexahydroterephthalic acid, hexachloroendomethylene-tetrahydrophthalic acid, phthalic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, adipic acid, succinic acid, trimellitic acid and maleic acid, fumaric acid, citraconic acid and mesaconic acid. These  
15 acids may be used as such or, insofar as available, in the form of their anhydrides, acid chlorides or lower alkylesters.

Use may also be made of hydroxycarboxylic acids and/or optionally lactones such as 12-  
20 hydroxystearic acid, hydroxypivalic acid and  $\epsilon$ -caprolactone.

Suitable polyalcohols, in particular diols, that can be caused to react with the carboxylic acids to obtain the polyester include aliphatic diols such as  
25 ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,4-diol, butane-1,3-diol, 2,2-dimethylpropanediol-1,3 (= neopentyl glycol), hexane-2,5-diol, hexane-1,6-diol, 2,2-bis-(4-hydroxycyclohexyl)-propane (hydrogenated bisphenol-A), 1,4-  
30 dimethylolcyclohexane, diethylene glycol, dipropylene glycol and 2,2-bis[4-(2-hydroxyethoxy)-phenyl]propane, the hydroxypivalic ester of neopentyl glycol.

Small amounts, for example less than about 4 wt.%, but preferably less than 2 wt.%, of trifunctional  
35 alcohols or acids can be used to obtain branched polyesters. Examples of suitable polyols and polyacids are glycerol, hexanetriol, trimethylolethane,

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trimethylolpropane, tris-(2-hydroxyethyl)-isocyanurate and trimellitic acid.

The preparation conditions and the COOH/OH ratio can be chosen so that end products are obtained  
5 that have a hydroxyl value that lies within the envisaged range of values.

The hydroxyl value may for example lie between 20 and 100 mg of KOH/gram and the molecular weight ( $M_n$ ) between 1000 and 10000.

10 The polyesters can be prepared both in the presence of catalysts according to the invention and in the presence of the usual catalysts, via the usual process, through esterification or re-esterification.

The use of a catalyst according to the  
15 invention, preferably titanium(IV), zirconium(IV), tin(IV) or aluminium(III) complexes, during the polyester synthesis for example presents the advantage that only one catalyst need be used in the various successive steps (the polymer synthesis, the reaction  
20 with a compound containing two or more isocyanate groups with different reactivities and optionally the curing step) and, moreover, that the desired reaction rates are coupled to an improved selectivity. It is also possible to use the usual catalysts during the  
25 polymer synthesis and during the curing.

In general, the acrylate polymer is based on alkylesters of (meth)acrylic acid, such as ethyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, n-propyl (meth)acrylate, isobutyl  
30 (meth)acrylate, ethylhexyl acrylate and/or cyclohexyl (meth)acrylate, vinyl compounds such as styrene and vinyl acetate, malate, fumarate and itaconate.

The hydroxyl-functional acrylate resins are generally based on hydroxyethyl (meth)acrylate,  
35 hydroxypropyl (meth)acrylate and alkyl (meth)acrylate.

Acrylate resins can be prepared in a polymerisation in which first a solvent, for example

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toluene, xylene or butylacetate, is added to the reactor. This is followed by heating to the desired reaction temperature, for example the reflux temperature of the solvent used, after which an  
5 initiator and optionally mercaptan are added in a period of for example between 2 and 4 hours. Then the temperature is kept at reflux temperature for for example two hours. The solution is refluxed for 1 to 4 hours. The solvent is then removed through distillation  
10 by raising the temperature, after which a vacuum distillation can be carried out, for for example one to two hours. Then the product is drained and cooled.

Before the solvent is removed through distillation at room temperature or elevated  
15 temperature, modification, for example using IMCI, may take place. The selective reaction results in isocyanate-functional polyacrylates without any chain lengthening taking place. In the case of highly functional polymers, chain lengthening may result in  
20 premature crosslinking. A further advantage of the selective reaction is that when the optimum ratio of OH and NCO groups is chosen to be at most 2, no free diisocyanate is observed after modification. The presence of free diisocyanate is unjustifiable in view  
25 of the toxic properties of the diisocyanate and the irritation that it causes.

Isocyanate-functional polyacrylates can be further modified with the aid of, for example, hydroxyethyl(meth)acrylate, aminopropyl vinylether or  
30 hydroxybutyl vinyl ether, but they can also be used as such with crosslinkers. If an OH : NCO ratio of 1 : 1 is chosen in the functionalisation of the acrylate with for example IMCI, the selective reaction may result in a latent self-crosslinking system. As the remaining  
35 tertiary isocyanates have a low reactivity, the isocyanate-functional polyacrylates can be extruded or be dispersed in water or emulsified.

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After the synthesis of the polymer, for example the polyester, mixing of the polymer with for example IMCI may take place at a temperature at which the polymer has a viscosity of less than 5000 dPas  
5 (measured according to Emila). This can be effected by using agents that result in a homogeneous composition, for example static or dynamic mixers.

At the mixing temperature the difference in reactivity is so great that the second isocyanate group  
10 of for example 3(4)-isocyanatomethyl-1-methylcyclohexylisocyanate shows no reactivity relative to the polymer's reactive group.

A high selectivity as a result of the catalyst according to the invention results in minimum  
15 chain lengthening, in better flow properties of the powder paint and in the absence of unreacted diisocyanate after functionalisation.

The weight ratio of the polymer and a compound containing two or more isocyanate groups with  
20 different reactivities is generally between 70 : 30 and 99 : 1, preferably between 70 : 30 and 97 : 3 and more in particular between 85 : 15 and 95 : 5. Different desired ratios may also be chosen. Usually at most one diisocyanate molecule will be used per reactive group  
25 of the polymer. The OH:NCO molar ratio is usually chosen so that this ratio lies between 1 : 0.3 and 1 : 3 and preferably between 1 : 0.5 and 1 : 2.5. In the case of self-crosslinking systems the ratio is preferably between 1 : 0.8 and 1 : 1.2 and in the case  
30 of isocyanate-functional resins between 1 : 1.5 and 1 : 2.0

The preparation of thermosetting powder paints and chemical reactions for curing these powder  
35 paints into cured coatings are described in general terms in for example Misev, "Powder Coatings, Chemistry and Technology" (1991, John Wiley), pp. 44-54, pp. 148 and pp. 225-226 (and what is disclosed therein is

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included here by way of reference).

The curing reaction between for example an IMCI-modified polymer and the crosslinker, as described in WO-A-95/20017, which results in the ultimate cured  
5 coating, will usually take place in the presence of an effective amount of catalyst. If the curing reaction is based on the reaction between isocyanate and groups that can react with isocyanate, use can be made of both the catalyst according to the invention and a different  
10 suitable catalyst. The importance of the ratio of the polymer and the crosslinker and of the amount of catalyst is explained in Misev, "Powder Coatings, Chemistry and Technology", pp. 174-223 (and what is disclosed therein is included here by way of  
15 reference).

Because the polymer is modified with IMCI, tertiary isocyanate-functionalised polymers are obtained. Such functional groups do not require a blocking agent because they have a relatively low  
20 reactivity towards a usual reactive component containing hydroxyl groups. That makes it possible for example to mix such polymers with a hydroxy-functional crosslinker in an extruder during the preparation of powder paint, without noticeable prereaction taking  
25 place.

The crosslinker and the modified polymer can be mixed with one another with the aid of, for example, an extruder or a static mixer. It is, for example, possible to couple two static mixers in series, so that  
30 the polymer can be modified in the first mixer and the mixing with the crosslinker can take place in the second mixer. The two static mixers may differ in shape and/or they may be brought to different temperatures to enable control of the specific processes in the in-line  
35 mixers.

It is also possible to use the reaction according to the invention by chemically curing into a

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powder coating for example a powder paint composition comprising a hydroxyl-functional polymer, IMCI as the crosslinker and the catalyst according to the invention. The temperature for this reaction is  
5 generally between 120°C and 200°C.

The invention will be further described based on the following non-limiting examples.

Examples I-VI and Comparative Examples A-I

10               194 parts by weight of IMCI and 88 parts of neopentylalcohol (2,2-dimethylpropanol) were introduced into a glass flask. Next, 3 parts by weight of catalyst according to Table 1 were added to the stirred  
15 suspension, at room temperature. The changes in temperature during the exothermal reaction were followed with the aid of a thermometer. After 1 hour's reaction time a sample was taken and analysed by means of proton-NMR. The degree of conversion and the selectivity could be determined from the spectra  
20 obtained. The selectivity, which was expressed in percents, represents the fraction of the most reactive isocyanate groups that have reacted with the equimolar amount of added alcohol to form a urethane group after full conversion of the alcohol.

25               At 100% selectivity all the alcohol groups present reacted exclusively with the most reactive isocyanate groups; at 50% selectivity the added alcohol groups reacted with IMCI without discrimination between the different isocyanate groups. The detection limit  
30 for the selectivity according to this method lies at approx. 99 %. When little catalytic activity was observed, i.e. incomplete conversion after 1 hour's reaction time, this procedure was repeated after 20 hours.

35               The various catalysts are summarised in Table 1.

Table 1

	Catalyst	E <sup>1)</sup>	Reaction		
			% after 1 hour	% after 20 hours	selec- tivity
5	I	Ti (OBu) <sub>4</sub>	+	> 99	≥ 99
	II	Zr (acac) <sub>4</sub>	+	> 99	≥ 99
	III	Zr (octoate) <sub>4</sub>	+	> 99	≥ 99
	IV	SnCl <sub>4</sub>	+	> 99	≥ 99
	V	Mn(acac) <sub>3</sub>	+	> 99	≥ 99
10	VI	Ti(acac) <sub>4</sub>	+/-	95	> 99
	VII	Al(iPrO) <sub>3</sub>	+/-	92	> 99
15	A	Ti(Cp) <sub>2</sub> Cl <sub>2</sub>	-	35	92
	B	Bu <sub>2</sub> Sn (laurate) <sub>2</sub>	+	> 99	81
	C	BuSnCl <sub>3</sub>	+	> 99	91
	D	Sn(octoate) <sub>2</sub>	+	> 99	65
	E	Pb(octoate) <sub>2</sub>	-	55	> 99
	F	Zn (octoate) <sub>2</sub>	-	70	> 99
	G	Cu (octoate) <sub>2</sub>	-	71	> 99
	H	Co (octoate) <sub>2</sub>	+	> 99	90
	I	Fe (acac) <sub>3</sub>	+	> 99	90

E<sup>1)</sup>:           + exothermal reaction,  
                  - no exothermal reaction observable,  
                  +/- slightly exothermal reaction.

25               This table shows that the use of titanium(IV)  
 butoxide, zirconium(IV) acetoacetate, zirconium(IV)  
 2-ethylhexanoate, tin(IV) chloride or manganese(III)  
 acetoacetate results in a rapid exothermal reaction  
 in which the reaction mixture reached a peak  
 30   temperature of 60°C or more. In addition, complete



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conversion was observed after 1 hour's reaction time (as demonstrated by NMR) and complete or almost complete selectivity was achieved: 99% or higher.

The use of titanium(IV) acetoacetate and  
5 aluminium(III) isopropoxide results in a slightly exothermal reaction in which the reaction mixture reached a peak temperature of less than 50°C. In addition, almost complete conversion was observed after 1 hour's reaction time (>90%) (as demonstrated by NMR)  
10 and complete or almost complete selectivity was achieved: 99% or higher.

When titanocene(IV) dichloride was used as the catalyst, no exothermal reaction was observed. In addition, conversion was not yet complete after 20  
15 hour's reaction time (92%) and complete or almost complete selectivity was achieved: 99% or higher.

When use was made of tin(II) 2-ethylhexanoate, butyl tin trichloride, dibutyl tin dilaurate, iron(III) acetoacetate and cobalt(II) 2-  
20 ethylhexanoate, a rapid exothermal reaction was observed, in which the reaction mixture reached a peak temperature of 40°C or more. In addition, complete conversion was observed after 1 hour's reaction time, but the selectivity was found to be incomplete (65-  
25 91%).

#### Example VII

Into a flask containing 1000 parts by weight dry tetrahydrofuran and 2 parts by weight zirconium  
30 (IV) acetylacetonate, 194 parts by weight IMCI and 45 parts trimethylolpropane were introduced. The reaction mixture was stirred at reflux temperature (65°C) for 4 hours. After cooling to room temperature 73 parts of diethylamine were introduced. After evaporation of the  
35 solvent a glassy material was obtained.

Analysis by GPC showed that more than 98% of the product material had a trimeric structure and that

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less than 2% of higher molecular weight compounds were formed.

#### Example VIII

5                   Into a flask containing 1000 parts by weight of dry tetrahydrofuran and 2 parts by weight of zirconium (IV) acetylacetonate 154 parts by weight 1,4-diisocyanate-4-methylpentane DIMP and 45 parts by weight trimethylolpropane were introduced. The reaction  
10 mixture was stirred at reflux temperatur (65°C) for 4 hours. After cooling to room temperature 73 parts of diethylamine were introduced. After evaporation of the solvent a glassy material was obtained.

                  Analysis by GPC showed that more than 98% of  
15 the product material had a trimeric structure and that less than 2% of higher molecular weight compounds were formed.

#### Comparative Example J

20                   Into a flask containing 1000 parts of dry tetrahydrofuran and 2 parts of zirconium (IV) acetylacetonate, 223 parts by weight isophorone diisocyanate (IPDI) and 45 parts by weight trimethylolpropane were introduced. The reaction  
25 mixture was stirred at reflux temperature (65°C) for 4 hours. After cooling to room temperature 73 parts of diethylamine were introduced. After evaporation of the solvent a glassy material was obtained.

                  Analysis by GPC showed that only about 50% of  
30 the product material had a trimeric structure and that about 35% of higher molecular weight compounds (pentamers, heptamers, monomers, etc.) were formed. Furthermore about 15% of the IPDI remained unreacted with hydroxyl groups whereas all trimethylolpropane had  
35 reacted.

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C L A I M S

1. Catalyst for a reaction between a compound that  
can react with isocyanate groups and an aliphatic  
5 diisocyanate with one isocyanate group bound to a  
primary carbon atom and one isocyanate group bound  
to a tertiary carbon atom, characterised in that  
the catalyst is an ionogenic metal complex based  
on a metallic element from one of the groups III,  
10 IV or VII of the Periodic System, with at least  
one exchangeable counterion.
2. Catalyst according to Claim 1, characterised in  
that the metallic element is titanium, zirconium,  
manganese or tin.
- 15 3. Catalyst according to Claim 1 or Claim 2,  
characterised in that the counterion is a  
halogenide, alkoxide, carboxylate or enolate.
4. Catalyst according to any one of Claims 1-3,  
characterised in that the catalyst is chosen from  
20 the group comprising titanium(IV) butoxide,  
zirconium(IV) acetoacetate, zirconium(IV)  
butoxide, tin(IV) acetate, titanium(IV)  
isopropoxide, zirconium(IV) 2-ethylhexanoate,  
manganese(III) acetoacetate and tin(IV)  
25 chloride.
5. Catalyst according to any one of Claims 1-4,  
characterized in that the isocyanate is 3(4)-  
isocyanatomethyl-1-methylcyclohexylisocyanate or  
1,4-diisocyanate-4-methylpentane.
- 30 6. Process for the reaction between a compound that  
can react with isocyanate groups and an aliphatic  
diisocyanate with one isocyanate group bound to a  
primary carbon atom and one isocyanate group bound  
to a tertiary carbon atom in the presence of a  
35 catalyst, characterised in that the catalyst is a  
catalyst according to any one of Claims 1-5.
7. Use of the reaction product obtained with the

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process according to Claim 6.

8. Use of the reaction product obtained with the process according to Claim 6 in a coating composition.

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/NL 97/00300

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C269/02 C07B43/00 C07C271/20 C08F8/30 C08G63/685  
C09D5/03 C08G18/22 C08G18/75 C09D175/04

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 6 C08G C07C

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)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 232 584 A (BASF) 3 January 1975 see claim 1 see page 3, line 2 - line 23 see page 6, line 23 - line 31 see example 1 ---	1
A	US 4 045 527 A (BABAYAN EDUARD P ET AL) 30 August 1977 see claims 1-3 see column 3, line 45 - line 49 ---	1
A	EP 0 153 561 A (BAYER AG) 4 September 1985 see claims 1-4,7 --- -/--	1

☒ 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
- "E" earlier document but published on or after the international filing date
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- "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

13 August 1997

Date of mailing of the international search report

15.09.97

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/NL 97/00300

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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