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alcohol. In this case the lower aliphatic alcohol may originate from a catalyst solution impregnated on a solid carrier.

Accordingly, it would be advantageous to apply a catalyst solution which contains a lower aliphatic alcohol as solvent.

5 However, it has been observed that the selection of a lower aliphatic alcohol as solvent for the catalyst system entails two problems, one relating to the preparation of the catalyst and another relating to its storability.

10 Initially, catalyst systems were applied which comprised, besides a palladium compound and an anion source, a bidentate bisphosphine ligand of the formula $(Q)_2P-R-P(Q)_2$ whereby Q represents an aromatic hydrocarbyl group and R represents a bivalent organic bridging group containing at least two carbon atoms in the bridge.

15 In a subsequent investigation it was found that the performance of the catalyst system could be improved significantly by replacing the ligand of the formula $(Q)_2P-R-P(Q)_2$ by a ligand of formula $R^1R^2P-R-PR^3R^4$ wherein R^1 , R^2 , R^3 and R^4 independently represent alkoxy substituted aromatic hydrocarbyl groups. However, the
20 solubility of these substituted bisphosphine ligands in methanol and other lower aliphatic alcohols proved to be poor and hence it was proposed to perform the preparation of the catalyst in another solvent such as toluene.

25 Another problem encountered with the use of a lower aliphatic alcohol, in particular methanol, as catalyst solvent, consists in the short shelflife of the catalysts thus prepared, which is apparent from significant plating out of palladium present in the catalyst system. In principle, this problem can be circumvented by preparing a fresh catalyst solution prior to its use in the
30 copolymerization process. Obviously it would be desirable to prepare in advance a larger amount of catalyst which can be stored so that in a batchwise polymerization for each batch a portion of the stored catalyst can be applied, or in a continuous polymerization the catalyst can be supplied from the same stock for a long period of
35 time.

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The said problems, encountered with the use of methanol as solvent in the preparation of the catalyst system are discussed in EP-A-360359. According to this document, the storability of the catalyst is improved by using an aprotic polar solvent, in particular acetone, in the preparation of the catalyst.

As it appears, the solubility of the ligands of the formula $R^1R^2P-R-PR^3R^4$ is higher in acetone than in methanol.

In the operation of a slurry copolymerization process, it is common practice to separate the product by removing the diluent from the reaction medium, e.g. by distillation and to recycle, or reuse, the diluent. Since fresh catalyst is supplied, this implies - following the procedure of EP-360359 - that the amount of acetone builds up after each recycle, necessitating a purifying treatment of the recycle stream, or a significant bleed of the said stream, both measures being unattractive for economic reasons. This could apply similarly to a gas phase process carried out in the presence of a lower aliphatic alcohol.

It could be considered to prepare the catalyst as a solution in acetone and to use the same liquid as a diluent in the copolymerization reaction, but as explained before, the use of acetone as the only diluent in the copolymerization reaction is less attractive, in view of the lower level of activity of the catalysts in that environment.

Surprisingly, it has now been found that by first combining the palladium compound, the bisphosphine ligand and a lower aliphatic alcohol as solvent and then admixing the resulting combination with an acid after a generation period, related to the temperature at which the catalyst preparation is performed, a catalyst solution of good storability is obtained, thus allowing the use of a single liquid in the preparation of the catalyst and in the production of the copolymers. It has been observed that the generation period is limited to a maximum value, related to the temperature at which the catalyst preparation is performed. The selection of a generation period beyond this maximum results in decomposition of the catalyst system which is apparent from significant plating out of palladium.

The invention relates to a process for the preparation of a solution of a catalyst system, suitable for use in a process for copolymerizing carbon monoxide and one or more ethylenically unsaturated compounds, which comprises (a) combining a palladium compound, a bisphosphine of the general formula $R^1R^2P-R-PR^3R^4$ (I) wherein each of R^1 , R^2 , R^3 and R^4 independently represents an aromatic hydrocarbyl group which is substituted with an alkoxy group and R represents a bivalent bridging group containing at least two carbon atoms in the bridge, and a lower aliphatic alcohol as solvent, and (b) admixing the obtained combination after a generation period G, during which a temperature T in the range of 0-70 °C is maintained, with an acid, whereby the said generation period G is selected such that the value for G (in hours) and the temperature T (in °C) are related as

$$G \leq 6.0 \times 10^{-21} \exp \left(\frac{14500}{T + 273.2} \right).$$

In step (a) of the process, i.e. the combination of a palladium compound, a bisphosphine and a solvent, as palladium compound conveniently a palladium salt is used. Suitable salts include salts of mineral acids such as sulphuric acid, nitric acid and phosphoric acid, salts of carboxylic acids and salts of sulphonic acids such as methanesulphonic acid, para-toluenesulphonic acid and trifluoromethanesulphonic acid.

Preferably, a palladium salt of a carboxylic acid is used, for example acetic acid, propionic acid, citric acid and halogenated carboxylic acids such as trichloroacetic acid and trifluoroacetic acid. A particularly preferred compound is palladium (II) acetate.

In view of the good performance exhibited by catalysts having a ligand of formula (I), whereby each of R^1 , R^2 , R^3 and R^4 represents a phenyl group, substituted with an alkoxy group at an ortho-position with respect to the phosphorus atom to which the phenyl group is bound, these substituted bisphosphines are in particular preferred. The alkyl groups in the alkoxy groups are usually C_1 - C_4 groups having their common meaning of indicating methyl, ethyl,

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propyl, isopropyl, n-butyl, sec. butyl, isobutyl and tertiary butyl groups. Preferably, each of R^1 , R^2 , R^3 and R^4 represents an ortho-methoxyphenyl group.

5 The bivalent bridging group R in the bisphosphines of formula (I), preferably comprises three atoms in the bridge, at least two of which are carbon atoms. Most preferably, R represents a trimethylene group.

Very good results can be obtained by selecting as the bisphosphine 1,3-bis[bis(2-methoxyphenyl)phosphino]propane.

10 The palladium compound and the bisphosphine of formula (I) are combined with a solvent which is a lower aliphatic alcohol, viz. an alcohol having from 1 to 4 carbon atoms, e.g. methanol, ethanol or butanol.

15 Although minor amounts of other solvents, for example up to 20% vol relative to the volume of the lower aliphatic alcohol, can be tolerated and also mixtures of more than one lower aliphatic alcohol are feasible, this is not recommended. Preferably, methanol is used as the only solvent.

20 According to a recommended embodiment of the invention, first the bisphosphine of formula (I) is dissolved or suspended in the solvent and subsequently the palladium compound is supplied.

25 Other procedures of combining the palladium compound, the bisphosphine and the solvent may be followed, e.g. adding the palladium compound and the bisphosphine simultaneously to the solvent, but it is generally preferred to disperse the bisphosphine in the solvent before the palladium compound is added, because the catalyst usually exhibits the highest level of activity if that sequence is adhered to.

30 For the same reason it is not recommended to combine only a portion of the total amount of palladium compound with the bisphosphine and the solvent and to supply the remainder of the palladium compound afterwards, e.g. during step (b) of the process, together with the supply of acid.

35 In the context of the present invention, the generation period G is deemed to start when the total or substantially total

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amounts of palladium compound and bisphosphine have been combined with the solvent.

In the recommended embodiment, described above, the generation period therefore starts as soon as the total amount of the palladium compound has been supplied.

The generation period G is deemed to end when the obtained combination is admixed with the acid. The admixing typically occurs by adding the acid to the obtained combination, for example within a period of addition ranging from 10 seconds up to 2 hours.

In practice, the temperature which is maintained during the generation period is advantageously the same as the temperature at which step (b), the mixing between the combination obtained in step (a) and the acid, is effected, and is also the same as the temperature prevailing during step (a). Preferably, in particular when the selected solvent is methanol, each of these temperatures is selected in the range of 20-50 °C.

The relation between the maximum value of the generation period G and the temperature T indicates that the generation period should not exceed a certain value, which depends on the temperature selected in the said range.

Preferably, the relation between the generation period and the temperature is determined by

$$G \leq 9.3 \times 10^{-22} \exp \left(\frac{15000}{T + 273.2} \right).$$

It has further been observed, that selecting a very short generation period may involve a complication in that the resulting mixture of the combination obtained in step (a) and the acid is not directly suitable to be used as catalyst, but only after some time of storage. In such cases a precipitate is formed upon admixing with the acid, which precipitate gradually dissolves upon standing.

Whilst in some cases this delay can be accepted, it would be generally desirable that after step (b) at least a portion of the

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resulting mixture can directly be used as catalyst in a first batch of a batchwise copolymerization process and that the remainder can be stored until it is needed in a subsequent batch of the process.

Accordingly, it is preferred to select the generation period such that

$$G \geq 7.1 \times 10^{-28} \exp \left(\frac{18800}{T + 273.2} \right).$$

The acid component of the catalyst system, used in step (b) of the process of the invention, may be a protic acid or a Lewis acid. Examples of Lewis acids are tris(perfluorophenyl)borane and trifluoroborane. The acid is in particular a protic acid, more in particular a protic acid which has a pKa of less than 2, measured in aqueous solution at 18 °C. The protic acid may be inorganic, such as fluoboric acid or organic, such as a sulphonic acid or a carboxylic acid. Preferably a carboxylic acid having a pKa value of less than 2 is used. Trifluoroacetic acid is a particularly preferred acid to be used in preparing the catalyst system. Examples of other suitable acids are the (1:2) adducts of boric acid with salicylic acids, 1,2-glycols or catechols.

The catalyst solutions prepared according to this invention contain typically 1-10000 mg palladium per kg solution, more typically 2-5000 mg/kg. The quantity of the bisphosphine of formula I used is typically 0.5-2 mole per gram atom palladium, more typically 0.75-1.5 mole per gram atom palladium. The acid is typically used in an amount of 0.5 to 50 equivalent per gram atom palladium, more typically 1 to 25 equivalent per gram atom palladium.

The catalyst solutions prepared according to the invention have good storage stability and are eminently suitable to be used in the copolymerization process for preparing linear alternating copolymers of carbon monoxide and one or more ethylenically unsaturated compounds.

The invention therefore also relates to a process for the preparation of copolymers of carbon monoxide and one or more ethylenically unsaturated compounds by reacting the monomers under polymerization conditions in the presence of a catalyst supplied as a solution which can be prepared according to this invention. In a preferred embodiment of this process the diluent used has substantially the same composition as the solvent used during the preparation of the catalyst solution.

Suitable ethylenically unsaturated compounds include compounds consisting of carbon and hydrogen only and compounds also comprising one or more heteroatoms such as oxygen or nitrogen. Examples are unsaturated esters such as vinylacetate and vinylpropionate.

Unsaturated hydrocarbons are preferred as starting materials for the copolymerization process. Suitable examples are ethene, propene, cyclopentene and styrene. The lower olefins are most preferred, in particular ethene, or a mixture of ethene and propene.

The copolymerization process may suitably be carried out in the presence of a diluent in which the copolymers are insoluble or virtually insoluble, so that they form a suspension in the diluent. In accordance with this invention it is advantageous to select as the diluent a lower aliphatic alcohol. If desired, the process may be carried out as a gas phase process.

The catalyst may be supplied to the copolymerization as a solution as prepared or it may be supplied impregnated on a carrier. Very suitable carriers are silica, polyethylene and a copolymer of carbon monoxide and an ethylenically unsaturated compound, in particular a copolymer which is based on the same monomers as the copolymer to be prepared.

The copolymerization process is preferably carried out at a temperature in the range from 30 to 150 °C, and at a pressure in the range from 20 to 100 bar, whereby the molar ratio between carbon monoxide and ethylenically unsaturated compound(s) is in the range from 5:1 to 1:5 and the amount of catalyst solution such that per mole of ethylenically unsaturated compound to be polymerized, from 10^{-7} to 10^{-2} gram-atom of palladium is present.

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The copolymerization process may be carried out in a batchwise manner or as a continuous process. It is very advantageous to recover the lower aliphatic alcohol after conducting the copolymerization and to reuse the recovered lower aliphatic alcohol in a subsequent copolymerization.

The invention is illustrated by the following examples.

EXAMPLE 1

A number of catalyst solutions were prepared as follows:

In each case a 1000 ml reactor vessel was charged with 395 grams of methanol at ambient pressure. The temperature was then raised to the pre-set value T and maintained at that value. Subsequently, 3.74 g of 1,3-bis[bis(2-methoxyphenyl)-phosphino]propane was added. A slurry was formed which was stirred for 20 minutes. To this slurry 1.50 g of solid palladium acetate was added, causing the ligand to dissolve to form an organo-metal complex.

After a generation period of G hours, 1.6 g of trifluoroacetic acid was added and the solution was allowed to react during 30 minutes.

Finally, the contents of the reactor were discharged into a 1000 ml jar and allowed to cool down to ambient temperature.

The obtained brown catalyst solutions were stored in a glass jar, air and daylight not being excluded during storage.

The production temperatures T and the generation periods G for each catalyst solution are listed below.

Catalyst solution	Production temp. (°C)	Generation period (hrs.)
1	23	8
2	26	4.5
3	32	2
4	40	0.5

The activity of all catalysts solutions was comparable to that of a conventional catalyst solution in acetone.

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It was observed that upon storage the solutions showed signs of catalyst decomposition visible by the formation of metallic palladium (plating) as a mirror on the glass wall. However, significant plating did only occur after storage for more than one week.

By plotting the temperature and generation period data, it can be seen that the relation between G and T fulfils the condition

$$G \leq 6.0 \times 10^{-21} \exp \left(\frac{14500}{T + 273.2} \right).$$

The relation between G and T approximately fulfils the equation

$$G = 9.3 \times 10^{-22} \exp \left(\frac{15000}{T + 273.2} \right),$$

such that the experimental values of G are equal or slightly below the calculated values for G.

EXAMPLE 2

A number of catalyst solutions were prepared, substantially as described in Example 1, whereby, however, at comparable temperature values shorter generation periods were applied.

The production temperatures T and the generation periods G for each catalyst solution are listed below.

Catalyst solution	Production temp. (°C)	Generation period (hrs.)
5	20	7.5
6	27	1.7
7	28	1
8	35	0.2

Again, it was observed that upon storage no significant plating did occur for more than one week.

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By plotting the temperature and generation period data, it can be seen that the relation between G and T approximately fulfils the equation

$$G = 7.1 \times 10^{-28} \exp \left(\frac{18800}{T + 273.2} \right).$$

EXAMPLE 3

5 A number of catalyst solutions were prepared, substantially as described in Example 1, whereby, however, generation periods were applied, which, for a certain temperature value, were intermediate between those applied in Example 1 and in Example 2.

10 The production temperatures T and the generation periods G for each catalyst solution are listed below.

Catalyst solution	Production temp. (°C)	Generation period (hrs.)
9	27	1.9
10	28	2.3
11	32	1
12	35	0.5
13	37	0.5
14	40	0.2

Upon storage, none of these catalyst solutions showed significant plating for more than one week.

EXAMPLE 4

15 A number of catalyst solutions were prepared, substantially as described in Example 1, whereby, however, at a certain temperature value, the applied generation periods were shorter than those applied in Example 2.

The production temperatures T and the generation periods G for each catalyst solution are listed below.

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Catalyst solution	Production temp. (°C)	Generation period (hrs.)
15	20	0.2
16	20	1.9
17	20	4.5
18	24	0.2
19	24	0.5
20	24	2
21	28	0.2
22	28	0.6
23	32	0.5

In all cases, instead of brown solutions, orange solutions containing a white precipitate were obtained.

5 Upon storage, the orange solutions gradually darkened and the precipitate gradually dissolved.

After a storage period of one to two weeks, brown solutions, as obtained in Example 1 resulted, which could be further stored for more than one week before significant plating was observed.

10 The activity of the eventually obtained brown solutions was again comparable to the activity of a conventional catalyst solution in acetone.

EXAMPLE A (for comparison, not according to the invention)

15 A number of catalyst solutions were prepared, substantially as described in Example 1, whereby however at comparable temperature values longer generation periods were applied.

The production temperatures T and the generation periods G for each catalyst solution are listed below.

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Catalyst solution	Production temp. (°C)	Generation period (hrs.)
24	20	20
25	27	16
26	27	5.0
27	32	4
28	35	1.9
29	40	1
30	43	0.6
31	50	0.2
32	55	0.5

In all cases, a brown solution was obtained, in which upon storage significant plating was observed in less than one week. By plotting the temperature and generation period data, it can be seen that the relation between G and T fulfils the condition

$$G > 6.0 \times 10^{-21} \exp \left(\frac{14500}{T + 273.2} \right).$$



C L A I M S

1. A process for the preparation of a solution of a catalyst system, suitable for use in a process for copolymerizing carbon monoxide and one or more ethylenically unsaturated compounds, which comprises (a) combining a palladium compound, a bisphosphine of the general formula $R^1R^2P-R-PR^3R^4$ (I) wherein each of R^1 , R^2 , R^3 and R^4 independently represents an aromatic hydrocarbyl group which is substituted with an alkoxy group and R represents a bivalent bridging group containing at least two carbon atoms in the bridge, and a lower aliphatic alcohol as solvent, and (b) admixing the obtained combination after a generation period G, during which a temperature T in the range of 0-70 °C is maintained, with an acid, whereby the said generation period G is selected such that the value for G (in hours) and the temperature T (in °C) are related as

$$G \leq 6.0 \times 10^{-21} \exp \left(\frac{14500}{T + 273.2} \right).$$

2. A process as claimed in claim 1, characterized in that as palladium compound a palladium salt of a carboxylic acid is used, in particular palladium (II) acetate, in the bisphosphine of formula (I) each of R^1 , R^2 , R^3 and R^4 independently represents a phenyl group, substituted with an alkoxy group at an ortho-position with respect to the phosphorus atom to which the phenyl group is bound, and R represents a trimethylene group.

3. A process as claimed in claim 2, characterized in that the bisphosphine is 1,3-bis[bis(2-methoxyphenyl)phosphino]propane.

4. A process as claimed in any one of claims 1-3, characterized in that as solvent methanol is used.

5. A process as claimed in any one of claims 1-4, characterized in that in (a) the bisphosphine of formula (I) is added to the solvent and that subsequently the palladium compound is supplied.



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6. A process as claimed in any one of claims 1-5, characterized in that the combination obtained in (a) is admixed with a carboxylic acid having a pKa of less than 2, in particular trifluoroacetic acid.

5 7. A process as claimed in any one of claims 1-6, characterized in that the temperature maintained during the generation period is selected in the range of 20-50 °C.

8. A process as claimed in any one of claims 1-7, characterized in that the generation period is selected such that

$$G \leq 9.3 \times 10^{-22} \exp \left(\frac{15000}{T + 273.2} \right).$$

10 9. A process as claimed in any one of claims 1-8, characterized in that the generation period is selected such that

$$G \geq 7.1 \times 10^{-28} \exp \left(\frac{18800}{T + 273.2} \right).$$

10. A solution of a catalyst system, characterized in that the solution is obtainable by a process as claimed in any one of claims 1-9.

15 11. A process for the preparation of copolymers of carbon monoxide and one or more ethylenically unsaturated compounds by reacting the monomers under polymerization conditions in the presence of a catalyst supplied as a solution which is obtainable by a process as claimed in any one of claims 1-9.

20 12. A process as claimed in claim 11, characterized in that it is carried out in the presence of a diluent in which the copolymers are insoluble or virtually insoluble, preferably in the presence of a lower aliphatic alcohol as a diluent.

25 13. A process as claimed in claim 11 or 12, characterized in that the process is carried out at a temperature in the range from 30 to



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5 150 °C, at a pressure in the range from 20 to 100 bar, whereby the molar ratio between carbon monoxide and ethylenically unsaturated compound(s) is in the range from 5:1 to 1:5 and the quantity of catalyst solution such that per mole of ethylenically unsaturated compound(s) to be polymerized from 10^{-7} to 10^{-2} gram-atom of palladium is present.

14. A process as claimed in any one of claims 11-13, characterized in that as ethylenically unsaturated compound(s) ethene or a mixture of ethene and propene is used.