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<p>(54) Title: POLYKETONE BARRIER MATERIALS HAVING IMPROVED BARRIER PROPERTIES</p>		
<p>(57) Abstract</p> <p>A barrier material comprising a linear polyketone polymer having an alternating structure of (a) units derived from carbon monoxide, and (b) units derived from ethylene, hexene and optionally a further alpha-olefin which has a low oxygen permeability and also a low variability of oxygen permeability with relative humidity.</p>		

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**POLYKETONE BARRIER MATERIALS HAVING IMPROVED BARRIER  
PROPERTIES**

The present invention relates to barrier materials comprising a terpolymer comprising units derived from carbon monoxide, ethylene, hexene, and optionally a further alpha olefin, and particularly to such barrier materials having low oxygen permeability and also a low variability of oxygen permeability with relative humidity.

5 For the purposes of this patent, polyketones are defined as linear polymers having an alternating structure of (a) units derived from carbon monoxide and (b) units derived from one or more olefinically unsaturated compounds.

Such polyketones have the general formula:



where the R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> groups are independently hydrogen or hydrocarbyl groups, and m is a large integer; they are disclosed in several patents e.g. US 3694412. Processes for preparing the polyketones are disclosed in US 3694412 and also in EP 181014A and EP 121965A. Although for the purposes of this patent  
15 polyketones correspond to this idealised structure, it is envisaged that materials corresponding to this structure in the main but containing small regimes (i.e. up to 10 wt%) of the corresponding homopolymer or copolymer derived from the olefinically unsaturated compound, also fall within the definition.

EP 213671A teaches that polyketones comprising units of carbon monoxide,  
20 ethylene and an alpha olefin have lower melting points than corresponding copolymers comprised only of carbon monoxide and ethylene units. A quantitative relationship is shown to exist between the proportion of further olefin units in the polyketone and the melting point. The most preferred range of melting points is said to be from 195 to 235°C, corresponding to a specific range of ethylene:further olefin ratios. Within  
25 this preferred range, in addition to examples employing propene as the further

monomer, there are examples of terpolymers of carbon monoxide, ethylene and butene-1 or octene-1, having melting points of 244°C and 225°C respectively. The amounts of butene-1 and octene-1 in the terpolymer are 0.7% and 5.4% respectively. Mention is also made of the possibility of the further alpha-olefin being a mixture of  
5 hexene-1 and octene-3, although this is not exemplified.

EP 0392759 relates to the use of a photodegrading agent preferably comprising a polyketone which is a linear copolymer having a melting point of between 150 and 245°C which consists of units  $-\text{CO}(\text{C}_2\text{H}_4)-$  and units of  $-\text{CO}(\text{B}')$ - where (B') is derived from one or more olefinically unsaturated monomers (B) having  
10 less than 20 carbon atoms. Preferred monomers B are represented by the formula  $\text{C}_n\text{H}_{2n}$  where n is 3 to 8. Example 6 of EP 0392759 discloses a photodegradable composition prepared by blending 5% by weight of an ethylene/hexene/carbon monoxide copolymer (E/H/CO) with 95% by weight of a low density polyethylene. The E/H/CO copolymer is said to comprise 4 mol % hexene. Sheets of the blend  
15 were prepared and subjected to accelerated UV ageing. However, the unblended E/H/CO copolymer was not formed into a sheet nor was the barrier performance of the E/H/CO copolymer discussed.

Although polyketones are known to exhibit good barrier properties, in particular against oxygen, it is desirable to improve these properties. It is known to  
20 do this by melt processing the polyketone or by drawing a film of the polyketone.

Thus, US 5,077,385 describes a polymer material having water, oxygen and/or carbon dioxide barrier properties prepared from a melt processed material comprising a linear alternating polymer of carbon monoxide and at least one ethylenically unsaturated hydrocarbon. Preferred polyketone polymers are said to include  
25 copolymers of carbon monoxide, ethylene and a second aliphatic  $\alpha$ -olefin of 3 or more carbon atoms, particularly propylene. However, carbon monoxide/ethylene/hexene copolymers are not specifically disclosed.

EP 0420331 relates to a process for producing a mono- or biaxially drawn film by drawing a non- or less-stretched polymer sheet along one or two axes,  
30 respectively, characterised by drawing a linear alternating terpolymer of carbon monoxide, ethylene and a second ethylenically unsaturated hydrocarbon of at least 3 carbon atoms, the terpolymer having a melting point of at least 214°C, at a draw temperature between 175°C and 205°C, to a draw ratio of at least 4. The hydrocarbons useful as the second ethylenically unsaturated hydrocarbon are aliphatic  
35 such as propylene and other  $\alpha$ -olefins including 1-hexene. The mono- or biaxially

stretched or drawn films are said to have a high degree of molecular orientation and have enhanced barrier properties towards oxygen and carbon dioxide, compared to, for example, orientated polyolefins. The examples all relate to terpolymers of carbon monoxide, ethylene and propylene i.e. the barrier properties of stretched or drawn  
5 films of ethylene/hexene/CO terpolymers are not specifically disclosed.

It is also known to improve the barrier properties of polyketones by blending the polyketone with a further polymer.

Where polyketones are used in packaging applications as an oxygen barrier one important feature in such applications is the variation of the barrier performance  
10 of the polyketone with relative humidity, especially for liquid packaging; generally the oxygen barrier performance deteriorates with increasing humidity. A typical liquid container may comprise a mono-layer structure or alternatively a multi-layer structure such as a co-extruded multilayer structure or a laminate. Where the container comprises a multi-layer structure, at least one internal layer of the multilayer structure  
15 comprises the oxygen barrier polyketone. In use, when the inside surface of the container is in contact with a liquid, the relative humidity (RH) is 100%, whilst the outer surface which is in contact with the atmosphere is generally at about 50% RH. The precise RH level in the region of the internal layer of oxygen barrier polyketone will depend on its relative distance from the inner and outer surfaces of the multi-layer  
20 structure. In mass manufacture this may vary somewhat, leading potentially to a variation in oxygen barrier performance from one container to another. Clearly a polymer whose oxygen barrier performance is relatively constant over a range of RH will be advantageous, as its position within such a multi-layer structure will have less effect on its performance, and thus the thickness of polyketone polymer required for  
25 satisfactory oxygen barrier can be calculated with more confidence.

We have now discovered that terpolymers of carbon monoxide, ethylene and hexene not only provide excellent oxygen barrier performance, but also have a surprisingly low variation of oxygen permeability with relative humidity compared with other polyketones, thereby making them particularly suitable for packaging  
30 applications such as those described above.

Accordingly, in a first aspect the present invention provides a barrier material comprising a linear polyketone polymer having an alternating structure of (a) units derived from carbon monoxide, and (b) units derived from ethylene, hexene and optionally a further alpha-olefin.

35 Preferably the total amount of units derived from hexene present in the linear

polyketone polymer is from 0.1 to 10 mole %, more preferably from 1 to 8 mole %, and most preferably from 2 to 6 mole % of the polymer. Particularly useful polyketone polymers contain between 3 and 4 mole % hexene based on total polymer. The form of hexene most conveniently employed is hexene-1.

5 As mentioned above, the barrier materials of the present invention have excellent oxygen barrier properties. Preferably the oxygen permeability of the barrier material at 23°C, 75%RH is less than  $5 \times 10^{-12}$  cc.cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>, and more preferably less than  $2 \times 10^{-12}$  cc.cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>. A major benefit of the barrier materials of the present invention is the combination of good oxygen barrier  
10 properties with low variability thereof over a range of humidity. The ratio of oxygen permeability at 75% RH to that at 0% RH is preferably less than 4, more preferably less than 3 and ideally less than 2.

Typically, the optional further alpha-olefin may be selected from the group consisting of propene, butene, pentene, heptene and octene, preferably propene and  
15 butene. The linear polyketone polymer may contain units derived from more than one further alpha olefin.

The Melt Flow Rate (5kg load at 240°C, 2.095 diameter die) of the linear polyketone polymer is typically in the range 5-200, preferably 10-150, more preferably 20-100, for example, 40-80g/10 mins.

20 The linear polyketone polymer may suitably have a number average molecular weight of between 30,000 and 1,000,000 preferably between 40,000 and 250,000 for example 60,000 to 180,000.

It is envisaged that the barrier material may comprise blends of the linear polyketone polymer defined above. Furthermore, the barrier material of the present  
25 invention may comprise blends of the linear polyketone polymer defined above with other linear polyketones, for example, ethylene/CO copolymer, ethylene/propene/CO, ethylene/butene/CO, ethylene/pentene/CO, ethylene/heptene/CO or ethylene/octene/CO terpolymers. It is also envisaged that the barrier materials of the present invention may contain other polymers which are blended with the linear  
30 polyketone polymers defined above (for example, polyethylene, polypropylene, PVC, polystyrene and polyesters); the nature and amount of such a polymer will depend upon what modifications of the polymer properties are required. Furthermore the barrier materials of the present invention may contain conventional polymer additives such as anti-oxidants, stabilisers, fillers, mould release agents, and processing aids  
35 (such as internal and external lubricants).

The linear polyketone polymer of the barrier material of the present invention can be prepared using conventional batch or continuous reactor techniques. Although in the Examples below the barrier materials of the present invention are prepared by compression moulding, articles can also be made by extrusion processes to produce coatings, films, sheets, pipes, tubes, containers (receptacles), liners (including liners for pipes, containers, and tanks, such liners being formed from monolayers of the barrier material of the present invention or from multi-layer structures comprising at least one layer of the barrier material of the present invention, and which are fitted internally to the pipe, container, tank etc.) and closures. Extrusion techniques can result in lower permeabilities than compression moulding, as is well known, due to molecular orientation.

The scope of the present invention extends to packaging materials such as films and articles (for example, moulded articles) made from the barrier materials as defined hereinbefore, which can be used in packaging applications requiring good oxygen barrier properties and optionally good aroma, flavour, or fragrance barrier properties and requiring low variability of the barrier performance with humidity. Suitable goods which may be packaged using packaging materials made from the barrier material of the present invention include foodstuffs, beverages, household goods, healthcare products, medical products, pharmaceuticals, industrial chemicals, agricultural products and fuels.

In a further aspect of the present invention there is provided goods, (for example, foodstuffs, beverages, household goods, healthcare products, medical products, pharmaceuticals, industrial chemicals, agricultural products and fuels) contained in a packaging material made from the barrier material as defined hereinbefore.

In yet another aspect of the present invention there is provided the use of the barrier material as defined hereinbefore as a packaging material to package goods (for example, foodstuffs, beverages, household goods, healthcare products, medical products, pharmaceuticals, industrial chemicals, agricultural products and fuels), particularly those in liquid, wet or dry form.

Thus, the barrier material of the present invention is particularly useful for packaging goods which are sensitive to oxygen and where it is important that the oxygen barrier performance of the barrier material has low variability over a range of humidity.

The packaging material may be a film (for example, a pouch, a seal for a tray,

bowl or other receptacle) or a moulded article (for example, a tray, cup, bowl, container, vessel or other receptacle).

The scope of the present invention also extends to applications requiring hydrocarbon or chemical resistance in addition to good oxygen barrier properties.

5 Thus, the barrier materials of the present invention are also resistant to hydrocarbons (for example, fuels, crude oils, and organic solvents such as toluene and heptane) and industrial chemicals (for example, ethanol, acetone, weak acids, weak bases, and other aqueous solutions). The barrier materials of the present invention are therefore particularly useful for the manufacture of fuel tanks or storage drums for solvents and  
10 industrial chemicals.

The barrier material of the present invention is also particularly useful for pipe applications where it is important to exclude oxygen from the material being conveyed by the pipe or to limit oxygen ingress into the material being conveyed by the pipe and where the performance of the pipe in excluding oxygen or limiting oxygen ingress  
15 should have low variability over a range of humidity.

In yet another aspect of the present invention there is provided a pipe comprising the barrier material as defined hereinbefore for use in conveying, for example, hydrocarbons or industrial chemicals.

In a further aspect of the present invention there is provided a multi-  
20 layered structure comprising at least one layer which is a barrier material as defined before.

The packaging material, fuel tank, storage drum or pipe may be formed from a monolayer of the barrier material as defined hereinbefore. Alternatively, the packaging material, fuel tank, storage drum or pipe may be formed from a multi-  
25 layered structure as defined hereinbefore. A multi-layered structure is preferred. Such multi-layered structures may be prepared by co-extrusion e.g. multi-layered film or pipe produced by co-extrusion or by lamination. Typically, the multi-layered structure comprises 2 to 12 layers, preferably 3 to 7 layers. Preferably, the multi-layered structure comprises 3 or 6 layers. Preferably, the layer of the barrier  
30 material is an internal layer. Where a packaging material is formed from a multi-layered structure, the layer(s) of the barrier material, as hereinbefore defined, suitably has a thickness of at least 3  $\mu\text{m}$  and up to 5000  $\mu\text{m}$ , preferably in the range 5 to 1000  $\mu\text{m}$ , more preferably for packaging of foodstuffs and beverages in the range 5 to 50  $\mu\text{m}$ . Where a pipe, fuel tank or storage drum is formed from a multi-  
35 layered structure, the layer(s) of the barrier material, as hereinbefore defined,

suitably has a thickness of at least 3  $\mu\text{m}$  and up to 10 mm, preferably in the range 5 to 5000  $\mu\text{m}$ , more preferably in the range 5 to 1000  $\mu\text{m}$  and most preferably in the range 25 to 500  $\mu\text{m}$ . Tie-layers may be required to bond the different layers of the multi-layer structure, for example, tie-layers for bonding polyolefins to polyketones are disclosed in EP 0670869.

The present invention also provides in another aspect a process for making a linear polyketone polymer having an alternating structure of (a) units derived from carbon monoxide, and (b) units derived from ethylene, hexene and optionally a further alpha-olefin, comprising contacting carbon monoxide with ethylene, hexene and the optional alpha-olefin in the presence of a catalyst composition comprising

- a) a group VIII metal compound containing at least one ligand capable of coordinating to the Group VIII metal, and
- b) a boron hydrocarbyl compound.

The catalyst composition is described in detail in EP 619335A.

Preferably the boron hydrocarbyl compound is a Lewis acid of the formula BXYZ where at least one of X, Y and Z is a monovalent hydrocarbyl group, preferably a  $\text{C}_1\text{-C}_6$  alkyl group or an optionally substituted phenyl group. Particularly preferred catalysts are where X, Y and Z are the same and are preferably all  $\text{C}_6\text{F}_5$ .

The Group VIII metal in the catalyst composition is preferably palladium, with the preferred compound having the formula  $\text{Pd}(\text{P-P})(\text{acetate})_2$  where P-P is a bidentate phosphine.

The ratio of the Group VIII metal to boron is preferred to be in the range of from 1:5 to 1:70.

The invention is illustrated by the following examples.

#### Characterisation

For barrier performance evaluation, 11cm diameter and 150 micron thick films of the barrier materials of the present invention were compression moulded between two polished aluminium sheets using a KOMTEC 40 tonne press. The barrier material was initially held at  $240^\circ\text{C}$  for 3 minutes at a dial pressure of 0.2MPa, following which the dial pressure was increased to 18MPa and simultaneously a cooling rate of  $15^\circ\text{C}/\text{minute}$  applied until the film reached a temperature of about  $30^\circ\text{C}$ . The dial pressure was maintained at a constant 18MPa during the cooling cycle.

The melting point and glass transition ( $T_g$ ) of the ex-reactor powder were determined by differential scanning calorimetry (DSC) and dynamic thermal analysis

respectively (DMTA respectively).

DSC measurements were carried out using a DuPont DSC Model No. 990315. A heating rate of 10°C/min from -50°C up to 240°C was used under a nitrogen purge, followed by cooling at a rate of 10°C/min back down to -50°C. A second heating cycle at the same rate was then applied: the melting point was evaluated from the second heating endotherm. The results are shown in the Examples.

DMTA measurements were determined by loading a sample of the material to be tested (150 µm thickness, 25 mm long and 4mm width) into a DMTA tensile controller to give a gauge length of 20 mm. The nuts clamping the samples were tightened evenly at room temperature to a torque of 10 cNm. A preload of 4N was applied to the sample to prevent buckling of the sample during the sinusoidal displacement and a frequency of 10 Hz and a low strain level (equivalent to a peak to peak displacement of 11 microns) were chosen for the test. The sample was positioned in an oven. The oven was rapidly cooled to -100°C with liquid nitrogen and a reducing force mode was selected so that the preload applied would decrease in accordance with the reduction of modulus at higher temperatures. The sample was then heated to 220°C at a heating rate of 2°C/m. E' (storage modulus), E'' (loss modulus), tan δ (mechanical loss factor) and sample displacement were recorded as a function of temperature. The results are reported below in Table 2.

Water uptake measurements were carried out using 5 cm<sup>2</sup> discs of samples cut from 150µm compression moulded sheets. The samples were dried at 80°C in a vacuum oven for 24 hours, prior to testing. The samples were weighed to the nearest 0.001 g and then fully immersed in distilled water at a temperature of 21°C. The weight of the samples was monitored as a function of time until an equilibrium water uptake was achieved. Three samples of each material were tested simultaneously and an average water uptake value taken. The results are reported below in Table 2.

Hexene content of the polymers was determined by proton <sup>1</sup>H NMR using a JEOL GSX 270 spectrometer. The polymer was analysed as a solution in HFIP/CD<sub>2</sub>Cl<sub>2</sub>. The hexene content is expressed in mole % of the total terpolymer.

The oxygen permeabilities were measured using a MOCON Oxtran (1000) machine according to ASTM D3985. The results are shown in Table 1.

#### EXAMPLE 1

A carbon monoxide/ethene/hexene terpolymer was prepared under the

following conditions:

85 ml dichloromethane and 43g hexene-1 were charged to a mechanically stirred autoclave having a volume of 300 ml. The contents of the autoclave were brought to a temperature of 65°C. A 1:1 carbon monoxide/ethene gas mixture was introduced  
5 until a pressure of 50 barg was reached. A boron solution was then introduced into the autoclave, consisting of 0.156 mmol tris(pentafluorophenyl)boron in 10 ml dichloromethane, followed by addition of a catalyst solution consisting of 0.007 mmol Pd(dppp)(OAc)<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino)propane) in 10 ml dichloromethane.

10 The autoclave pressure was maintained at 50 barg pressure by introducing under pressure a 1:1 carbon monoxide/ethene gas mixture. Polymerisation was stopped after 4 hours by depressurising the autoclave. The polymer was filtered, washed with methanol and dried. 13.5g of terpolymer was produced having a melting point determined by DSC of 210°C. The content of units derived from hexene in the  
15 terpolymer was 3.0 weight %.

#### **EXAMPLE 2**

A further carbon monoxide/ethene/hexene terpolymer was prepared under the following conditions:

480 ml dichloromethane and 320 g hexene-1 were charged to a mechanically stirred  
20 autoclave having a volume of 2000 ml. The contents of the autoclave were brought to a temperature of 65°C. A 1:1 carbon monoxide/ethene gas mixture was introduced until a pressure of 50 bar was reached. A boron solution was then introduced into the autoclave, consisting of 0.64 mmol tris(pentafluorophenyl)boron in 20 ml dichloromethane, followed by addition of a catalyst solution consisting of 0.048 mmol  
25 Pd(dppp)(OAc)<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino)propane) in 20 ml dichloromethane.

The autoclave pressure was maintained at 50 barg pressure by introducing under pressure a 1:1 carbon monoxide/ethene gas mixture. Polymerisation was stopped after 4 hours by depressurising the autoclave. The polymer was filtered,  
30 washed with methanol and dried. 120 g of terpolymer was produced having a melting point determined by DSC of 211°C. The content of units derived from hexene in the terpolymer was 3.5 weight %.

#### **EXAMPLE 3**

A further carbon monoxide/ethene/hexene terpolymer was prepared under the  
35 following conditions:

70 ml dichloromethane and 53g hexene-1 were charged to a mechanically stirred autoclave having a volume of 300 ml. The contents of the autoclave were brought to a temperature of 65°C. A 1:1 carbon monoxide/ethene gas mixture was introduced until a pressure of 50 barg was reached. A boron solution was then introduced into the autoclave, consisting of 0.160 mmol tris(pentafluorophenyl)boron in 10 ml dichloromethane, followed by addition of a catalyst solution consisting of 0.007 mmol Pd(dppp)(OAc)<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino)propane) in 10 ml dichloromethane.

The autoclave pressure was maintained at 50 barg pressure by introducing under pressure a 1:1 carbon monoxide/ethene gas mixture. Polymerisation was stopped after 4 hours by depressurising the autoclave. The polymer was filtered, washed with methanol and dried. 12.6g of terpolymer was produced having a melting point determined by DSC of 211°C. The content of units derived from hexene in the terpolymer was 3.9 weight %.

#### 15 **EXAMPLE 4**

A further carbon monoxide/ethene/hexene terpolymer was prepared under the following conditions:

80 ml dichloromethane and 80 ml hexene-1 were charged to a mechanically stirred autoclave having a volume of 300 ml. The contents of the autoclave were brought to a temperature of 65°C. A 1:1 carbon monoxide/ethene gas mixture was introduced until a pressure of 50 barg was reached. A boron solution was then introduced into the autoclave, consisting of 0.15 mmol tris(pentafluorophenyl)boron in 20 ml dichloromethane, followed by addition of a catalyst solution consisting of 0.016 mmol Pd(dppp)(PhCN)<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino)propane) in 20 ml dichloromethane.

The autoclave pressure was maintained at 50 barg pressure by introducing under pressure a 1:1 carbon monoxide/ethene gas mixture. Polymerisation was stopped after 1.5 hours by depressurising the autoclave. The polymer was filtered, washed with methanol and dried. 21 g of terpolymer was produced having a melting point determined by DSC of 212 °C. The content of units derived from hexene in the terpolymer was 4.8 weight %.

#### 30 **EXAMPLE 5**

A carbon monoxide/ethene/propene terpolymer was prepared under the following conditions:

35 80 ml dichloromethane and 10.2g propene were charged to a mechanically stirred

autoclave having a volume of 300 ml. The contents of the autoclave were brought to a temperature of 73°C. A 1:1 carbon monoxide/ethene gas mixture was introduced until a pressure of 50 barg was reached. A boron solution was then introduced into the autoclave, consisting of 0.3 mmol of tris(pentafluorophenyl)boron in 20 ml of dichloromethane. This was followed by addition of a catalyst solution comprising:  
5 0.017 mmol [Pd(dppp)(PhCN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino)propane) in 20 ml of dichloromethane.

The autoclave pressure was maintained at 50 barg by introducing under pressure a 1:1 carbon monoxide/ethene gas mixture. Polymerisation was stopped  
10 after 1.5 hours by depressurising the autoclave. The polymer was filtered, washed with methanol and dried at 40°C. 20g of terpolymer was produced having a melting point determined by DSC of 227°C. The content of units derived from propene was determined by NMR as 2.9 mol %.

#### EXAMPLE 7

15 A carbon monoxide/ethene/propene terpolymer was prepared under the following conditions:

80 ml dichloromethane and 20.2g propene were charged to a mechanically stirred autoclave having a volume of 300 ml. The contents of the autoclave were brought to a temperature of 70°C. A 1:1 carbon monoxide/ethene gas mixture was introduced  
20 until a pressure of 50 barg was reached. A boron solution was then introduced into the autoclave, consisting of 0.3mmol of tris(pentafluorophenyl)boron in 20 ml of dichloromethane. This was followed by addition of a catalyst solution comprising: 0.015mmol [Pd(dppp)(PhCN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino)propane) in 20 ml of dichloromethane.

25 The autoclave pressure was maintained at 50 barg by introducing under pressure a 1:1 carbon monoxide/ethene gas mixture. Polymerisation was stopped after 2 hours by depressurising the autoclave. The polymer was filtered, washed with methanol and dried at 40°C. 21.9g of terpolymer was produced having a melting point determined by DSC of 218°C. The content of units derived from propene was  
30 determined by NMR as 4.6 mol %.

#### EXAMPLE 8

A carbon monoxide/ethene/propene terpolymer was prepared under the following conditions:

35 7.6 litres of dichloromethane were charged to a mechanically stirred autoclave having a volume of 20 litres. The water content of the dichloromethane was

adjusted to 139 ppm by the addition of 1 ml of distilled water. The autoclave was pressurised with nitrogen to about 20 barg and the contents stirred for a minimum of 20 minutes at ambient temperature. The autoclave was vented slowly back to atmospheric pressure and this procedure was then repeated three more times so as to reduce the oxygen dissolved in the dichloromethane to an acceptable level. The contents of the autoclave were brought to a temperature of 68°C and a 1:1 carbon monoxide/ethene gas mixture was introduced until a pressure of 20 barg was reached. 5.04 litres of propene were then added before the pressure in the autoclave was increased to 44 barg by feeding a further quantity of the 1:1 carbon monoxide/ ethene gas mixture. A boron solution was then introduced to the autoclave, which consisted of 17.8 mmol tris(4-chlorophenyl)borane in 250 ml of deoxygenated dichloromethane, followed by 0.47 mmol [Pd(dppp) (PhCN)<sub>2</sub>] [BF<sub>4</sub>]<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino)propane) in 80 ml of deoxygenated dichloromethane. The autoclave pressure was then maintained at 45 barg pressure by introducing under pressure a 1:1 carbon monoxide/ethene gas mixture. Polymerisation was allowed to continue for 2.7 hours, whereupon a second charge of catalyst, comprising 0.47 mmol [Pd(dppp) (PhCN)<sub>2</sub>] [BF<sub>4</sub>]<sub>2</sub> in 80 ml of deoxygenated dichloromethane, was added to the autoclave. Polymerisation was maintained as before until a total reaction time of 4.3 hours had elapsed, whereupon the autoclave was cooled back to ambient temperature and depressurised. A 2 litre sample of polymer slurry was removed from the reactor. 2 litres of methanol was added to the slurry sample, and the diluted slurry was stirred for about 15 minutes under ambient conditions. The diluted slurry was then filtered to give a damp cake of polymer. The polymer cake was re-slurried in 2 litres of methanol and the resulting slurry was stirred for about 15 minutes at room temperature before being filtered once more to give a damp cake. This washing and filtering step was repeated. The damp cake was then dried in air at room temperature and then under vacuum at a temperature of 60°C. The melting point of the terpolymer was determined by DSC to be 140°C while the content of units derived from propene in the terpolymer was determined by NMR as 13.6 mol %.

The oxygen permeability of the above terpolymers was then determined as described above, at relative humidities of 0%, 75% and 90%.

The results are shown in Table 1 below.

**TABLE 1**

EX. NO.	HEXENE CONTENT (mol %)	OXYGEN PERMEABILITY (cc.cm cm <sup>-2</sup> s <sup>-1</sup> cmHg <sup>-1</sup> )			RATIO 75% : 0%
		(23°C, 0%RH)	(23°C, 75%RH)	(23°C, 90%RH)	
1	3.0 %	3.66 x 10 <sup>-13</sup>	5.45 x 10 <sup>-13</sup>	6.52 x 10 <sup>-13</sup>	1.5
2	3.5%	6.24 x 10 <sup>-13</sup>	7.58 x 10 <sup>-13</sup>	7.88 x 10 <sup>-13</sup>	1.2
3	3.9%	9.78 x 10 <sup>-13</sup>	1.39 x 10 <sup>-12</sup>	1.73 x 10 <sup>-12</sup>	1.4
4	4.8%	2.03 x 10 <sup>-12</sup>	2.71 x 10 <sup>-12</sup>	--	1.3
5 <sup>a</sup>	2.9 % propene	3.23 x 10 <sup>-14</sup>	6.12 x 10 <sup>-13</sup>	--	18.9
6 <sup>a,b</sup>	3.7% propene	4.03 x 10 <sup>-14</sup>	3.47 x 10 <sup>-13</sup>	--	8.6
7 <sup>a</sup>	4.6 % propene	1.20 x 10 <sup>-14</sup>	8.32 x 10 <sup>-14</sup>	--	6.9
8 <sup>a</sup>	13.6% propene	9.17 x 10 <sup>-13</sup>	5.72 x 10 <sup>-12</sup>	--	6.2

a Comparative examples using propene instead of hexene-1.

5 b Carilon P1000 (ex Shell)

The results given in Table 1 show that there is very little variability in the oxygen permeability of the barrier materials of the present invention with relative humidity. However in the case of barrier materials comprising terpolymers containing similar levels of propene instead of hexene, the variation is substantially greater.

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**TABLE 2**

EX. NO.	HEXENE CONTENT (mol %)	% Water Uptake <sup>c</sup>	DMTA Tg shift dry/wet <sup>c</sup> (°C)
2	3.5%	1.01	4
6 <sup>a, b</sup>	3.7% propene	2.00	22

- a. Comparative example using propene instead of hexene-1.
- 5 b. Carilon P1000 (ex Shell)
- c. Saturated with water at a temperature of 21°C.

The results given in Table 2 show that the barrier materials of the present invention are particularly insensitive to plasticisation in aqueous environments.

Claims:

1. A barrier material comprising a linear polyketone polymer having an alternating structure of (a) units derived from carbon monoxide, and (b) units derived from ethylene, hexene and optionally a further alpha-olefin.
2. A barrier material as claimed in claim 1 wherein the amount of units derived  
5 from hexene present in the linear polyketone polymer is from 1 to 8 mole % of the polymer.
3. A barrier material as claimed in claim 2 wherein the amount of units derived from hexene is from 2 to 6 mole %.
4. A barrier material as claimed in any one of the preceding claims wherein the  
10 oxygen permeability of the barrier material at 23°C, 75%RH is less than  $5 \times 10^{-12}$  cc.cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>.
5. A barrier material as claimed in claim 4 wherein the oxygen permeability of the barrier material at 23°C, 75%RH is less than  $2 \times 10^{-12}$  cc.cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>.
6. A barrier material as claimed in any one of the preceding claims wherein the  
15 ratio of oxygen permeability at 75% RH to that at 0% RH is less than 4.
7. A barrier material as claimed in claim 6 wherein the ratio of oxygen permeability at 75% RH to that at 0% RH is less than 2.
8. A barrier material as claimed in any one of the preceding claims wherein the  
20 optional further alpha-olefin is selected from the group consisting of propene, butene, pentene, heptene and octene.
9. A multi-layered structure comprising at least one layer which is a barrier material as defined in any one of claims 1 to 8.
10. A multi-layered structure as claimed in claim 9 wherein the layer of the barrier material has a thickness in the range 3 to 5000µm.
- 25 11. A multi-layered structure as claimed in claim 9 or claim 10 wherein the

multi-layered structure comprises 3 to 7 layers.

12. A multi-layered structure as claimed in any one of claims 9 to 11 wherein the layer of the barrier material is an internal layer.

13. Use of a barrier material as defined in any one of claims 1 to 8 as a packaging material to package goods selected from the group consisting of foodstuffs, beverages, household goods, healthcare products, medical products, pharmaceuticals, industrial chemicals, agricultural products and fuels.

14. Use of a multi-layered structure as defined in any one of claims 9 to 12 as a packaging material to package goods selected from the group consisting of foodstuffs, beverages, household goods, healthcare products, medical products, pharmaceuticals, industrial chemicals, agricultural products and fuels.

15. A use as claimed in claim 13 or claim 14 wherein the packaging material is a film or a moulded article.

16. A pipe, fuel tank or storage drum comprising a barrier material as defined in any one of claims 1 to 8.

17. A pipe, fuel tank or storage drum formed from a multi-layered structure as defined in any one of claims 9 to 12.

18. A liner comprising a barrier material as defined in any one of claims 1 to 8.

19. A liner formed from a multi-layered structure as defined in any one of claims 9 to 12.

20. A process for making a linear polyketone polymer as defined in any one of claims 1 to 3, which comprises contacting carbon monoxide with ethylene, hexene and an optional alpha-olefin in the presence of a catalyst composition comprising

a) a group VIII metal compound containing at least one ligand capable of

coordinating to the Group VIII metal, and

b) a boron hydrocarbyl compound.

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/02036

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 C08G67/02

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 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 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.
X	EP 0 704 471 A (BP CHEMICALS) 3 April 1996 see page 2, line 34 - line 42; claims ---	1,4-8,20
X	EP 0 213 671 A (SHELL) 11 March 1987 cited in the application see column 4, line 29; claim 1 see column 6, line 555 - line 56 ---	1-8,13, 16,18
X	EP 0 392 759 A (BP CHEMICALS) 17 October 1990 cited in the application see example 6 ---	1-8
X,Y	EP 0 420 331 A (SHELL) 3 April 1991 cited in the application see page 2, line 28; claims ---	1-8,13, 16,18
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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

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"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

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No  
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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 5 077 385 A (L. GERLOWSKI ET AL.) 31 December 1991 cited in the application see claims ---	1-8,13, 16,18
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X	EP 0 396 268 A (BRITISH PETROLEUM COMPANY) 7 November 1990 see example 7 ---	1-8
X	EP 0 569 101 A (SHELL INT RESEARCH) 10 November 1993 see page 3, line 17 see page 1, line 5 - line 13; claims -----	1-19

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