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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 June 2005 (30.06.2005)

PCT

(10) International Publication Number
WO 2005/058996 A1

(51) International Patent Classification[7]: C08G 18/22, 18/16

(21) International Application Number:
PCT/GB2004/005368

(22) International Filing Date:
17 December 2004 (17.12.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0329272.9 18 December 2003 (18.12.2003) GB

(71) Applicant *(for all designated States except US)*: **JOHNSON MATTHEY PLC** [US/US]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **STENGEL, Bruno, Frederic** [FR/GB]; 3 Prestwick Court, Eaglescliffe, Stockton on Tees, Cleveland TS16 9ED (GB).

(74) Agents: **GIBSON, Sara, Hillary, Margaret** et al.; Intellectual Property Department, Johnson Matthey Catalysts, P.O. Box 1, Belasis Avenue, Billingham, Cleveland TS23 1LB (GB).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CATALYST AND METHOD OF MAKING POLYURETHANE MATERIALS

(57) Abstract: The invention is a catalyst composition which is suitable for use in catalysing the reaction between a polyol and an isocyanate composition comprising a mixture of a) an organotitanium or organozirconium compound and b) a bismuth compound, optionally in the presence of an amine. The catalyst composition is especially useful for curing polyurethane-forming mixtures in which the polyol component contains secondary hydroxyl groups.

WO 2005/058996 A1

Catalyst and method of making polyurethane materials

The present invention relates to catalyst compositions which are suitable for catalysing the reaction between a polyol and an isocyanate composition for i.e. for preparing and curing polyurethane materials.

In polyurethane manufacture the catalysts of choice in many applications have, for many years, been organic mercury compounds. This is because these catalysts provide a desirable reaction profile which offers an initial induction period in which the reaction is either very slow or does not take place, followed by a rapid reaction which continues for sufficient time to produce a relatively hard polymer article. The induction time, also known as the pot life, is desirable because it allows the liquid reaction mixture to be poured or moulded after addition of the catalyst and therefore gives the manufacturer more control over the manufacturing process. The rapid and complete reaction after the pot life is important to provide finished articles which are not sticky and which develop their desired physical properties quickly to allow fast turnaround in the production facility.

It is, however, known that mercury compounds are toxic and so there is a need for catalysts which do not contain mercury and yet which offer the manufacturer the desirable reaction profile which is offered by the known mercury-containing catalysts. Less toxic catalyst systems have been proposed, for example those based on titanium or bismuth.

Catalysts comprising compounds of titanium or zirconium are well known for use in many applications such as in esterification reactions and for curing reaction mixtures containing isocyanate and hydroxylic species to form polyurethanes. Typically, such catalysts comprise a metal alkoxide, such as titanium tetra isopropoxide, or a chelated species derived from the alkoxides. Although titanium alkoxides provide very effective catalysts for polyurethane cure reactions, they may not produce a reaction profile with the desirable pot life and cure profile described above. In many cases the reaction may be very rapid but offers only a short induction period so that the polyurethane mixture tends to gel very quickly, often before it can be cast into its final shape. A further problem is that, despite the rapid initial reaction, the resulting polyurethane does not achieve a satisfactory degree of cure within a reasonable time. This presents a particular problem when the polyurethane reaction mixture contains polyols having secondary terminal hydroxy groups, which are less readily catalysed using titanium catalysts. This results in finished articles which are sticky and difficult to handle and which may have inferior physical properties compared with articles made using a mercury catalyst.

A paper by W.J. Blank, "New Developments in Catalysis" published on the internet at www.wernerblank.com/pdfiles/paper32.pdf, describes to use of different catalysts for curing

a variety of industrial polyurethane coating systems. A bismuth catalyst was found to provide rapid cure for one system containing methoxytripropylene glycol, containing a secondary hydroxyl group.

US3714077 describes the use of organic bismuth and/or antimony compounds, optionally in the presence of certain tertiary amines, as catalyst systems for curing polyurethane foams. US4584362 describes processes for preparing polyurethane elastomers by reacting a polyether or polyester polyol with a polyisocyanate in the presence of a catalytic amount of a bismuth salt of a carboxylic acid having from 2 to 20 carbon atoms. US5011902 describes polyurethane elastomers prepared by reacting a polyether or polyester polyol with a polyisocyanate in the presence of a catalytic amount of a co-catalyst system comprising an organo-bismuth compound, preferably a bismuth salt of a carboxylic acid, and at least one organo-metallic compound, preferably a metal salt of a carboxylic acid, wherein the metal is selected from the group consisting of zinc, antimony and lithium.

US5,902,835 describes a range of catalysts for blowing polyurethane foams. The catalysts are titanium, zirconium or hafnium compounds. The use of a combination of such catalysts with other catalysts such as bismuth, zinc, cobalt etc compounds is mentioned. US6,590,057 describes polyurethane materials formed in the presence of amine catalysts and a catalyst mixture comprising an organic titanium or zirconium compound and a lithium carboxylate, optionally also containing a bismuth compound.

The bismuth catalysts of these prior art processes are relatively non-toxic. However, bismuth catalysts are rather reactive leading to relatively short pot-life and cure reactions which may be difficult to control. Furthermore, we have found that mixtures of bismuth catalysts in polyols tend to become less reactive after storage for several days.

It is an object of the invention to provide an effective catalyst compound which does not contain mercury and which may be used to manufacture polyurethane articles which overcomes some of the disadvantages of known catalyst systems.

We have found a catalyst composition which may replace mercury catalysts in certain polyurethane preparations but which has improved pot-life and hardening characteristics compared with the use of conventional mercury-free catalyst compositions.

According to a first aspect of the invention we provide a catalyst composition suitable for use in catalysing the reaction between a polyol and an isocyanate composition comprising

a) an organometallic compound which is a compound of titanium, zirconium, hafnium, iron (III), cobalt (III) or aluminium and

b) a bismuth compound.

According to a further aspect of the invention we also provide a composition comprising:

a) either

i) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or

ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane, or

iii) a mixture of (i) and (ii)

b) a catalyst composition comprising an organometallic compound which is a mixture of a compound of titanium, zirconium, hafnium, iron (III), cobalt (III) or aluminium and a bismuth compound.

c) one or more further components selected from chain modifiers, diluents, flame retardants, blowing agents, release agents, water, coupling agents, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, colourants, impact modifiers, surfactants, thixotropic agents, flame retardants, plasticisers, and other binders.

According to a further aspect of the invention, we also provide a process for the manufacture of a polyurethane elastomer, adhesive or thermoplastic polyurethane comprising the steps of :

a) forming a mixture by mixing together either

i) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or

ii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

with a catalyst composition comprising a mixture of

(iii) an organometallic compound which is a compound of titanium, zirconium, hafnium, iron (III), cobalt (III) or aluminium and

(iv)a bismuth compound,

b) adding to said mixture the other of the compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or the a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

c) forming said mixture into the required shape for the polyurethane article,

d) allowing said mixture to cure

e) optionally subjecting the mixture to specified conditions for post-cure conditioning.

The catalyst composition comprises an organometallic compound which is a compound of titanium, zirconium, hafnium, iron (III), cobalt (III) or aluminium and a bismuth compound,

which are mixed together before the catalyst composition is added to the polyol or isocyanate component of the polyurethane-forming mixture. Alternatively the mixed catalyst composition may be added to a mixture of polyol and isocyanate compound.

The catalyst composition does not contain a lithium carboxylate in contrast to the catalyst systems used in US6,590,057.

The organometallic compound is preferably of general formula:
$M(L^1)_w (L^2)_x (L^3)_y (L^4)_z$
wherein M is a metal selected from titanium(IV), zirconium(IV), hafnium(IV), iron (III), cobalt (III) or aluminium;
R is alkyl or a hydroxy-alkyl, hydroxyalkoxyalkyl, or (hydroxy)polyoxyalkyl group, and
L^1, L^2, L^3 and L^4 are each independently selected from:-

a) RO-, where R is selected from alkyl, hydroxy-alkyl, hydroxyalkoxyalkyl, or (hydroxy)polyoxyalkyl group,
b) a β-diketonate,
c) an ester or amide of acetoacetic acid,
d) a hydroxycarboxylic acid or ester thereof,
e) R^1COO- where R^1 is substituted or unsubstituted $C_1 - C_{30}$ branched or linear alkyl,
f) substituted or unsubstituted aryl including polycyclic structures such as naphthyl or anthracyl,
g) phosphate, phosphinate, phosphonate, siloxy or sulphonato or
h) a substituted or unsubstituted alkoxy or aryloxy;

w, x, y and z are each either 0 or 1,
$(w+x+y+z) \leq V$, where V= the valency of the metal M
provided that when one of L^1, L^2, L^3 and L^4 is a ligand which forms two or more covalent bonds with the metal atom, then $(w+x+y+z) < V$.

The metal M is preferably selected from titanium(IV) and zirconium(IV).
When M is titanium then it is believed that compounds containing three or four β-diketonate, acetoacetate ester or carboxylic acid, phosphate, phosphinate, phosphonate, siloxy or sulphonato ligands attached to one metal atom do not form and so such compounds are not included in the scope of the organometallic compounds shown above.

The organometallic compounds, although represented by the empirical formula shown above and throughout this specification, may form bridged structures so that a molecule of the compound may contain more than one metal atom. When present in a liquid form, the ligands L1 – L4 may exchange so that the composition is a dynamic mixture of components approximating, on average, to the composition represented by the general formulae shown.

At least one of L^1- L^4 is preferably –OR. The group OR, is labile and provides an active site for catalysis. By labile, we mean that under the conditions of the reaction which is to be catalysed, the group OR may undergo substitution or insertion by one of the reactant molecules to facilitate the reaction mechanism. The relatively labile OR group may detach readily from the metal atom and exchange with other molecules which have an active proton as in -OH or -COOH functional groups for example. R may be an alkyl group, such as a $C_1 – C_{22}$ alkyl, more preferably a $C_1 – C_8$ alkyl. R may be a hydroxy-alkyl group derived from a diol such as 1,4-butane diol or a polyoxyalkyl group (also known as a glycol-ether group) such as a dialkylene glycol, polyalkylene glycol, for example diethylene glycol or polyethylene glycol. Preferred R groups include ethyl, n-propyl, isopropyl, n-butyl, t-butyl, pentyl, hexyl or 2-ethyl-hexyl, hydroxybutyl, polyoxyethyl and 2-(2-hydroxyethoxy)-ethyl.

In one embodiment, -OR is an alkoxide derived from a diol, e.g. 1,4-butane diol, diethylene glycol, ethylene glycol or a polyalkylene glycol. In the manufacture of polyurethanes, a short-chain polyol, normally a diol such as1,4-butane diol, is often used as a chain extender as part of a mixture of polyols to be reacted with a polyisocyanate. It may therefore be beneficial to provide as the labile OR group of the catalyst a functionalised alkoxide, which is capable of forming a bis or poly functional alcohol on leaving the organometallic compound and thereby functioning as a chain extender rather than forming a singly functional alcohol which may have a tendency to terminate the growing polymer chains.

The organometallic compound may, for example, be a titanium or zirconium tetraalkoxide of formula $M(OR)_4$ where R is alkyl or hydroxy alkyl , preferably $C_1 – C_{22}$ alkyl, more preferably C_1 to C_8 alkyl. Preferred R groups include ethyl, n-propyl, isopropyl, n-butyl, t-butyl, pentyl, hexyl or 2-ethyl-hexyl, hydroxybutyl, polyoxyethyl and 2-(2-hydroxyethoxy)-ethyl.

L^1- L^4 may alternatively be derived from a β-diketone such as acetylacetone, an alkylacetoacetate or an N-alkylacetoacetamide (where alkyl is preferably a C_1 to C_8 alkyl group), such as ethylacetoacetate or N,N-diethylacetoacetamide, a hydroxycarboxylic acid or ester thereof, such as salicylic acid, mandelic acid, levulinic acid, naphthalene dicarboxylic acid, citric acid, lactic acid, tartaric acid; substituted or unsubstituted aryloxy such as phenoxy or naphthoxy, an alkyl phenoxy, benzoic acid or a $C_2 – C_{30}$ carboxylic acid, preferably a $C_6 – C_{22}$ carboxylic acid such as stearic, isostearic or 2-ethyl-hexylcarboxylic acid.

When one of L^1- L^4 is a ligand which forms two covalent bonds with the metal atom such as for example when L^1 is salicylic acid or mandelic acid, and x = 1 then y may be 0 and in this case w+x+y+z is less than V. So for example, when M is Ti(IV) and L^1 is salicylic acid, V = 4, y = 0 and w+x+y+z = 3. Examples of ligands which form two covalent bonds with the metal atom include hydroxycarboxylic acids, such as salicylic acid or esters thereof, a bis-hydroxy compound such as 2-hydroxy-benzyl alcohol (salicyl alcohol), or esters thereof e.g. with a carboxylic acid having a β-carbonyl group such as 3-oxo-butyric acid for example; a substituted phenol, especially a bisphenol compound where two phenol moieties are linked by a hydrocarbon or nitrogen-containing bridge such as 2,2'ethylidene bis (4,6-di-*tert*-butyl phenolate), symmetrical or unsymmetrical hydrazine- or amine-bridged phenol derivatives.

L^1, L^2, $L^3$and L^4 may be capable of forming a coordinating bond with the metal atom in addition to a covalent bond so that the total number of bonds formed between M and the L groups is greater than V. This may occur, for example, when L^1 or L^2 is a diketonate such as acetylacetone or an alkyl acetoacetate or acetoacetamide which can react with the metal atom at the carbonyl group through the enolate form of the compound and also form a coordinating bond between the electron-donating ester or amide group and the metal. When M is titanium, for example, this leads to a stable complexed form of titanium.

In preferred compositions the organometallic compound is of general formula

$RO\text{-}M(L^1)_x (L^2)_y (L^3)_z$

wherein M is a metal selected from titanium, zirconium, hafnium, iron (III), cobalt (III) or aluminium;

R is alkyl or a hydroxy-alkyl, hydroxyalkoxyalkyl, or (hydroxy)polyoxyalkyl group, and

L^1 , L^2 and L^3 are each independently selected from a diketonate, an ester or amide of acetoacetic acid, a hydroxycarboxylic acid or ester thereof, R^1COO- where R^1 is substituted or unsubstituted $C_1 - C_{30}$ branched or linear alkyl, substituted or unsubstituted aryl including polycyclic structures such as naphthyl or anthracyl, phosphate, phosphinate, phosphonate, siloxy or sulphonato, substituted or unsubstituted aryloxy, a polyoxyalkoxy or hydroxyalkoxyalkoxy group;

provided that when L^1 is a ligand which forms two covalent bonds with the metal atom, and x=1 then y = 0;

x and y are each either 0 or 1,

z=1

$(x+y+z) \leq V-1$, where V= the valency of the metal M.

More preferably, when R is alkyl, L^1 and L^2 are each independently selected from a β-diketonate, an ester or amide of acetoacetic acid, a hydroxycarboxylic acid or ester thereof or siloxy.

Alternatively, when R is a hydroxy-alkyl hydroxyalkoxyalkyl, or (hydroxy)polyoxyalkyl group, L^1 and L^2 are preferably each independently selected from a diketonate, an ester or amide of acetoacetic acid, a hydroxycarboxylic acid or ester thereof, R^1COO- where R^1 is substituted or unsubstituted $C_1 - C_{30}$ branched or linear alkyl, substituted or unsubstituted aryl including polycyclic structures such as naphthyl or anthracyl, phosphate, phosphinate, phosphonate, siloxy or sulphonato.

In the preferred formulations, L^3 is selected from substituted or unsubstituted aryloxy, R^2COO- where R^2 is a linear or branched $C_1 - C_{30}$ alkyl or a substituted or unsubstituted aryl, a polyoxyalkoxy or hydroxyalkoxyalkoxy group;

For clarity, some examples of suitable organotitanium and organozirconium compounds include:- tetraethyl titanate, tetraisopropyltitanate, $Ti(DEAA)_2(1\text{-naphthoxy})(OCH(CH_3)_2)$, (DEAA = N,N-diethylacetoacetamido), $Ti(DEAA)_2(propylphenoxy)(OCH(CH_3)_2)$, $Zr(OCH(CH_3)_2)\ (OCOC_6H_4O)(OCOC_{17}H_{35})$, $Ti(OCH(CH_3)_2)\ (OCOC_{17}H_{35})_3$, $Ti(OCH(CH_3)_2)_2(CH_3COCH_2COCH_3)_2$, $Ti(OC_2H_4OC_2H_4OH)_2(CH_3COCH_2COCH_3)_2$, $Ti(OC_2H_4OC_2H_4OH)(CH_3COCH_2COCH_3)_2(OCOC_{17}H_{35})$, $Ti(OC_2H_4OC_2H_4OH)(OC_6H_5)_3$, $Ti(OCH(CH_3)_2)(OCOC_6H_4O)(OCOC_{17}H_{35})$, $Ti(OCH(CH_3)_2)(OC_6H_5)(C_2H_5OCOCH_2COCH_3)_2$, $Ti(OCH(CH_3)_2)(CH_3COCH_2COCH_3)_2(OCOC_{17}H_{35})$, $Ti(OCH(CH_3)_2)(CH_3COCH_2COCH_3)_2(OC_6H_5)$, $Ti(OCH(CH_3)_2)\ (OC_6H_4CH_3)_3$, $Ti(OCH(CH_3)_2)(OC_6H_5)_3$, $Ti(OCH(CH_3)_2)_2(CH_3COCH_2COCH_3)_2$, $Zr(OCH(CH_3)_2)_2(CH_3COCH_2COCH_3)_2$, $Ti(OCH(CH_3)_2)_2\ (C_2H_5OCOCH_2COCH_3)_2$, $Ti(OCH(CH_3)_2)_2\ (C_2H_5OCOCH_2COCH_3)_2$, $Ti(DEAA)_2(4\text{-dodecylphenoxy})(OCH(CH_3)_2)$, $Zr(DEAA)_2(4\text{-dodecylphenoxy})\ (OCH(CH_3)_2)$, $Ti(DEAA)_2(phenoxy)\ (OCH(CH_3)_2)$, $Ti(OCH(CH_3)_2)\ (OCOC_{17}H_{35})\ (C_2H_5OCOCH_2COCH_3)_2$, $Zr(OCH(CH_3)_2)\ (OCOC_{17}H_{35})\ (C_2H_5OCOCH_2COCH_3)_2$

The bismuth compound may be inorganic, e.g. bismuth trioxide but is preferably an organobismuth compound, especially compounds of bismuth with $C_2 - C_{20}$ carboxylic acids, e.g. bismuth triacetate or more especially with $C_8 - C_{12}$ carboxylic acids. Suitable organobismuth catalysts are known for use as catalysts in polyurethane systems and typical examples include bismuth tris(neodecanoate) and bismuth tris(2-ethyl-hexylcarboxylate). The bismuth compounds may be made by reacting a bismuth salt such as bismuth trioxide with a carboxylic acid. The bismuth compound is preferably present as a solution in e.g. a carboxylic acid.

The catalyst composition preferably contains the organometallic compound and bismuth compound in a ratio of about 1 -10 :10 - 1 by weight more preferably about 1 :1 by weight.

The catalyst composition may additionally include an amine. Amines are known catalysts for polyurethane reactions and any known amine for this purpose may be used. Secondary and especially tertiary amines are preferred. Suitable amines include morpholines, e.g.2,2'-dimorpholinodiethyl ether (DMDEE), n-alkyl-morpholines, alkyl or aryl amines, e.g. triethylenediamine, N,N-dimethylcyclohexylamine, bis-(2-dimethylaminoethyl)ether, N,N-dimethylaminoethanol, N,N- dimethylcyclohexylamine, bis-(2-diemthylaminoethyl)ether, N,N,N',N',N"-pentamethyldiethylene-triamine, N,N-dimethylbenzylamine, N,N-dimethylcetylamine, N-ethylmorpholine, methylene-bis-dimethylcyclohexylamine, N,N,N',N',N"-pentamethyldipropylene-triamine, N,N'-diethylpiperazine, N,N,N'-trimethylaminoethyl-ethanolamine, 1-(2-hydroxypropyl)imidazole, 1,4-bis(2-hydroxypropyl)-2-methylpiperazine and similar compounds. The catalyst composition preferably contains the organotitanium and/or organozirconium compound and amine compound in a ratio of about 1 -10 :10 - 1 by weight more preferably about 1 :1 by weight.

The organometallic compound or its mixture with the bismuth compound may contain one or more additional components. In particular we have found that the presence of a liquid diluent or solvent may provide a benefit. The liquid component may be selected from an acid, a diol or polyol, a β-diketonate or a ketone. Suitable acids include alkyl carboxylic acids, for example a $C_2 - C_{30}$ carboxylic acid, especially a $C_4 - C_{22}$ carboxylic acid such as butyric, stearic, isostearic, oleic or 2-ethyl-hexylcarboxylic acid. Suitable diols or polyols include 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butane diol or a dihydric alcohol containing a longer chain such as diethylene glycol or a polyethylene glycol or polypropylene glycol. Suitable β-diketonates include acetyl acetone, alkyl acetoacetates, especially ethylacetoacetate or 2-ethylhexylacetoacetate. The additional liquid component may be mixed with the compound of the invention in all proportions, suitably the proportions of the catalyst composition : additional liquid used will be in the range 1:99 – 99:1, more usually 10:90 – 90:10 by weight, depending upon the molecular weight of the additional liquid and the catalyst composition. Preferably, when present, the additional liquid is added at a ratio of from 0.1 to 10 moles of the liquid compound per mole of titanium or zirconium, e.g. from about 0.5 to 5, preferably from about 0.5 to 3 moles of the liquid compound per mole of titanium or zirconium.

It is preferred that catalysts for curing polyurethanes are supplied in a liquid form. The organometallic compositions of the invention may be supplied neat (particularly when the composition is, itself a liquid) or as a solution in a suitable solvent, such as toluene, hexane, heptane etc. More preferably it is supplied in a liquid component which is already present in or which is compatible with the polyurethane reaction components, such as a diol or glycol e.g. butane diol or diethylene glycol.

The compound having more than one hydroxy group which is capable of reacting with an isocyanate group-containing material to form a polyurethane or the compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane may comprise a mixture of such compounds or a mixture of such compounds with different compounds, e.g. fillers or other additives etc.

The process of the invention is comprises the reaction between a hydroxy-functionalised molecule, such as a polyol, and an isocyanate-functionalised molecule, such as a polyisocyanate to form an elastomer, an adhesive or a thermoplastic mouldable material. This reaction forms the basis of many commercially available two-component polyurethane systems. The process is not intended to include the formation of polyurethane foams in which the catalyst is a blowing agent. Therefore the reactants preferably do not contain water in sufficient amounts as to produce a blown foam by reaction of the water with the isocyanate material. In particular, the polyol component should contain less than 0.3%, more preferably less than 0.1%, of water by weight.

The polyol component may be any suitable for the manufacture of polyurethanes and includes polyester-polyols, polyester-amide polyols, polyether-polyols, polythioetherpolyols, polycarbonate polyols, polyacetal polyols, polyolefin polyols polysiloxane polyols, dispersions or solutions of addition or condensation polymers in polyols of the types described above, often referred to as "polymer" polyols. A very wide variety of polyols has been described in the prior art and is well known to the formulator of polyurethane materials.

Typically, a mixture of polyols is used to manufacture polyurethane having particular physical properties. The polyol or polyols is selected to have a molecular weight, backbone type and hydroxy functionality which is tailored to the requirements of the formulator. Typically the polyol includes a chain extender, which is often a relatively short-chain diol such as 1,4-butane diol or diethylene glycol or a low molecular weight polyethylene glycol. Alternative chain extenders in commercial use, such as diamines, e.g. MOCA (4,4-methylene bis (2-chloroaniline)) may also be used.

The isocyanate compositions used for polyurethane manufacture suitable for use with the catalysts of the present invention may be any organic polyisocyanate compound or mixture of organic polyisocyanate compounds which are commercially useful for the purpose. Preferably the polyisocyanate is liquid at room temperature.
Suitable organic polyisocyanates include diisocyanates, particularly aromatic diisocyanates, and isocyanates of higher functionality. Examples of suitable organic polyisocyanates

include aliphatic isocyanates such as hexamethylene diisocyanate and isophorone diisocyanate; and aromatic isocyanates such as m- and p-phenylene diisocyanate, tolylene-2,4- and tolylene- 2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, chlorophenylene-2,4-diisocyanate, naphthylene-1,5-diisocyanate, diphenylene-4,4'-diisocyanate, 4,4'-diisocyanate-3,3'-dimethyl-diphenyl, 3-methyldiphenylmethane-4,4'-di- isocyanate and diphenyl ether diisocyanate; and cycloaliphatic diisocyanates such as cyclohexane-2,4- and -2,3-diisocyanate, 1-methylcyclohexyl-2,4- and -2,6-diisocyanate and mixtures thereof and bis-(isocyanatocyclohexyl)methane and triisocyanates such as 2,4,6-triisocyanatotoluene and 2,4,4-tri- isocyanatodiphenylether.

Modified polyisocyanates containing isocyanurate, carbodiimide or uretonimine groups may be used. The polyisocyanate may also be an isocyanate-ended prepolymer made by reacting an excess of a diisocyanate or higher functionality polyisocyanate with a polyol for example a polyether polyol or a polyester polyol. The use of prepolymers is common in commercially available polyurethane systems. In these cases, polyols may already be incorporated in the isocyanate or prepolymer whilst further components such as chain extenders, polyols etc may be mixed with the isocyanate prepolymer mixture before polymerisation.

Mixtures of isocyanates may be used in conjunction with the organometallic composition of the invention, for example a mixture of tolylene diisocyanate isomers such as the commercially available mixtures of 2,4- and 2,6-isomers. A mixture of di- and higher polyisocyanates, such as trimers (isocyanurates) or pre-polymers, may also be used. Polyisocyanate mixtures may optionally contain monofunctional isocyanates such as p-ethyl phenylisocyanate.

The organometallic composition of the invention is typically added to the polyol prior to mixing together the polyol component with the isocyanate component to form the polyurethane. However, the organometallic composition may instead be added to the isocyanate component if required.

A composition containing a catalyst composition of the present invention and a polyisocyanate and compounds reactive therewith may further comprise conventional additives such as chain modifiers, diluents, flame retardants, blowing agents, release agents, water, coupling agents, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, colourants, impact modifiers, surfactants, thixotropic agents, flame retardants, plasticisers, and other binders. The selection of these and other ingredients for inclusion in a formulation for a polyurethane composition is well known to the skilled person and may be selected for the particular purpose. When the mixture has been allowed to

cure it may be further conditioned to allow for post-cure. Typically this occurs when the polyurethane article, coating etc has hardened to a state in which it may be handled, demoulded etc and then it may be held at elevated temperature, e.g. by placing in an oven, to develop or enhance the full cured properties of the article.

The catalysts of the present invention are useful for the manufacture of polyurethane foams, flexible or rigid articles, coatings, adhesives, elastomers, sealants, thermoplastic polyurethanes, and binders e.g. for oriented strand board manufacture. The catalysts of the present invention may also be useful in preparing polyurethane prepolymers, i.e. urethane polymers of relatively low molecular weight which are supplied to end-users for curing into polyurethane articles or compositions of higher molecular weight.

The catalysts are typically present in the isocyanate and/or alcohol mixture to give a concentration in the range 1 x 10^{-4} to 10% by weight, preferably up to about 4% by weight based upon the weight of the total reaction system, i.e. the total weight of the polyisocyanate and polyol components .

The invention will be further described in the following examples.

Example 1

In this example the organotitanium compound is Ti(N,N-diethylacetoacetamido)$_2$ (2-isopropylphenoxy)(isopropoxy). The bismuth compound is Coscat™ 83, a commercially available bismuth trisneodecanoate in neodecanoic acid, containing 16.5% by weight of bismuth. The amine is 2,2'-dimorpholinodiethyl ether (DMDEE).

Preparation of the titanium compound

110g (0.70 moles) of N,N-diethylacetoacetamide (DEAA) was added very slowly, with stirring, to 100g (0.35 moles) of tetraisopropyl titanium (Vertec™ TIPT) in a rotary flask. The reaction was exothermic. The mixture was distilled under reduced pressure (30" Hg) at a temperature of 60°C to remove 42g (0.75 moles) of 2–propanol. 48g (0.35 moles) of 2-isopropyl phenol was added to the mixture in the flask. The remaining 2–propanol (0.35 mol, 21g) was then removed by reduced pressure distillation.

Preparation of the catalyst composition

The ingredients indicated in Table 1 were mixed together in equal parts by weight and then made up to a total weight of 10g with a commercial polyol and mixed.

0.1g of the total catalyst composition, (i.e of the polyol and catalyst composition mixture prepared as described above) was put in a cup, together with 75g of the polyol used to make up the catalyst composition. The catalyst and polyol were mixed in a high-speed mixer at 3000 rpm for 30 seconds. An isocyanate prepolymer based on 4,4'methylenebis(phenyl isocyanate) (30g)

was added and the mixture was again mixed in the high-speed mixer for 30 seconds. The mixture was then divided between a disposable smooth-walled aluminium weighing dish and a 50ml beaker. When the moulding in the aluminium dish became tack-free, it was subjected to hardness measurement using a BAREISS HHP-2001 hardness tester to measure Shore A hardness as described in DIN 53505. The sample in the beaker was immediately introduced to a Trombotech™ integrated viscosity and temperature measurement instrument and the viscosity and exotherm was recorded over 90 minutes or until a gel-time could be determined. The gel-time is calculated as the point at which the tangent to the steepest part of the viscosity vs time curve cuts the time axis. It is a representation of the time at which the curing polymer / monomer mixture ceases to flow. A gel-time of about 600s normally provides a convenient balance between providing a period in which the mixture may flow to enable a mould to be filled or a coating to flow on application whilst providing a sufficiently rapid cure for a fast throughput in the manufacture of polyurethane articles. The cure and testing was also carried out using also a commercially available mercury-based catalyst, phenyl mercury neodecanoate, as a comparison. The results are shown in Table 1.

Table 1

Catalyst composition	Ti (g)	Bi (g)	Amine (g)	Gel time(s)	Shore A hardness at specified time(hours) after mixing								
					1	2	3	4	5	6	24	48	72
Phenyl mercury neodecanoate (comparison)	-	-	-	610	44	48	53	55	57	57	65	68	68
Comparison	0.5	-	-	186	0	0	0	0	2	2	10**	20	33
Invention	0.5	0.5	-	882	53	57	58	59	60	60	64	68	68
Invention	0.5	0.5	0.5	181	55	59	61	63	63	64	65	68	68
Comparison	-	0.5	-	285	43	50	50	50	52	54	61*	65	65
Comparison	-	-	0.5	262	0	0	0	0	0	0	0	7	14
Comparison	0.5	-	0.5	827	0	0	0	0	5	6	16**	21	30
Comparison	-	0.5	0.5	3459	48	53	55	57	59	59	61	60	65

Notes * sample slightly tacky after 24 hours; ** sample very tacky after 24 hours

Example 2

A catalyst composition according to the invention was prepared by mixing together the following components in a glass vial:-

(i) 40g of Vertec™ TAA, available from Johnson Matthey Catalysts, a commercially available liquid titanium complex of di(isopropoxy)titanium bis(2,4-pentanedionate) in 2-propanol, containing about 10% Ti,

(ii) 20g BiCAT™ HM available from Shepherd Chemical, a commercially available bismuth 2-ethylhexanoate in 2-ethylhexanoic acid containing about 28% Bi and

(iii) 40g of a solution of 25g triethylene diamine in 100g of 1,4-butane diol.

Example 3

A catalyst composition according to the invention was prepared by mixing together the following components in a glass vial:-

(i) 40g of a titanium compound made by the following method: a reactor was charged with tetra(isopropoxy)titanium (140 g, Vertec™ TIPT from Johnson Matthey Catalysts). Ethylacetoacetate (128 g) was then added with stirring. The resulting product was a pale red liquid. The displaced alcohol (48 g , isopropanol) was then removed by evaporation to leave a red liquid, containing about 11% Ti,

(ii) 20g "Coscat™ 16" available from CasChem, a commercially available bismuth carboxylate in dipropylene glycol containing about 16.5% Bi and

(iii) 40g of a solution of 25g triethylene diamine in 100g of 1,4-butane diol.

Example 4

A catalyst composition according to the invention was prepared by mixing together the following components in a glass vial:-

(i) 50.4g of $Ti(OCH(CH_3)_2)(OCOC_6H_4O)(OCOC_{17}H_{35})$ made by the following method: a rotary flask was charged with tetra(isopropoxy)titanium Vertec™ TIPT from Johnson Matthey Catalysts) (50 g, 0.1761moles). 50.02g (0.1761 mole) of isostearic acid was added very slowly. Then, 10g (0.1761 mole) of 2-propanol was removed by reduced pressure distillation at 91°C. 24.33g (0.1761 mole) of salicylic acid was added to the flask very slowly. Then a further 20g (0.3522 mole) of 2-propanol was stripped at 95°C and 25 inches Hg.

(ii) 50.4g of BiCAT™ HM.

Claims

1. A process for the manufacture of a polyurethane elastomer, adhesive or thermoplastic polyurethane comprising the steps of :

a) forming a mixture by mixing together either

j) a compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or

iii) a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

with a catalyst composition comprising a mixture of

(iii) an organometallic compound which is a compound of titanium, zirconium, hafnium, iron (III), cobalt (III) or aluminium and

(iv)a bismuth compound,

b) adding to said mixture the other of the compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane or the a compound having more than one isocyanate group which is capable of reacting with a hydroxyl group-containing material to form a polyurethane,

c) forming said mixture into the required shape for the polyurethane article,

d) allowing said mixture to cure

e) optionally subjecting the mixture to specified conditions for post-cure conditioning.

2. A process as claimed in claim 1, wherein the catalyst composition further comprises an amine.

3. A process as claimed in claim 1 or claim 2 , wherein the organometallic compound is of general formula:

$M(L^1)_w (L^2)_x (L^3)_y (L^4)_z$

In which M is a metal selected from titanium, zirconium, hafnium, iron (III), cobalt (III) or aluminium;

R is alkyl or a hydroxy-alkyl, hydroxyalkoxyalkyl, or (hydroxy)polyoxyalkyl group, and

L^1, L^2, L^3 and L^4 are each independently selected from:-

RO-, where R is selected from alkyl, hydroxy-alkyl, hydroxyalkoxyalkyl, or (hydroxy)polyoxyalkyl group,

a β-diketonate,

an ester or amide of acetoacetic acid,

a hydroxycarboxylic acid or ester thereof,

R^1COO- where R^1 is substituted or unsubstituted $C_1 - C_{30}$ branched or linear alkyl, substituted or unsubstituted aryl including polycyclic structures such as naphthyl or anthracyl,

phosphate, phosphinate, phosphonate, siloxy or sulphonato or

a substituted or unsubstituted alkoxy or aryloxy;
w, x, y and z are each either 0 or 1,
(w+x+y+z) ≤ V, where V= the valency of the metal M
provided that when one of L^1, L^2, L^3 and L^4 is a ligand which forms two or more covalent bonds with the metal atom, then (w+x+y+z) < V.

4. A process as claimed in any one of claims 1 - 3, wherein the organometallic composition is an organotitanium or organozirconium compound.

5. A process as claimed in claim 4, wherein the organotitanium or organozirconium compound is selected from a titanium or zirconium tetra-alkoxide

6. A process as claimed in any one of claims 1 - 5, wherein the organotitanium or organozirconium compound is selected from tetraethyl titanate, tetraisopropyltitanate, $Ti(DEAA)_2(1\text{-naphthoxy})(OCH(CH_3)_2)$, (DEAA = N,N-diethylacetoacetamido), $Ti(DEAA)_2(propylphenoxy)(OCH(CH_3)_2)$, $Zr(OCH(CH_3)_2)\ (OCOC_6H_4O)(OCOC_{17}H_{35})$, $Ti(OCH(CH_3)_2)\ (OCOC_{17}H_{35})_3$, $Ti(OCH(CH_3)_2)_2(CH_3COCH_2COCH_3)_2$, $Ti(OC_2H_4OC_2H_4OH)_2(CH_3COCH_2COCH_3)_2$, $Ti(OC_2H_4OC_2H_4OH)(CH_3COCH_2COCH_3)_2(OCOC_{17}H_{35})$, $Ti(OC_2H_4OC_2H_4OH)(OC_6H_5)_3$, $Ti(OCH(CH_3)_2)(OCOC_6H_4O)(OCOC_{17}H_{35})$, $Ti(OCH(CH_3)_2)(OC_6H_5)(C_2H_5OCOCH_2COCH_3)_2$, $Ti(OCH(CH_3)_2)(CH_3COCH_2COCH_3)_2(OCOC_{17}H_{35})$, $Ti(OCH(CH_3)_2)(CH_3COCH_2COCH_3)_2(OC_6H_5)$, $Ti(OCH(CH_3)_2)\ (OC_6H_4CH_3)_3$, $Ti(OCH(CH_3)_2)(OC_6H_5)_3$, $Ti(OCH(CH_3)_2)_2(CH_3COCH_2COCH_3)_2$, $Zr(OCH(CH_3)_2)_2(CH_3COCH_2COCH_3)_2$, $Ti(OCH(CH_3)_2)_2\ (C_2H_5OCOCH_2COCH_3)_2$, $Ti(OCH(CH_3)_2)_2\ (C_2H_5OCOCH_2COCH_3)_2$, $Ti(DEAA)_2(4\text{-dodecylphenoxy})(OCH(CH_3)_2)$, $Zr(DEAA)_2(4\text{-dodecylphenoxy})\ (OCH(CH_3)_2)$, $Ti(DEAA)_2(phenoxy)\ (OCH(CH_3)_2)$, $Ti(OCH(CH_3)_2)\ (OCOC_{17}H_{35})\ (C_2H_5OCOCH_2COCH_3)_2$, $Zr(OCH(CH_3)_2)\ (OCOC_{17}H_{35})\ (C_2H_5OCOCH_2COCH_3)_2$.

7. A process as claimed in claim 1, wherein the organometallic composition is of general formula
$RO\text{-}M(L^1)_x\ (L^2)_y\ (L^3)_z$
wherein M is a metal selected from titanium, zirconium, hafnium, iron (III), cobalt (III) or aluminium;
R is alkyl or a hydroxy-alkyl, hydroxyalkoxyalkyl, or (hydroxy)polyoxyalkyl group, and
L^1 , L^2 and L^3 are each independently selected from a diketonate, an ester or amide of acetoacetic acid, a hydroxycarboxylic acid or ester thereof, R^1COO- where R^1 is substituted or unsubstituted $C_1 - C_{30}$ branched or linear alkyl, substituted or unsubstituted aryl including polycyclic structures such as naphthyl or anthracyl, phosphate, phosphinate, phosphonate,

siloxy or sulphonato, substituted or unsubstituted aryloxy, a polyoxyalkoxy or hydroxyalkoxyalkoxy group;
provided that when L^1 is a ligand which forms two covalent bonds with the metal atom, and x= 1 then y = 0;
x and y are each either 0 or 1,
z=1
$(x+y+z) \leq V-1$, where V= the valency of the metal M.

8. A process as claimed in claim 7, wherein when R is alkyl, L^1 and L^2 are each independently selected from a β-diketonate, an ester or amide of acetoacetic acid, a hydroxycarboxylic acid or ester thereof or siloxy.

9. A process as claimed in claim 7, wherein when R is a hydroxy-alkyl hydroxyalkoxyalkyl, or (hydroxy)polyoxyalkyl group, L^1 and L^2 are each independently selected from a diketonate, an ester or amide of acetoacetic acid, a hydroxycarboxylic acid or ester thereof, R^1COO- where R^1 is substituted or unsubstituted $C_1 - C_{30}$ branched or linear alkyl, substituted or unsubstituted aryl including polycyclic structures such as naphthyl or anthracyl, phosphate, phosphinate, phosphonate, siloxy or sulphonato.

10. A process as claimed in any one of claims 7 - 9, wherein L^3 is selected from substituted or unsubstituted aryloxy, R^2COO- where R^2 is a linear or branched $C_1 - C_{30}$ alkyl or a substituted or unsubstituted aryl, a polyoxyalkoxy or hydroxyalkoxyalkoxy group;

11. A process as claimed in any of the preceding claims, which is carried out in the presence of from 0 – 0.3% by weight of water.

12. A process as claimed in claim 11, which is carried out in the presence of from 0 – 0.1% by weight of water.

13. A process as claimed in any of the preceding claims, wherein the compound having more than one hydroxy group which is capable of reacting with an isocyanate group - containing material to form a polyurethane contains less than 0.3% by weight of water.

14. A process as claimed in claim 13, wherein the compound having more than one hydroxy group which is capable of reacting with an isocyanate group -containing material to form a polyurethane contains less than 0.1% by weight of water.

15. A process as claimed in any of the preceding claims, wherein the catalyst composition does not contain a lithium carboxylate.

16. A catalyst composition, suitable for in catalysing the reaction between a polyol and an isocyanate composition comprising

a) an organometallic composition of general formula

$RO\text{-}M(L^1)_x(L^2)_y(L^3)_z$

wherein M is a metal selected from titanium, zirconium, hafnium, iron (III), cobalt (III) or aluminium;

R is alkyl or a hydroxy-alkyl, hydroxyalkoxyalkyl, or (hydroxy)polyoxyalkyl group, and

L^1, L^2 and L^3 are each independently selected from a diketonate, an ester or amide of acetoacetic acid, a hydroxycarboxylic acid or ester thereof, R^1COO- where R^1 is substituted or unsubstituted $C_1 - C_{30}$ branched or linear alkyl, substituted or unsubstituted aryl including polycyclic structures such as naphthyl or anthracyl, phosphate, phosphinate, phosphonate, siloxy or sulphonato, substituted or unsubstituted aryloxy, a polyoxyalkoxy or hydroxyalkoxyalkoxy group;

provided that when L^1 is a ligand which forms two covalent bonds with the metal atom, and $x = 1$ then $y = 0$;

x and y are each either 0 or 1,

$z=1$

$(x+y+z) \leq V-1$, where V= the valency of the metal M.

and

b) a bismuth compound.

17. A catalyst composition as claimed in claim 16, wherein

when R is alkyl, L^1 and L^2 are each independently selected from a β-diketonate, an ester or amide of acetoacetic acid, a hydroxycarboxylic acid or ester thereof or siloxy and

when R is a hydroxy-alkyl hydroxyalkoxyalkyl, or (hydroxy)polyoxyalkyl group, L^1 and L^2 are each independently selected from a diketonate, an ester or amide of acetoacetic acid, a hydroxycarboxylic acid or ester thereof, R^1COO- where R^1 is substituted or unsubstituted $C_1 - C_{30}$ branched or linear alkyl, substituted or unsubstituted aryl including polycyclic structures such as naphthyl or anthracyl, phosphate, phosphinate, phosphonate, siloxy or sulphonato,

and L^3 is selected from substituted or unsubstituted aryloxy, R^2COO- where R^2 is a linear or branched $C_1 - C_{30}$ alkyl or a substituted or unsubstituted aryl, a polyoxyalkoxy or hydroxyalkoxyalkoxy group.

18. A catalyst composition as claimed in either claim 16 or claim 17, wherein the metal M is selected from titanium or zirconium.

19. A catalyst composition as claimed in claim 18, wherein the organometallic composition is selected from $Ti(DEAA)_2(1\text{-naphthoxy})(OCH(CH_3)_2)$,

$Ti(DEAA)_2$(propylphenoxy)$(OCH(CH_3)_2)$, $Zr(OCH(CH_3)_2)$ $(OCOC_6H_4O)(OCOC_{17}H_{35})$, $Ti(OCH(CH_3)_2)$ $(OCOC_{17}H_{35})_3$, $Ti(OC_2H_4OC_2H_4OH)(CH_3COCH_2COCH_3)_2(OCOC_{17}H_{35})$, $Ti(OC_2H_4OC_2H_4OH)(OC_6H_5)_3$, $Ti(OCH(CH_3)_2)(OCOC_6H_4O)(OCOC_{17}H_{35})$, $Ti(OCH(CH_3)_2)(OC_6H_5)(C_2H_5OCOCH_2COCH_3)_2$, $Ti(OCH(CH_3)_2)(CH_3COCH_2COCH_3)_2(OCOC_{17}H_{35})$, $Ti(OCH(CH_3)_2)(CH_3COCH_2COCH_3)_2(OC_6H_5)$, $Ti(OCH(CH_3)_2)$ $(OC_6H_4CH_3)_3$, $Ti(OCH(CH_3)_2)(OC_6H_5)_3$, $Ti(OCH(CH_3)_2)_2$ $(C_2H_5OCOCH_2COCH_3)_2$, $Ti(DEAA)_2$(4-dodecylphenoxy)$(OCH(CH_3)_2)$, $Zr(DEAA)_2$(4-dodecylphenoxy) $(OCH(CH_3)_2)$, $Ti(DEAA)_2$(phenoxy) $(OCH(CH_3)_2)$, $Ti(OCH(CH_3)_2)$ $(OCOC_{17}H_{35})$ $(C_2H_5OCOCH_2COCH_3)_2$, $Zr(OCH(CH_3)_2)$ $(OCOC_{17}H_{35})$ $(C_2H_5OCOCH_2COCH_3)_2$; where DEAA = N,N-diethylacetoacetamido.

20. A catalyst composition as claimed in any on claims 16 – 19, in the form of a solution in a solvent selected from toluene, hexane, heptane, a carboxylic acid, a diol, a polyol, a β-diketonate or a ketone.

INTERNATIONAL SEARCH REPORT

Internati pplication No
PCT/GB2004/005368

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/22 C08G18/16

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 902 835 A (MEIER ET AL) 11 May 1999 (1999-05-11) cited in the application claim 1 column 5, line 18 - line 20	1-20
X	US 6 590 057 B1 (BRECHT KLAUS ET AL) 8 July 2003 (2003-07-08) cited in the application experiment 19	1-20
X	EP 1 241 234 A (KANSAI PAINT CO., LTD; HONDA GIKEN KOGYO KABUSHIKI KAISHA) 18 September 2002 (2002-09-18) example 1	1-20

☐ 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

"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	Date of mailing of the international search report
1 April 2005	18/04/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Müller, M

INTERNATIONAL SEARCH REPORT

Internat ılication No
PCT/GB2004/005368

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5902835 A	11-05-1999	BR 9901754 A	11-04-2000
		EP 0960894 A1	01-12-1999
		JP 2000026564 A	25-01-2000
US 6590057 B1	08-07-2003	DE 10142296 C1	13-02-2003
		WO 03020783 A1	13-03-2003
		EP 1432749 A1	30-06-2004
		HU 0401279 A2	28-09-2004
		JP 2005501940 T	20-01-2005
		TW 593395 B	21-06-2004
EP 1241234 A	18-09-2002	CA 2376376 A1	12-09-2002
		EP 1241234 A1	18-09-2002
		JP 3602828 B2	15-12-2004
		JP 2002338879 A	27-11-2002
		US 2002198290 A1	26-12-2002