

Patent Claims

1. Composition, comprising:

- a) an inert, porous support material;
- b) an ionic liquid,
- 5 c) a metal, selected from group 9 of the periodic table of the elements,
- d) a phosphorus-containing organic ligand, and
- e) at least one organic amine.

2. Composition according to Claim 1, characterized in that the inert, porous support material is selected from the group comprising aluminium oxide, silicon dioxide, titanium dioxide, zirconium dioxide, silicon carbide, carbon and mixtures of these components.

3. Composition according to Claim 2, characterized in that the inert, porous support material has the following parameters:

- a) BET surface area from 50 to 800 m²/g
- b) pore volume from 0.1 to 2.0 ml/g and
- c) mean pore diameter from 2 - 80 nm.

4. Composition according to Claims 1 - 3, characterized in that from the inert, porous support material with the use of an additional binder, selected from the group comprising:

- a) alumina,
- b) ceramic clays, and
- 25 c) colloids

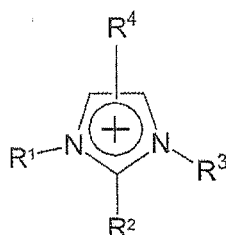
shaped bodies of different three-dimensional form selected from the group comprising:

- i) spherical,
- ii) cylindrical,
- 30 iii) ellipsoidal, and

iv) polylobular bodies

are formed in a size range from 1 - 10 mm.

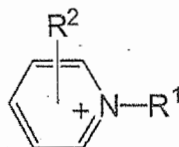
5. Composition according to Claims 1 - 4, characterized in that as the ionic liquid compounds are used wherein the anion is selected from the group comprising:
- 5 tetrafluoroborate ($[\text{BF}_4]^-$), hexafluorophosphate ($[\text{PF}_6]^-$), dicyanamide ($[\text{N}(\text{CN})_2]^-$), bis(trifluoromethylsulphonyl)imide ($[\text{NTf}_2]^-$), tricyanomethide ($[\text{C}(\text{CN})_3]^-$), tetracyanoborate ($[\text{B}(\text{CN})_4]^-$), halide (Cl^- , Br^- , F^- , I^-), hexafluoroantimonate ($[\text{SbF}_6]^-$), hexafluoroarsenate ($[\text{AsF}_6]^-$), sulphate ($[\text{SO}_4]^{2-}$), tosylate ($[\text{C}_7\text{H}_7\text{SO}_3]^-$), triflate ($[\text{CF}_3\text{SO}_3]^-$), nonaflate ($[\text{C}_4\text{F}_9\text{SO}_3]^-$), tris-(pentafluoroethyl) trifluorophosphate ($[\text{PF}_3(\text{C}_2\text{F}_5)_3]^-$), thiocyanate ($[\text{SCN}]^-$), carbonate ($[\text{CO}_3]^{2-}$), $[\text{R}'\text{-COO}]^-$, $[\text{R}'\text{-SO}_3]^-$, $[\text{R}'\text{PO}_4\text{R}'']^-$ or $[(\text{R}'\text{-SO}_2)_2\text{N}]^-$ with R' and R'' the same or different, and each is a linear or branched aliphatic or alicyclic residue containing 1 to 12 carbon atoms or a $\text{C}_5\text{-C}_{18}$ substituted aryl, $\text{C}_5\text{-C}_{18}$ substituted aryl- $\text{C}_1\text{-C}_6$ alkyl or $\text{C}_1\text{-C}_6$ alkyl- $\text{C}_5\text{-C}_{18}$ substituted aryl residue, which can be substituted with halogen atoms;
- 10 wherein the cation is selected from the group comprising:
- quaternary ammonium cations of the general formula $[\text{NR}^1\text{R}^2\text{R}^3\text{R}^4]^+$;
- phosphonium cations of the general formula $[\text{PR}^1\text{R}^2\text{R}^3\text{R}^4]^+$; and
- imidazolium cations of the general formula



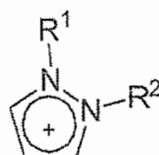
wherein the imidazole nucleus can be substituted with at least one group R, which is selected from $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ alkoxy, $\text{C}_1\text{-C}_6$ substituted aminoalkyl, $\text{C}_5\text{-C}_{12}$ substituted aryl or $\text{C}_5\text{-C}_{12}$ substituted aryl- $\text{C}_1\text{-C}_6$ alkyl groups;

pyridinium cations of the general formula

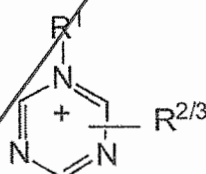
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wherein the pyridine nucleus can be substituted with at least one group R, which is selected from C1-C6 alkyl, C1-C6 alkoxy, C1-C6 substituted aminoalkyl, C5-C12 substituted aryl or C5-C12 substituted aryl-C1-C6 alkyl groups;
 5 pyrazolium cations of the general formula



wherein the pyrazole nucleus can be substituted with at least one group R, which is selected from C1-C6 alkyl, C1-C6 alkoxy, C1-C6 substituted aminoalkyl, C5-C12 substituted aryl or C5-C12 substituted aryl-C1-C6 alkyl groups; and
 10 triazolium cations of the general formula



wherein the triazole nucleus can be substituted with at least one group R, which is selected from C1-C6 alkyl, C1-C6 alkoxy, C1-C6 substituted aminoalkyl, C5-C12 substituted aryl or C5-C12 substituted aryl-C1-C6 alkyl groups,
 15 and the residues R¹, R², R³ independently of one another are selected from the group consisting of:

hydrogen;

linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl groups with 1 to 20 carbon atoms;

heteroaryl-, heteroaryl-C1-C6 alkyl groups with 3 to 8 carbon atoms in the

20 heteroaryl residue and at least one hetero atom selected from N, O and S, which

can be substituted with at least one group selected from C1-C6 alkyl groups and/or halogen atoms; and
aryl and aryl-C1-C6 alkyl groups with 5 to 12 carbon atoms in the aryl residue,
which can optionally be substituted with at least one C1-C6 alkyl group and/or a
5 halogen atom.

6. Composition according to Claims 1- 5, characterized in that the ionic liquid is selected from the group comprising :

- a) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide,
- 10 b) 1-butyl-3-methylimidazolium hexafluorophosphate, and
- c) 1-butyl-3-methylimidazolium tetrafluoroborate.

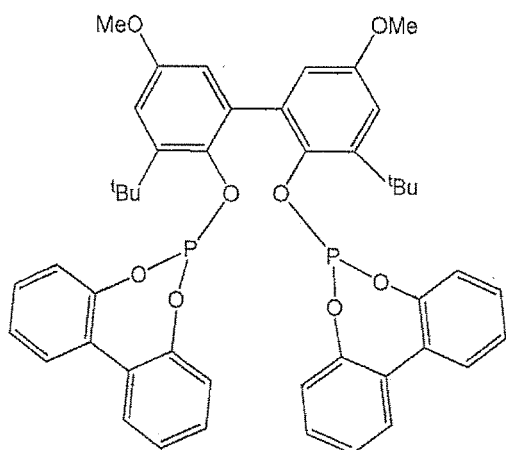
7. Composition according to Claims 1 - 6, characterized in that the metal is rhodium.

15 8. Composition according to Claims 1-7, characterized in that the phosphorus-containing organic ligand contains at least one covalent bond, which is selected from the group consisting of:

- a) phosphorus-oxygen; and
- b) phosphorus-nitrogen.

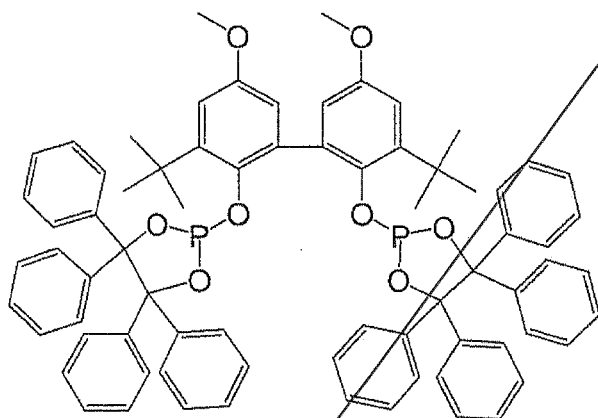
20 9. Composition according to Claim 8, characterized in that the phosphorus-containing organic ligand is selected from the group comprising:

- a) [6,6'-((3,3'-di-tert-butyl-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)bis(oxy))bis(dibenzo[d,f][1,3,2]dioxaphosphepine)] according to formula VII



VII

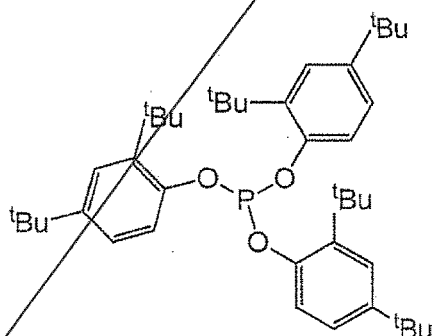
b) [2,2'-((3,3'-di-tert-butyl-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)bis(oxy))bis(4,4,5,5-tetraphenyl-1,3,2-dioxaphospholane)] according to formula VIII, and



VIII

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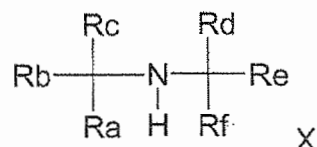
c) Tris-(2,4-di-tert-butylphenyl) phosphite according to formula IX



IX

10. Composition according to Claims 1 - 9, characterized in that the organic amine is selected from the group comprising:

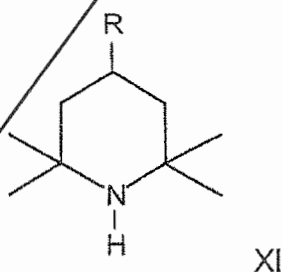
a) at least one amine according to formula X



wherein Ra, Rb, Rc, Rd, Re and Rf are the same or different hydrocarbon residues, which can also be bound to one another, and

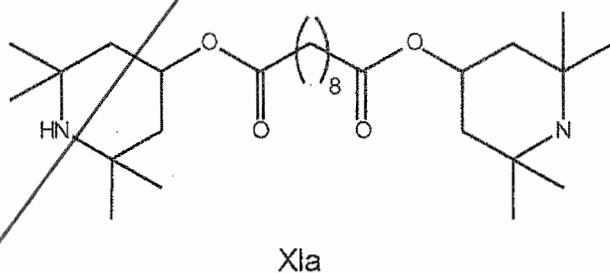
b) a tertiary amine, selected from the group of the aliphatic, aromatic, cycloaliphatic and heteroaromatic amines, or combinations thereof.

11. Composition according to Claim 10, characterized in that the organic amine contains at least one compound with a 2,2,6,6-tetramethylpiperidine unit according to formula XI:

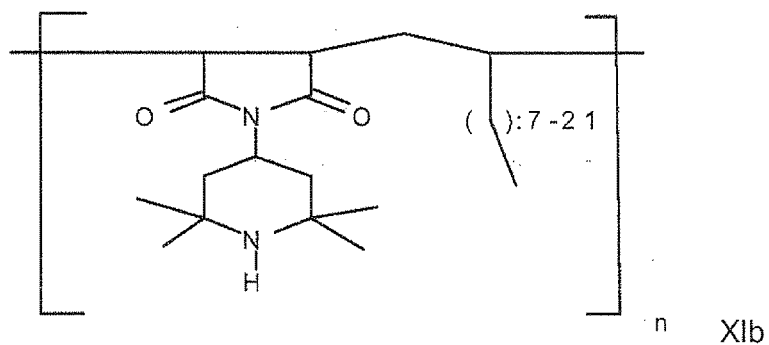
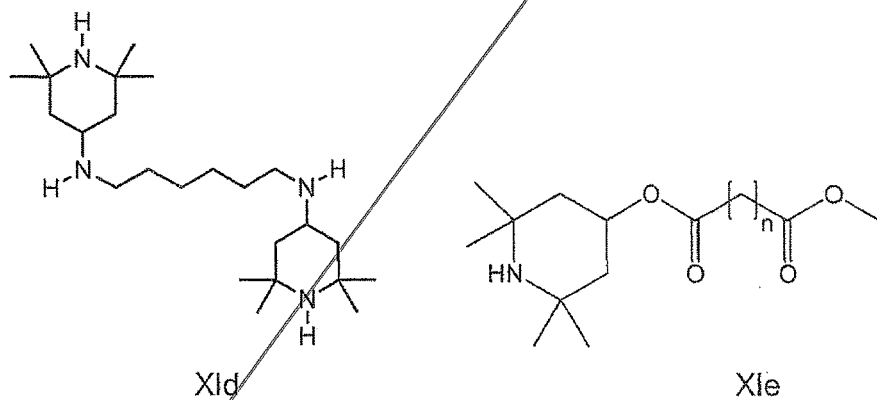
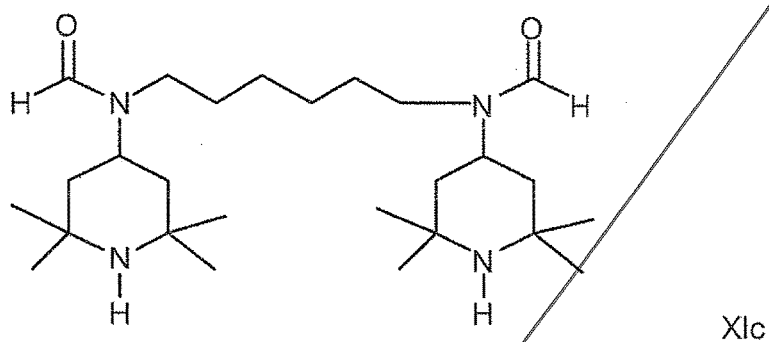
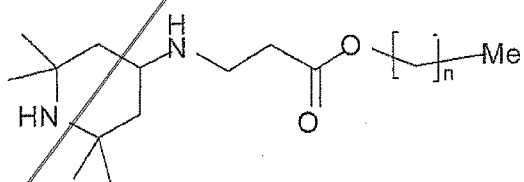


where R represents an organic residue, H, a hydroxyl group or a halogen.

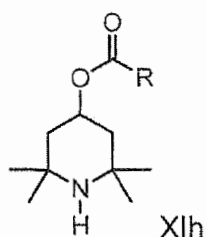
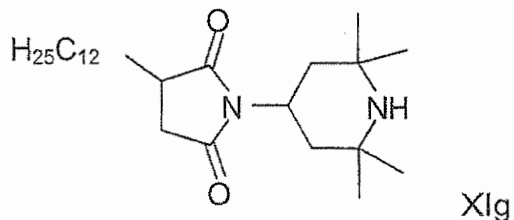
12. Composition according to Claim 11, characterized in that the organic amine contains at least one of the compounds according to the formulae Xla to Xlh:



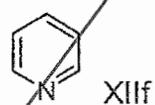
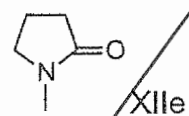
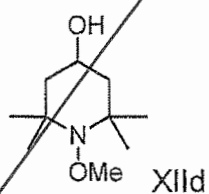
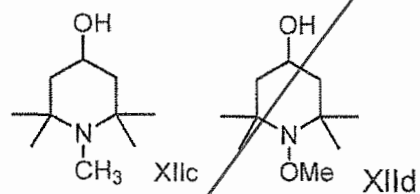
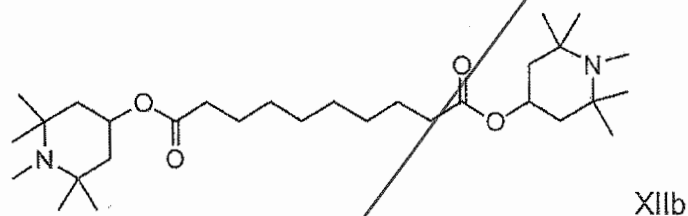
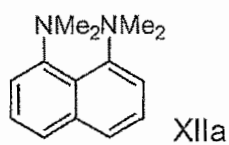
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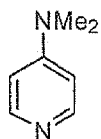
with $n = 1$ to 20XIe
with $n = 1$ to 12XIIf
with $n = 1$ to 17

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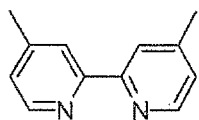
with R = C₆ to C₂₀ alkyl

- 5 13. Composition according to Claims 10 - 12, characterized in that contains a further organic amine according to the formulae XIIa to XIIj:

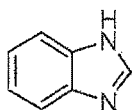




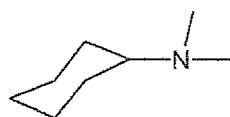
XIIg



XIIh



XIIi



XIIj

14. Multiphase reaction mixture, containing:

- a) an olefin-containing hydrocarbon mixture,
- b) a gas mixture comprising carbon monoxide and hydrogen and
- c) aldehydes,

characterized by a composition according to one of the previous claims as the catalytically active composition.

15. Process for the hydroformylation of olefin-containing hydrocarbon mixtures to aldehydes, with addition of a composition according to the previous claims as the catalytically active composition, wherein:

- a) the water content of the olefin-containing hydrocarbon mixtures is adjusted to at most 20 ppm,
- b) the content of multiply unsaturated compounds in the olefin-containing hydrocarbon mixture is adjusted to at most 3000 ppm,
- c) a molar ratio of organic amines according to Claims 10-13 to phosphorus-containing organic ligands according to Claims 8 - 9 of at least 4:1 is set,
- d) a molar ratio of phosphorus-containing organic ligands according to Claims 8 - 9

to rhodium of at least 10:1 is set.

16. Process for the hydroformylation of olefin-containing hydrocarbon mixtures according to Claim 15, characterized in that the reaction mixture is periodically
5 subjected to a stripping gas treatment for removal of the aldehyde.

17. Process according to Claims 15-16, characterized in that the stripping gas is selected from the group comprising:

- a) mixtures of carbon monoxide and hydrogen;
- 10 b) mixtures of C2-C6 alkanes;
- c) mixtures of C2-C6 alkanes and C2-C6 alkenes; and
- d) inert gases.

18. Process according to Claims 15-17, characterized in that after conclusion of the
15 reaction a part of the gaseous reaction mixture is fed back into the reaction zone again.

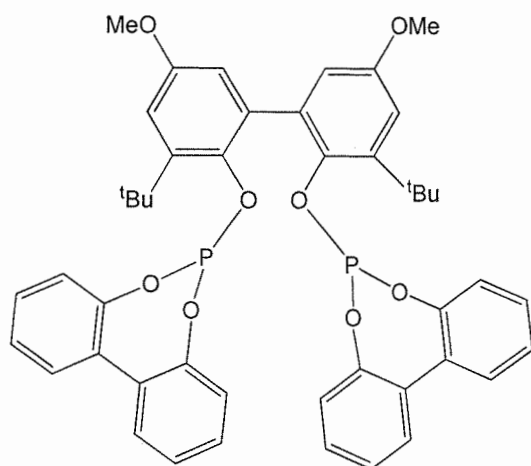
19. Process according to Claims 15-18, characterized in that the olefin-containing hydrocarbon mixture is selected from the group comprising:

- 20 a) ethylene,
- b) propylene,
- c) C4 olefins and multiply unsaturated compounds, and
- d) C5 olefins and multiply unsaturated compounds.

Patent Claims

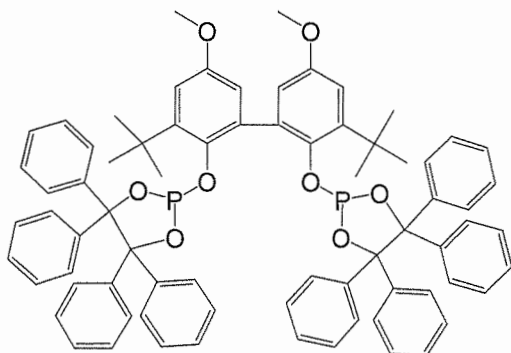
1. Composition, comprising:

- a) an inert, porous support material;
- b) an ionic liquid selected from the group consisting of:
 - b1) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide,
 - b2) 1-butyl-3-methylimidazolium hexafluorophosphate, and
 - b3) 1-butyl-3-methylimidazolium tetrafluoroborate,
- c) a metal, selected from group 9 of the periodic table of the elements,
- d) a phosphorus-containing organic ligand selected from the group consisting of:
 - d1) [6,6'-((3,3'-di-tert-butyl-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)bis(oxy))bis(dibenzo[d,f][1,3,2]dioxaphosphine)] according to formula VII



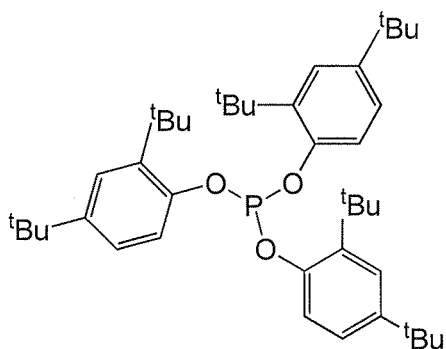
VII;

- d2) [2,2'-((3,3'-di-tert-butyl-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)bis(oxy))bis(4,4,5,5-tetraphenyl-1,3,2-dioxaphospholane)] according to formula VIII



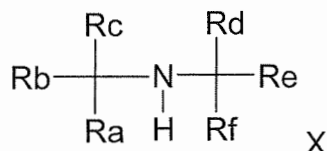
VIII; and

- d3) Tris-(2,4-di-tert-butylphenyl) phosphite according to formula IX



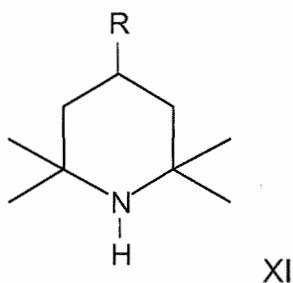
- e) at least one organic amine with a 2,2,6,6-tetramethylpiperidine unit.
2. Composition according to Claim 1, characterized in that the inert, porous support material is selected from the group comprising aluminium oxide, silicon dioxide, titanium dioxide, zirconium dioxide, silicon carbide, carbon and mixtures of these components.
 3. Composition according to Claim 2, characterized in that the inert, porous support material has the following parameters:
 - a) BET surface area from 50 to 800 m²/g
 - b) pore volume from 0.1 to 2.0 ml/g and
 - c) mean pore diameter from 2 - 80 nm.
 4. Composition according to Claims 1 - 3, characterized in that from the inert, porous support material with the use of an additional binder, selected from the group comprising:
 - a) alumina,
 - b) ceramic clays, and
 - c) colloidsshaped bodies of different three-dimensional form selected from the group comprising:
 - i) spherical,
 - ii) cylindrical,
 - iii) ellipsoidal, and
 - iv) polylobular bodiesare formed in a size range from 1 - 10 mm.

5. Composition according to Claims 1 - 4, characterized in that the metal is rhodium.
6. Composition according to Claims 1 - 5, characterized in that the organic amine is selected from the group comprising:
 - a) at least one amine according to formula X



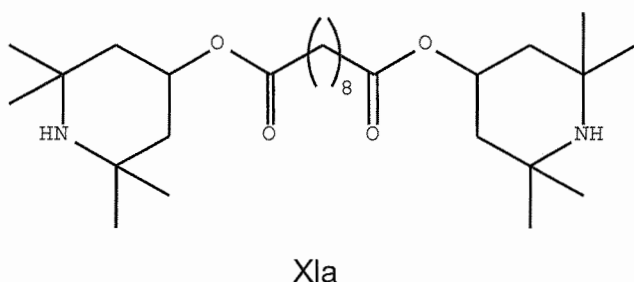
wherein Ra, Rb, Rc, Rd, Re and Rf are the same or different hydrocarbon residues, which can also be bound to one another, and

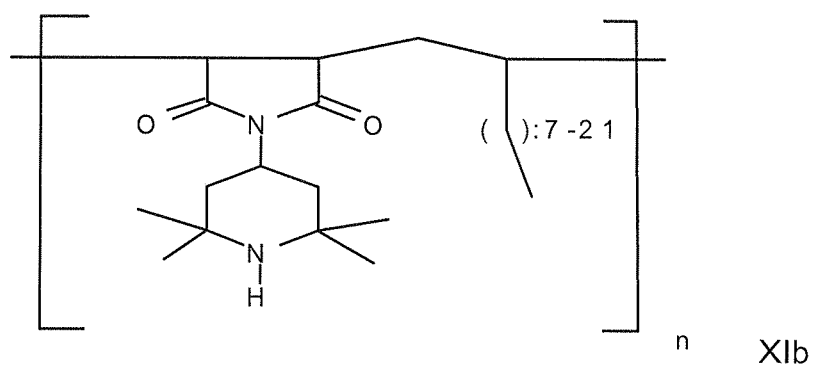
- b) a tertiary amine, selected from the group of the aliphatic, aromatic, cycloaliphatic and heteroaromatic amines, or combinations thereof.
7. Composition according to Claim 6, characterized in that the organic amine contains at least one compound according to formula XI:



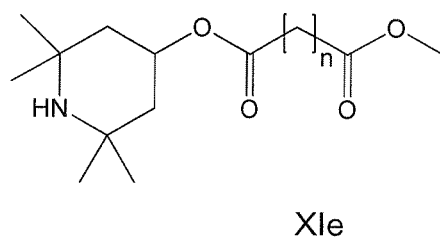
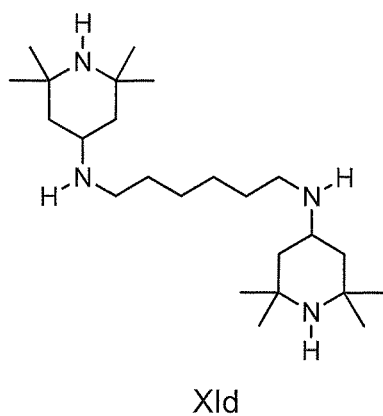
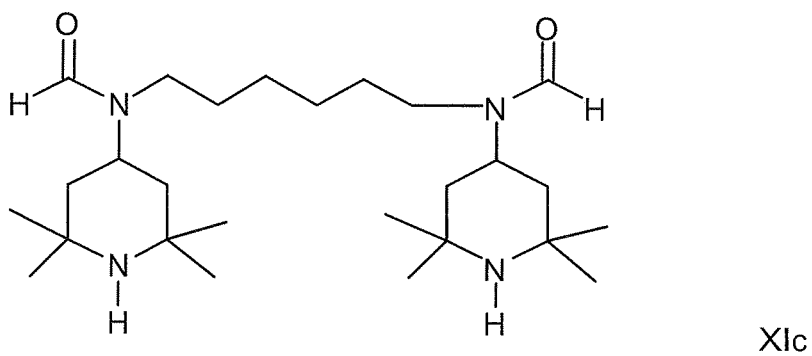
where R represents an organic residue, H, a hydroxyl group or a halogen.

8. Composition according to Claim 7, characterized in that the organic amine contains at least one of the compounds according to the formulae Xla to XIh:

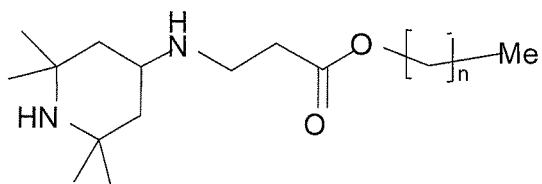




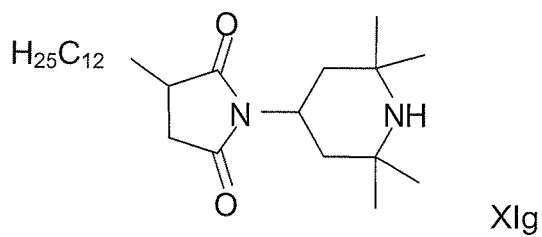
with $n = 1$ to 20

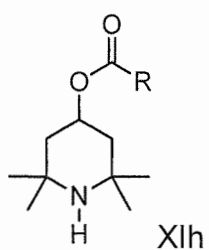


with $n = 1$ to 12



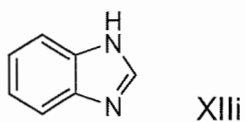
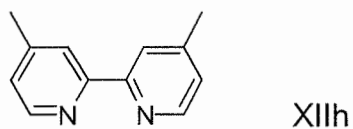
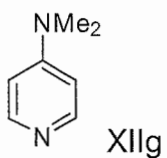
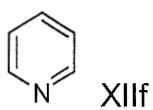
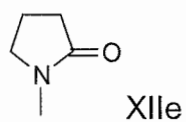
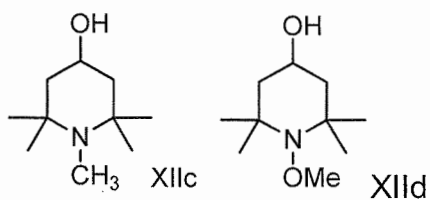
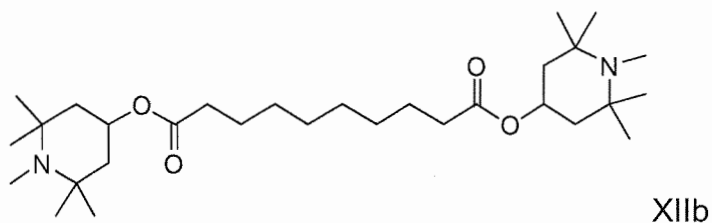
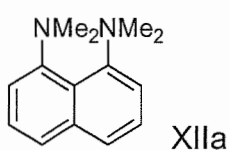
with $n = 1$ to 17

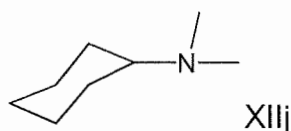




with R = C6 to C20 alkyl

9. Composition according to Claims 6 - 8, characterized in that the composition contains a further organic amine according to the formulae XIIa to XIIj:





10. Multiphase reaction mixture, containing:

- a) an olefin-containing hydrocarbon mixture,
 - b) a gas mixture comprising carbon monoxide and hydrogen and
 - c) aldehydes,
- characterized by a composition according to one of the previous claims as the catalytically active composition.

11. Process for the hydroformylation of olefin-containing hydrocarbon mixtures to aldehydes, with addition of a composition according to the previous claims as the catalytically active composition, wherein:

- a) the water content of the olefin-containing hydrocarbon mixtures is adjusted to at most 20 ppm,
- b) the content of multiply unsaturated compounds in the olefin-containing hydrocarbon mixture is adjusted to at most 3000 ppm,
- c) a molar ratio of organic amines according to Claims 6-9 to phosphorus-containing organic ligands according to Claim 1 of at least 4:1 is set,
- d) a molar ratio of phosphorus-containing organic ligands according to Claim 1 to rhodium of at least 10:1 is set.

12. Process for the hydroformylation of olefin-containing hydrocarbon mixtures according to Claim 11, characterized in that the reaction mixture is periodically subjected to a stripping gas treatment for removal of the aldehyde.

13. Process according to Claims 11-12, characterized in that the stripping gas is selected from the group comprising:

- a) mixtures of carbon monoxide and hydrogen;
- b) mixtures of C2-C6 alkanes;
- c) mixtures of C2-C6 alkanes and C2-C6 alkenes; and
- d) inert gases.

14. Process according to Claims 11-13, characterized in that after conclusion of the reaction a part of the gaseous reaction mixture is fed back into the reaction zone again.
15. Process according to Claims 11-14, characterized in that the olefin-containing hydrocarbon mixture is selected from the group comprising:
- a) ethylene,
 - b) propylene,
 - c) C4 olefins and multiply unsaturated compounds, and
 - d) C5 olefins and multiply unsaturated compounds.