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AUSTRALIA

PATENTS ACT 1990

**PATENT REQUEST: STANDARD PATENT**

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

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**[54] Invention Title:**

Catalyst Compositions Suitable for the Preparation of Polymers of Carbon Monoxide and  $\alpha$ -olefins

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Shell Internationale Research Maatschappij B.V.

By:



Registered Patent Attorney

IRN: 216030

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NOTICE OF ENTITLEMENT

I, Albertus Wilhelmus Joannes ZEESTRATEN, of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands, being authorised by the Applicant/Nominated Person in respect of Application No. 20810/92 state the following:-

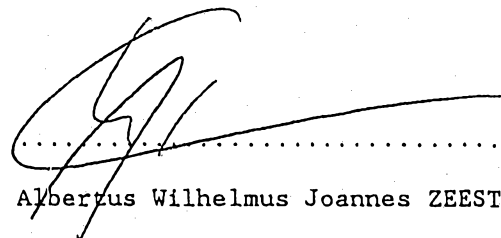
The Applicant/Nominated Person has entitlement from the actual inventor(s) as follows:-

The Applicant/Nominated Person is the assignee of the actual inventor(s).

The Applicant/Nominated Person is the applicant of the basic application(s) listed on the Patent Request.

The basic application(s) listed on the Patent Request is/are the application(s) first made in a Convention Country in respect of the invention.

DATED this 6th day of July, 1992

  
.....  
Albertus Wilhelmus Joannes ZEESTRATEN



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(54) Title  
CATALYST COMPOSITIONS SUITABLE FOR THE PREPARATION OF POLYMERS OF CARBON MONOXIDE AND ALPHA-OLEFINS

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(57) Claim

1. Catalyst compositions based upon:

- a) a Group VIII metal,
- b) an acid with a pKa of less than 2 in a quantity of more than 5 mol per gram atom Group VIII metal, and
- c) a phosphorus bidentate ligand of the general formula  $R^5R^6P-R-PR^7R^8$  in which  $R^5$  to  $R^8$  represent identical or different, optionally polar substituted hydrocarbyl groups containing a carbon atom which carbon atom carries at most one hydrogen atom and is linked to the corresponding phosphorus atom via a methylene bridge, and in which R is a divalent organic bridging group containing at least two carbon atoms in the bridge connecting the two phosphorus atoms.

9. Process for the preparation of polymers, characterized in that polymers of carbon monoxide with ethene and optionally also with one or more other  $\alpha$ -olefins are prepared by contacting the monomers in the presence of a liquid diluent in which the polymers are insoluble or virtually insoluble with a catalyst composition according to one or more of claims 1-8.

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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

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Invention Title:

Catalyst Compositions Suitable for the Preparation of  
Polymers of Carbon Monoxide and  $\alpha$ -olefins

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

CATALYST COMPOSITIONS SUITABLE FOR THE PREPARATION  
OF POLYMERS OF CARBON MONOXIDE AND  $\alpha$ -OLEFINS

The invention relates to novel catalyst compositions which are suitable for the preparation of polymers of carbon monoxide with one or more  $\alpha$ -olefins.

Linear alternating polymers of carbon monoxide with ethene and optionally one or more other  $\alpha$ -olefins, i.e. linear polymers in which the units originating in carbon monoxide and the units originating in the olefin(s) are present in a substantially alternating order, can be prepared by contacting the monomers in the presence of a liquid diluent in which the polymers are insoluble or virtually insoluble with a catalyst composition based upon:

- a) a Group VIII metal,
- b) an acid with a pKa of less than 2, and
- c) a phosphorus bidentate ligand of the general formula  $R^1R^2P-R-PR^3R^4$  in which  $R^1$  to  $R^4$  represent identical or different, optionally polar substituted monovalent hydrocarbyl groups and R is a divalent organic bridging group containing at least two carbon atoms in the bridge connecting the two phosphorus atoms.

As phosphorus bidentate ligands, compounds are eligible in which the groups  $R^1$  to  $R^4$  are unbranched alkyl groups, such as ethyl or n-butyl groups, and also in which these groups are branched alkyl groups, such as 2-propyl or 2-butyl groups. Compounds in which the groups  $R^1$  to  $R^4$  are aryl groups, such as phenyl groups, are also very suitable as catalyst components. As regards the quantity of acid to be included in the catalyst compositions, active catalyst compositions can be formulated both with small quantities of acid, such as 1 mol per gram atom Group VIII metal, and with larger quantities of acid, such as 1.0 mol per gram atom Group VIII metal.

The bulk density is one of the most important properties of

the polymer powder obtained from the polymerisation process. The bulk density plays an important role in the preparation, the purification, the storage, the transport and the processing of the alternating polymers. In the polymer preparation the bulk density determines the quantity of polymer that can be prepared in a certain reactor volume. In the polymer purification, such as in filtering, washing and drying, the quantity of adhering liquid is largely determined by the polymer bulk density. As far as transport and storage are concerned, the rule is that the higher the polymers' bulk density, the more attractive the flow behaviour they will have and the less space they will occupy. As far as the processing of the polymers into shaped objects is concerned, polymer powders with a high bulk density may not need to be compacted in order to make them suitable for further processing in the usual equipment.

The applicant has experienced that by modifying the composition of the applied catalyst composition, it is possible to influence the bulk density of the prepared polymers. The use of catalyst compositions containing the various aforementioned phosphorus bidentate ligands and containing different quantities of acid enabled polymers to be prepared which exhibited some variation in bulk density, their bulk density was however generally less than  $300 \text{ kg/m}^3$ .

It has now surprisingly been found that polymers of the present type with a bulk density of more than  $300 \text{ kg/m}^3$  can be prepared by using a catalyst composition of the above-mentioned type in which each of the optionally polar substituted hydrocarbyl groups of the phosphorus bidentate ligand contains a carbon atom which carbon atom carries at most one hydrogen atom and is linked to the corresponding phosphorus atom via a methylene bridge, and which catalyst composition additionally contains more than 5 mol of the acid per gram atom Group VIII metal. These catalyst compositions are novel.

The present patent application therefore relates to catalyst compositions based upon:

- a) a Group VIII metal,
- b) an acid with a pKa of less than 2 in a quantity of more than 5 mol per gram atom Group VIII metal, and
- 5 c) a phosphorus bidentate ligand of the general formula  $R^5R^6P-R-PR^7R^8$  in which  $R^5$  to  $R^8$  represent identical or different, optionally polar substituted hydrocarbyl groups containing a carbon atom which carbon atom carries at most one hydrogen atom and is linked to the corresponding phosphorus atom via a methylene bridge, and in which R is a divalent  
10 organic bridging group containing at least two carbon atoms in the bridge connecting the two phosphorus atoms.

The patent application further relates to a process for the preparation of polymers of carbon monoxide with ethene and optionally also with one or more other  $\alpha$ -olefins by contacting the  
15 monomers in the presence of a liquid diluent in which the polymers are insoluble or virtually insoluble with a catalyst composition according to the invention.

In this patent application, Group VIII metals are understood to be the noble metals ruthenium, rhodium, palladium, osmium, iridium and platinum, as well as the iron group metals iron, cobalt and nickel. The Group VIII metal in the catalyst compositions is preferably selected from palladium, nickel and cobalt. There is particular preference for palladium as Group VIII metal. The incorporation of the Group VIII metal in the catalyst compositions  
20 preferably takes place in the form of a salt, typically a salt of a carboxylic acid, in particular in the form of an acetate.

As acids with a  $pK_a$  of less than 2, both mineral acids and organic acids are eligible. Examples of suitable mineral acids are sulphuric acid and perchloric acid. Examples of suitable organic  
30 acids are sulphonic acids, such as para-toluenesulphonic acid and trifluoromethanesulphonic acid, and halocarboxylic acids such as trifluoroacetic acid. Preferably, the acid with a pKa of less than 2 incorporated in the catalyst compositions according to the invention is a sulphonic acid or a halocarboxylic acid. The  
35 quantity of acid in the catalyst compositions is preferably less

than 100 mol and in particular 10-50 mol per gram atom Group VIII metal.

5 In the phosphorus bidentate ligands of the general formula  $R^5R^6P-R-PR^7R^8$ , the groups  $R^5$  to  $R^8$  preferably contain each not more than 10 carbon atoms. There is also preference for phosphorus bidentate ligands in which the groups  $R^5$  to  $R^8$  are identical hydrocarbyl groups. Examples of suitable  $R^5$  to  $R^8$  groups are the 2-methylpropyl, the 2-methylbutyl, the benzyl, the ortho-, meta- and para-methylbenzyl, the ortho- and para-chlorobenzyl and the 10 ortho-methoxybenzyl groups. As regards the bridging group R, present in the phosphorus bidentate ligands, there is preference for bridging groups containing three atoms in the bridge. Examples of suitable bridging groups R are the  $-CH_2-CH_2-CH_2-$  group, the  $-CH_2-C(CH_3)_2-CH_2-$  group and the  $-CH_2-Si(CH_3)_2-CH_2-$  group. Very 15 suitable phosphorus bidentate ligands are 1,3-bis[bis(2-methylpropyl)phosphino]propane and 1,3-bis(dibenzylphosphino)propane. In the catalyst compositions the phosphorus bidentate ligands are preferably employed in a quantity of 0.5-2 and in particular 0.75-1.5 mol per gram atom Group VIII metal.

20 In addition to a phosphorus bidentate ligand and an acid with a pKa of less than 2, the catalyst compositions according to the invention contain preferably also an organic oxidizing agent. Examples of suitable organic oxidizing agents are 1,2- and 1,4-quinones, aliphatic nitrites such as butyl nitrite and aromatic 25 nitro compounds such as nitrobenzene and 2,4-dinitrotoluene. There is preference for 1,4-quinones and in particular 1,4-benzoquinone and 1,4-naphthoquinone. The organic oxidizing agent is preferably present in the catalyst compositions in a quantity of 5-5000 and in particular 10-1000 mol per gram atom Group VIII metal.

30 When the catalyst compositions according to the invention are employed for the preparation of polymer of carbon monoxide with ethene and additionally with one or more other  $\alpha$ -olefins, the latter  $\alpha$ -olefins preferably contain less than 10 carbon atoms per molecule. The catalyst compositions according to the invention are



particularly important for the preparation of copolymers of carbon monoxide with ethene and terpolymers of carbon monoxide with ethene and propene.

5 The preparation of the polymers is carried out in the presence of a liquid diluent. As diluents, polar liquids are preferably used. These liquids can be protic or aprotic. Suitable protic liquids are lower alcohols, such as methanol. Examples of suitable aprotic liquids are acetone and tetrahydrofuran. The polymer preparation can be carried out both batchwise and continuously.

10 The quantity of catalyst composition used in the preparation of the polymers may vary within wide limits. Per mol olefinically unsaturated compound to be polymerized, a quantity of catalyst composition is preferably used which contains  $10^{-7}$ - $10^{-3}$  and in particular  $10^{-6}$ - $10^{-4}$  gram atom Group VIII metal.

15 The preparation of the polymers is preferably carried out at a temperature of 20-150°C and a pressure of 2-150 bar and in particular at a temperature of 30-130°C and a pressure of 5-100 bar. The molar ratio of the olefinically unsaturated compounds relative to carbon monoxide is preferably 10:1-1:10 and in particularly 5:1-1:5.

20 The invention will now be illustrated with reference to the following examples.

Example 1 (for comparison)

25 A carbon monoxide/ethene copolymer was prepared as follows. Into a stirred autoclave with a volume of 250 ml a catalyst solution was introduced consisting of:

- 50 ml methanol,  
0.1 mmol palladium acetate,  
2 mmol para-toluenesulphonic acid, and  
30 0.12 mmol 1,3-bis(diphenylphosphino)propane.

After introducing 20 bar ethene and 30 bar carbon monoxide, the content of the autoclave was heated to 70°C. After 1 hour the polymerization was terminated by cooling the reaction mixture to room temperature and releasing the pressure. The polymer was

filtered off, washed with methanol and dried. 14 g copolymer was obtained with a bulk density of 230 kg/m<sup>3</sup>.

Example 2 (for comparison)

5 A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the difference that the catalyst solution contained 0.3 mmol trifluoromethane-sulphonic acid instead of para-toluenesulphonic acid and 0.12 mmol 1,3-bis(diethylphosphino)propane instead of 1,3-bis(diphenylphosphino)propane.

10 14 g copolymer was obtained with a bulk density of 200 kg/m<sup>3</sup>.

Example 3 (for comparison)

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- 15 a) the catalyst solution contained 2 mmol trifluoroacetic acid instead of para-toluenesulphonic acid and 0.12 mmol 1,3-bis(diethylphosphino)propane instead of 1,3-bis(diphenylphosphino)propane, and
- b) the reaction time was 3 hours instead of 1 hour.

20 12 g copolymer was obtained with a bulk density of 280 kg/m<sup>3</sup>.

Example 4 (for comparison)

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- 25 a) the catalyst solution contained 0.12 mmol 1,3-bis(di-n-butylphosphino)propane instead of 1,3-bis(diphenylphosphino)propane, and
- b) the reaction time was 5 hours instead of 1 hour.

14 g copolymer was obtained with a bulk density of 200 kg/m<sup>3</sup>.

30 Example 5 (for comparison)

A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 2 mmol trifluoroacetic acid instead of para-toluenesulphonic acid and 0.12 mmol 1,3-bis(di-2-propylphosphino)propane instead of 1,3-bis(diphenylphosphino)propane, and
- 5 b) the reaction time was 5 hours instead of 1 hour.  
12.5 g copolymer was obtained with a bulk density of 220 kg/m<sup>3</sup>.

Example 6 (for comparison)

10 A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 2 mmol trifluoroacetic acid instead of para-toluenesulphonic acid and 0.12 mmol 1,3-bis(di-2-butylphosphino)propane instead of 1,3-bis(diphenylphosphino)propane, and
- 15 b) the reaction time was 3 hours instead of 1 hour.  
10 g copolymer was obtained with a bulk density of 200 kg/m<sup>3</sup>.

Example 7 (for comparison)

20 A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 0.3 mmol trifluoromethane-sulphonic acid instead of para-toluenesulphonic acid and 0.12 mmol 1,3-bis[bis(2-methylpropyl)phosphino]propane instead of 1,3-bis(diphenylphosphino)propane, and
- 25 b) the reaction time was 2 hours instead of 1 hour.  
13 g copolymer was obtained with a bulk density of 200 kg/m<sup>3</sup>.

Example 8

30 A carbon monoxide/ethene copolymer was prepared in substantially the same way as in example 1, but with the following differences:

- a) the catalyst solution contained 2 mmol trifluoroacetic acid instead of para-toluenesulphonic acid and 0.12 mmol

1,3-bis[bis(2-methylpropyl)phosphino]propane instead of  
1,3-bis(diphenylphosphino)propane, and

b) the reaction time was 5 hours instead of 1 hour.

5 12.5 g copolymer was obtained with a bulk density of  
460 kg/m<sup>3</sup>.

Example 9

A carbon monoxide/ethene copolymer was prepared in  
substantially the same way as in example 1, but with the following  
differences:

10 a) the catalyst solution contained 2 mmol trifluoroacetic acid  
instead of para-toluenesulphonic acid and 0.12 mmol

1,3-bis(dibenzylphosphino)propane instead of  
1,3-bis(diphenylphosphino)propane, and

b) the reaction time was 5 hours instead of 1 hour.

15 10 g copolymer was obtained with a bulk density of 450 kg/m<sup>3</sup>.

Example 10

A carbon monoxide/ethene copolymer was prepared in  
substantially the same way as in example 1, but with the following  
differences:

20 a) the catalyst solution contained 0.12 mmol

1,3-bis[bis(2-methylpropyl)phosphino]propane instead of  
1,3-bis(diphenylphosphino)propane, and

b) the reaction time was 2 hours instead of 1 hour.

14 g copolymer was obtained with a bulk density of 470 kg/m<sup>3</sup>.

25 Example 11

A carbon monoxide/ethene copolymer was prepared in  
substantially the same way as in example 1, but with the difference  
that the catalyst solution contained 2 mmol  
trifluoromethanesulphonic acid instead of para-toluenesulphonic  
30 acid and 0.12 mmol 1,3-bis[bis(2-methylpropyl)phosphino]propane  
instead of 1,3-bis(diphenylphosphino)propane.

14 g copolymer was obtained with a bulk density of 480 kg/m<sup>3</sup>.

Of the examples 1-11, examples 8-11 are according to the invention. According to these examples, carbon monoxide/ethene copolymers with a bulk density of more than  $300 \text{ kg/m}^3$  were prepared by using catalyst compositions according to the invention which contained 20 mol acid per gram atom palladium and in which the tetrahydrocarbylbisphosphines contained 2-methylpropyl or benzyl groups as hydrocarbyl groups. Examples 1-7 fall outside the scope of the invention and have been included in the patent application for comparison. The carbon monoxide/ethene copolymers according to these examples had a bulk density of less than  $300 \text{ kg/m}^3$ . In examples 1-6, catalyst compositions were used in which the tetrahydrocarbylbisphosphines contained phenyl, ethyl, n-butyl, 2-propyl or 2-butyl groups as hydrocarbyl groups. In example 2 the catalyst composition additionally contained only 3 mol acid per gram atom palladium. In example 7, although a catalyst composition was used in which the tetrahydrocarbylbisphosphines contained 2-methylpropyl groups as hydrocarbyl groups, the composition contained only 3 mol acid per gram atom palladium.

It was established by NMR analysis that the polymers prepared according to examples 1-11 were built up of linear chains in which the units originating in carbon monoxide and the units originating in ethene occurred in an alternating order.

~~CLAIMS~~

The claims defining the invention are as follows:

1. Catalyst compositions based upon:
  - a) a Group VIII metal,
  - b) an acid with a pKa of less than 2 in a quantity of more than 5 mol per gram atom Group VIII metal, and
  - 5 c) a phosphorus bidentate ligand of the general formula  $R^5R^6P-R-PR^7R^8$  in which  $R^5$  to  $R^8$  represent identical or different, optionally polar substituted hydrocarbyl groups containing a carbon atom which carbon atom carries at most one hydrogen atom and is linked to the corresponding phosphorus atom via a methylene bridge, and in which R is a divalent organic bridging group containing at least two carbon atoms in the bridge connecting the two phosphorus atoms.
- 10 2. Catalyst compositions according to claim 1, characterized in that they contain palladium as Group VIII metal which is incorporated therein in the form of a salt of a carboxylic acid
- 15 such as an acetate.
3. Catalyst compositions according to claim 1 or 2, characterized in that they contain 10-50 mol acid per gram atom Group VIII metal.
4. Catalyst compositions according to one or more of claims 1-3,
- 20 characterized in that they contain a sulphonic acid or a halocarboxylic acid as acid.
5. Catalyst compositions according to one or more of claims 1-4 characterized in that the groups  $R^5$  to  $R^8$  in the phosphorus bidentate ligand contain each not more than 10 carbon atoms.
- 25 6. Catalyst compositions according to one or more of claims 1-5, characterized in that the groups  $R^5$  to  $R^8$  in the phosphorus bidentate ligand are identical hydrocarbyl groups and in that the bridging group R contains three atoms in the bridge.
7. Catalyst compositions according to claim 6, characterized in
- 30 that they contain 1,3-bis[bis(2-methylpropyl)phosphino]propane or 1,3-bis(dibenzylphosphino)propane as phosphorus bidentate ligand.

8. Catalyst compositions according to one or more of claims 1-7, characterized in that they contain the phosphorus bidentate ligand in a quantity of 0.75-1.5 mol per gram atom Group VIII metal.
- 5 9. Process for the preparation of polymers, characterized in that polymers of carbon monoxide with ethene and optionally also with one or more other  $\alpha$ -olefins are prepared by contacting the monomers in the presence of a liquid diluent in which the polymers are insoluble or virtually insoluble with a catalyst composition according to one or more of claims 1-8.
- 10 10. Process according to claim 9, characterized in that it is employed for the preparation of copolymers of carbon monoxide with ethene or terpolymers of carbon monoxide with ethene and an  $\alpha$ -olefin containing less than 10 carbon atoms, such as propene.
- 15 11. Process according to claim 9 or 10, characterized in that it is carried out at a temperature of 30-130°C, a pressure of 5-100 bar and a molar ratio of the olefinically unsaturated compounds relative to carbon monoxide of 5:1-1:5, using a quantity of catalyst composition which per mol olefinically unsaturated compound to be polymerized contains  $10^{-6}$ - $10^{-4}$  gram atom Group VIII metal and using as the diluent a protic liquid such as methanol or an aprotic liquid such as acetone or tetrahydrofuran.
- 20 12. A process for the preparation of polymers substantially as hereinbefore described with reference to any one of the Examples but excluding the comparative examples.
- 25 13. The product of the process of any one of claims 9 to 12.
- 30 14. A catalyst composition substantially as hereinbefore described with reference to any one of the Examples but excluding the comparative examples.

DATED this TWENTY-SEVENTH day of JULY 1992  
Shell Internationale Research Maatschappij B.V.

Patent Attorneys for the Applicant  
SPRUSON & FERGUSON

A B S T R A C T

CATALYST COMPOSITIONS SUITABLE FOR THE PREPARATION  
OF POLYMERS OF CARBON MONOXIDE AND  $\alpha$ -OLEFINS

Catalyst compositions based upon:

- a) a Group VIII metal,
  - b) an acid with a pKa of less than 2 in a quantity of more than 5 mol per gram atom Group VIII metal, and
  - c) a phosphorus bidentate ligand of the general formula  $R^5R^6P-R-PR^7R^8$  in which  $R^5$  to  $R^8$  represent identical or different, optionally polar substituted hydrocarbyl groups containing a carbon atom which carbon atom carries at most one hydrogen atom and is linked to the corresponding phosphorus atom via a methylene bridge, and in which R is a divalent organic bridging group containing at least two carbon atoms in the bridge connecting the two phosphorus atoms,
- and a process for the preparation of polymers of carbon monoxide with ethene and optionally also with one or more  $\alpha$ -olefins by contacting the monomers with the catalyst composition.