

PROCESS FOR THE ELECTROCHEMICAL PREPARATION OF
CATALYSTS BASED ON TRANSITION METAL AND PHOSPHINE

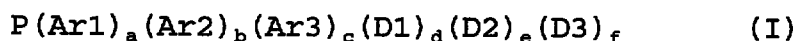
The present invention relates to an electrochemical process for the preparation of compounds which can be used as catalysts.

The compounds towards which the process of the invention is directed contain at least one transition metal in oxidation state 0 or 1 combined with at least one monodentate or bidentate water-soluble phosphine.

Such compounds can be used, for example, as catalysts in place of the catalysts used in the hydrocyanation reaction of ethylenic compounds, as described in patent FR-A-2,338,253. In the present text, they will be referred to as catalysts without this being a limitation on their field of use.

The process for the electrochemical synthesis of the catalysts consists of the electrolytic treatment of an aqueous solution containing at least one transition metal compound and at least one monodentate or bidentate water-soluble phosphine, placed in the cathode compartment of an electrolysis cell of an electrolyser.

The water-soluble phosphine used in the process of the invention [lacuna] a monodentate phosphine corresponding to the general formula (I):



in which:

- Ar₁ and Ar₂, which may be identical or different, represent aryl groups or aryl groups containing one or more substituents such as:

- 5 - alkyl or alkoxy radical having 1 to 4 carbon atoms,
- halogen atom,
- nitrile group,
- nitro group,
- 10 - hydrophilic group such as:
 -COOM, -SO₃M, -PO₃M, M representing an inorganic or organic cationic residue chosen from a proton, cations derived from alkali metals or alkaline-earth metals, ammonium cations -N(R)₄ in which formula
15 the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, the other cations derived from metals whose arylcarboxylic acid, arylsulphonic acid or arylphosphonic acid salts are water-soluble,
20 -N(R)₃ in which formula the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms,
 -OH
- 25 - Ar₃ represents an aryl group containing one or more substituents such as:
 - alkyl or alkoxy radical having 1 to 4 carbon atoms,

- halogen atom,
- nitrile group,
- nitro group,
- hydrophilic group such as:

5 -COOM, -PO₃M, M representing an inorganic or
 organic cationic residue chosen from a proton, cations
 derived from alkali metals or alkaline-earth metals,
 ammonium cations -N(R)₄ in which formula the symbols R,
 which may be identical or different, represent a
 10 hydrogen atom or an alkyl radical having from 1 to 4
 carbon atoms, the other cations derived from metals
 whose arylcarboxylic acid or arylphosphonic acid salts
 are water-soluble,

 -N(R)₃ in which formula the symbols R, which
 15 may be identical or different, represent a hydrogen
 atom or an alkyl radical having from 1 to 4 carbon
 atoms,

-OH

at least one of the said substituents of Ar₃ being a
 20 hydrophilic group as defined above,

- a represents 0 or 1,
- b represents 0 or 1,
- c represents 0 or 1,
- D1, D2 and D3, which may be identical or different,
- 25 represent an alkyl group, a cycloalkyl group or an
 alkyl or cycloalkyl group containing one or more
 substituents such as:

- alkoxy radical having 1 to 4 carbon atoms,

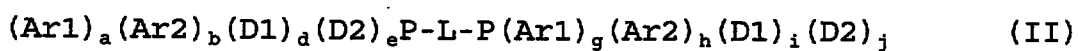
- halogen atom,
- nitrile group,
- nitro group,
- hydrophilic group such as:

5 -COOM, -SO₃M, -PO₃M, M representing an
 inorganic or organic cationic residue chosen from a
 proton, cations derived from alkali metals or alkaline-
 earth metals, ammonium cations -N(R)₄ in which formula
 the symbols R, which may be identical or different,
 10 represent a hydrogen atom or an alkyl radical having
 from 1 to 4 carbon atoms, the other cations derived
 from metals whose carboxylic acid, sulphonic acid or
 phosphonic acid salts are water-soluble,

 -N(R)₃ in which formula the symbols R, which
 15 may be identical or different, represent a hydrogen
 atom or an alkyl radical having from 1 to 4 carbon
 atoms,

 -OH

- d, e and f represent 0 or 1,
 20 - the sum (a+b+c+d+e+f) is equal to 3
 or a bidentate phosphine corresponding to the general
 formula (II):



in which:

25 - Ar1, Ar2, D1 and D2 have the meanings given above for
 formula (I),
 - a, b, d, e, g, h, i and j each represent 0 or 1,
 - the sum (a+b+d+e) is equal to 2,

- the sum (g+h+i+j) is equal to 2,
- L represents a single valency bond or a divalent hydrocarbon-based radical such as an alkylene radical, a cycloalkylene radical, an arylene radical, a radical
5 derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being directly attached to one of the phosphorus atoms or to the two phosphorus atoms or being attached to one of the phosphorus atoms or to
10 the two via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring(s) which may form part of the divalent radical L to contain one or more substituents as defined for Ar1, Ar2, D1 and D2.

15 As examples of metals whose carboxylic acid, sulphonc acid or phosphonic acid salts are water-soluble, mention may be made of lead, zinc and tin.

In the present text, the term water-soluble is understood to refer to a compound which is soluble
20 to at least 0.01 g per litre of water.

The preferred water-soluble phosphines are the phosphines of formula (I) or of formula (II) in which Ar1 and Ar2 are phenyl groups or phenyl groups containing one or two substituents as defined above,
25 Ar3 is a phenyl group containing one or two substituents as defined above, D1, D2 and D3, which may be identical or different, represent an alkyl group having from 1 to 6 carbon atoms or a cycloalkyl group

having 5 to 8 carbon atoms, or represent an alkyl group having from 1 to 6 carbon atoms or cycloalkyl group having 5 to 8 carbon atoms containing one or more substituents as defined above, L is a single valency bond, an alkylene radical having from 1 to 6 carbon atoms, a monocyclic or bicyclic cycloalkylene radical having from 4 to 12 carbon atoms, a phenylene radical, a diphenylene radical, a naphthylene radical, a dinaphthylene radical, a radical derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being directly attached to one of the phosphorus atoms or to the two phosphorus atoms or being attached to one of the phosphorus atoms or to the two via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring(s) which may form part of the divalent radical L to contain one or more substituents such as an alkyl group having 1 to 4 carbon atoms.

The preferred water-soluble phosphines are the phosphines of formula (I) or of formula (II) in which:

- the substituent(s) of Ar₁ and Ar₂, which may be identical or different, represent(s) groups such as:
- alkyl or alkoxy radical having 1 to 2 carbon atoms,
- chlorine atom,
- hydrophilic group such as:

-COOM, -SO₃M, -PO₃M, M representing an inorganic or organic cationic residue chosen from a proton, cations derived from sodium, potassium, calcium or barium, ammonium, tetramethylammonium, tetraethyl-
 5 ammonium, tetrapropylammonium and tetrabutylammonium cations, cations derived from zinc, lead or tin,

-N(R)₃, in which formula the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon
 10 atoms,

-OH

- the substituent(s) of Ar₃, which may be identical or different, represent(s) groups such as:

- alkyl or alkoxy radical having 1 to 2 carbon
 15 atoms,
- chlorine atom,
- hydrophilic group such as:

-COOM, -PO₃M, M representing an inorganic or organic cationic residue chosen from a proton, cations
 20 derived from sodium, potassium, calcium or barium, ammonium, tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium cations, cations derived from zinc, lead or tin,

-N(R)₃, in which formula the symbols R, which may be identical or different, represent a hydrogen
 25 atom or an alkyl radical having from 1 to 4 carbon atoms,

-OH

overall, at least two of the said substituents of Ar1, Ar2, Ar3, D1, D2 and D3 for the phosphines of formula (I) and of Ar1, Ar2, D1 and D2 for the phosphines of formula (II) being a hydrophilic group as defined
 5 above.

As non-limiting examples of phosphines of general formula (I), mention may be made in particular of tris(hydroxymethyl)phosphine, tris(2-hydroxyethyl)-phosphine, tris(3-hydroxypropyl)phosphine, tris-
 10 (2-carboxymethyl)phosphine, the sodium salt of tris(3-carboxyphenyl)phosphine, tris(3-carboxyethyl)phosphine, tris(4-trimethylammonio-phenyl)phosphine iodide, the sodium salt of tris(2-phosphoethyl)phosphine, bis(2-carboxyethyl)phenylphosphine, hydroxymethylbis(2-
 15 hydroxyethyl)phosphine, the sodium salt of tris(para-phosphophenyl)phosphine, the sodium salt of bis(meta-sulphophenyl)-para-carboxyphenylphosphine and the sodium salt of bis(meta-sulphophenyl)-2-sulphoethylphosphine.

As non-limiting example of phosphines of general formula (II), mention may be made in particular of the sodium salt of 2,2'-bis[di(sulphonatophenyl)-phosphino]-1,1'-binaphthyl, the sodium salt of
 1,2-bis[di(sulphonatophenyl)phosphinomethyl]cyclobutane
 25 (CBDTs), 1,2-bis(dihydroxymethylphosphino)ethane, 1,3-bis(dihydroxymethylphosphino)propane and the sodium salt of 2,2'-bis[di(sulphonatophenyl)phosphinomethyl]-1,1'-binaphthyl.

Needless to say, mixtures of several water-soluble phosphines defined above can be used.

Some of the water-soluble phosphines of formula (I) or (II) are commercially available.

5 For the preparation of the others, reference may be made to the general or specific processes for the synthesis of phosphines described in the general treatises such as Houben-Weyl, Method der organischen Chemie, organische Phosphor Verbindungen, Part 1
10 (1963).

 Lastly, for the preparation of the water-soluble derivatives not described, it is possible, starting with phosphines not containing any water-soluble substituents defined above, to readily
15 introduce one or more of these hydrophilic substituents. Thus, sulphonate groups, for example, can be introduced by reacting SO_3 with sulphuric acid. Similarly, carboxylate, phosphonate and quaternary ammonium groups can be introduced by applying the known
20 chemical methods for this type of synthesis.

 Nickel, cobalt, iron, palladium, platinum, rhodium and iridium compounds are preferably used as transition metal compounds. Water-soluble compounds or compounds capable of dissolving under the reaction
25 conditions are used. The residue attached to the metal is not critical provided that it satisfies these conditions.

 Among the abovementioned compounds, the ones

most preferred are the nickel compounds. As non-limiting examples, mention may be made of compounds such as nickel carboxylates (in particular nickel acetate, nickel formate and nickel citrate), nickel
5 carbonate, nickel bicarbonate, nickel borate, nickel bromide, nickel chloride, nickel iodide, nickel thiocyanate, nickel cyanide, nickel hydroxide, nickel hydrophosphite, nickel phosphite, nickel phosphate and derivatives, nickel nitrate, nickel sulphate, nickel
10 sulphite, nickel arylsulphonates and nickel alkylsulphonates.

It is not necessary for the nickel compound itself to be water-soluble. For example, nickel cyanide, which is sparingly soluble in water, dissolves
15 well in an aqueous solution of water-soluble phosphine.

The electrolysis cell of the electrolyser used in the present process contains a cathode compartment and an anode compartment separated by a separating member.

20 The cathode of the electrolysis cell can be made of a material such as platinum, gold, iridium, ruthenium, palladium, nickel, graphite, vitreous carbon, iron, a stainless steel, a special steel, lead, zinc, cadmium, mercury or an amalgam. It can also
25 consist of titanium, tantalum, nickel or a stainless steel, coated with a layer of platinum, gold, iridium or ruthenium, with a mixture of several of these metals, with platinum oxide, palladium oxide, iridium

oxide, rhodium oxide, ruthenium oxide, osmium oxide or tantalum oxide, or with a mixture of several of these oxides.

5 The cathode can have a flat structure such as a plate or grille or a voluminous structure; it can, in particular, be perforated or unfolded. Granular piles of the materials mentioned above, felts or foams of these materials can be used as voluminous-type structures.

10 The anode can be made of a material such as platinum, gold, iridium, ruthenium, palladium, nickel, graphite, vitreous carbon, a stainless steel, a special steel or lead. It can also consist of titanium or tantalum coated with a layer of platinum, gold,
15 iridium, ruthenium, with a mixture of several of these metals, with platinum oxide, palladium oxide, iridium oxide, rhodium oxide, ruthenium oxide, osmium oxide or tantalum oxide, or with a mixture of several of these oxides.

20 The structure of the anode can be of various types, as has been defined for the cathode.

 The separating member of the electrolysis cell consists of an ion-exchange membrane or a porous diaphragm.

25 The membranes can be of the cationic type, in particular prepared from cation-exchange resins containing acidic groups, such as sulphonic groups or carboxylic groups. Preferably, membranes prepared with

sulphonic resins will be used. As membranes of this type, mention may be made, for example, of those sold under the brand names Nafion® (perfluoro sulphonic membranes) or Selemion®.

5 The membranes can also be of anionic type, but cationic membranes are generally preferred since they have a certain number of advantages. In particular, they are more solid than anionic membranes and they also make it possible to work with higher
10 current intensities.

The porous diaphragms can be, in particular, diaphragms made of porous ceramic, diaphragms made of woven or nonwoven synthetic fibres, or deposited diaphragms made of asbestos fibres or synthetic fibres.

15 The separating member can be mounted supported on the anode or on the cathode.

As mentioned above, the aqueous solution comprising the monodentate or bidentate water-soluble phosphine and the transition metal compound is found in
20 the cathode compartment. The initial concentration of monodentate or bidentate water-soluble phosphine is generally between 10^{-3} mol/litre and 1 mol/litre. The initial concentration of transition metal compound, in particular of nickel compound, is generally between
25 10^{-5} mol/litre and 1 mol/litre.

Other compounds which allow the electrolyte conductivity to be increased, such as, for example, soluble salts, can be added to the cathode compartment.

Complexing agents capable of modifying the potential at which the reduction of the transition metal is carried out can also be added. As examples of such complexing agents, mention may be made of cyanides
5 and chlorides.

The solution in the cathode compartment can also comprise compounds whose role is to complete the catalyst prepared by the process of the invention. These compounds are, in particular, Lewis acids.

10 In the present text, the term Lewis acid is understood, according to the usual definition, to refer to electron-pair-acceptor compounds.

The Lewis acids mentioned in the treatise edited by G.A. Olah "Friedel-Crafts and Related
15 Reactions", volume I, pages 191 to 197, (1963) can be used in particular.

The Lewis acids which can be used in the cathode compartment are chosen from compounds of the elements from groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va,
20 Vb, VIb, VIIb and VIII of the Periodic Table of the Elements, as published in the Handbook of Chemistry and Physics, 51st edition (1970-1971) of The Chemical Rubber Co., provided that the said compounds are at least partially soluble and stable in water or more
25 generally in the aqueous solution to be treated by electrolysis. These compounds are usually, but in a non-limiting manner, salts, in particular halides, preferably chlorides and bromides, sulphates, nitrates,

sulphonates, in particular trifluoromethanesulphonates, carboxylates, acetylacetonates, tetrafluoroborates and phosphates.

As non-limiting examples of such Lewis acids, mention may be made of zinc chloride, zinc bromide, zinc iodide, zinc trifluoromethanesulphonate, zinc acetate, zinc nitrate, zinc tetrafluoroborate, manganese chloride, manganese bromide, nickel chloride, nickel bromide, nickel cyanide, nickel acetylacetonate, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, chlorides, bromides, sulphates, nitrates, carboxylates or trifluoromethanesulphonates of rare-earth elements such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium, cobalt chloride, ferrous chloride or yttrium chloride.

Needless to say, mixtures of several Lewis acids can be used.

Among the Lewis acids which can be used, mention may be made most particularly of zinc chloride, zinc bromide, zinc sulphate, zinc tetrafluoroborate, stannous chloride, stannous bromide, zinc chloride/stannous chloride mixtures, nickel chloride, nickel bromide and nickel acetylacetonate.

The Lewis acid used generally represents from 0 to 50 mol per mole of transition metal compound, more particularly of nickel compound, and preferably from 0

to 10 mol per mole.

The anode compartment contains an aqueous solution of an anolyte which can consist of an acid such as, in particular, sulphuric acid, nitric acid, 5 water-soluble carboxylic acids such as acetic acid, of their salts, in particular the sodium, potassium, ammonium or quaternary ammonium salts, or of a base such as, in particular, sodium hydroxide or potassium hydroxide. Preferably, the anolyte will be chosen from 10 sulphuric acid and its salts, in particular dipotassium sulphate, potassium hydrogensulphate, disodium sulphate and sodium hydrogensulphate.

The anolyte can also consist of one or more water-soluble phosphines defined above.

15 The initial concentration of the anolyte in the solution in the anode compartment is generally from 10^{-3} mol/litre to 3 mol/litre.

The electric current used in the process of the invention is defined by its intensity and the 20 cathode potential. The potential can be kept constant throughout the electrolysis (potentiostatic). Another possibility is to keep the intensity constant (intensistatic). In the continuous running of the process of the invention, these two variants are 25 equivalent.

When the process is performed at constant potential, the value of this potential can readily be determined by those skilled in the art by plotting

intensity/potential curves.

The current density can reach 30 A/dm². It is adjusted as a function of the amount of transition metal to be reduced.

5 The temperature at which the process is performed is generally from 0°C to 95°C.

 An advantageous variant of the process of the invention consists in regenerating a spent catalyst, i.e. a catalyst which has been used and has become at
10 least partially inactive. Thus, a catalyst based on monodentate or bidentate water-soluble phosphine and on a transition metal in oxidation state 0 or 1, also optionally containing one or more Lewis acids, used in the hydrocyanation reaction of butadiene and/or of
15 pentenenitriles, gradually becomes deactivated, in particular by oxidation of the transition metal. This transition metal, and more particularly nickel, is converted at least partly into cyanide. At the end of the hydrocyanation reaction, the aqueous phase
20 containing, in particular, the monodentate or bidentate water-soluble phosphine and the transition metal compound can readily be separated from the organic phase. This aqueous phase can contain variable amounts of compounds initially introduced, such as butadiene
25 and/or pentenenitriles, or compounds formed during the reaction, such as adiponitrile, methylglutaronitrile, ethylsuccinonitrile, pentenenitriles and methylbutene-nitriles. The aqueous phase is treated

electrochemically as described above in order to regenerate the catalyst.

The example which follows illustrates the invention.

5

EXAMPLE

Apparatus used

The electrolysis cell is composed of a glass cylindrical container with a working volume of about 100 ml, in which there is a cathode in the form of a platinum grille, a cylindrical anode well, placed
10 inside the cathode grille and comprising at the base a membrane made of Nafion 417® type resin and in which the anode in the form of a platinum plate is inserted.

The electrolyser is connected to a
15 potentiostat which allows the cathode potential to be kept at a value of -1.2 volts relative to an Ag/AgCl reference electrode.

Abbreviations used:

3PN = 3-pentenitrile
20 ADN = adiponitrile
RC = selectivity towards a compound obtained relative to the starting compound converted
t.o. = turnover = number of mmol of dinitriles formed per mmol of Ni(0) used
25 COD = cyclooctadiene.

The cathode compartment of an electrolyser is loaded with 50 ml of an aqueous solution containing 7.5 mmol of nickel cyanide $\text{Ni}(\text{CN})_2$ and 15 mmol of the

sodium salt of 1,2-bis[di(sulphonatophenyl)phosphino-methyl]cyclobutane (CBDTS).

50 ml of aqueous sulphuric acid solution (0.02 N) are loaded into the anode compartment.

5 The electrolysis is carried out at 25°C at a controlled potential of -1.2 volts. Samples are taken regularly in order to assay the remaining Ni(II) by polarography.

After electrolysis for 15 h, 80% of the
10 Ni(II) are converted into Ni(0).

Hydrocyanation tests of the 3-pentenitrile in the catalyst solution 1 generated electrochemically.

Tests	Catalyst	Ni(0) (mmol)	HCN (mmol/h)	RCADN (%)	t.o.
CT1*	Ni(COD) ₂ /CBDTS	4.5	44	81	4
15 CT2**	Ni(CN) ₂ (CBDTS)	0	44	0	0
Example	solution 1	3.6	35	80	5

Operating conditions of the hydrocyanation tests:

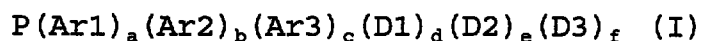
- 3PN: 204 mmol; ZnCl₂: 20 mmol; 65°C; 0.5 h.

20 CT1* = comparative test with a catalyst prepared by exchanging the COD ligands of Ni(COD)₂ with CBDTS,

CT2** = comparative test with an Ni(CN)₂(CBDTS) solution which has not been treated
25 electrochemically.

CLAIMS

1. Process for the electrochemical preparation of catalysts containing at least one transition metal in oxidation state 0 or 1, combined
5 with at least one monodentate or bidentate water-soluble phosphine, characterized in that it consists of the electrolytic treatment of an aqueous solution containing at least one transition metal compound and at least one monodentate or bidentate water-soluble
10 phosphine, placed in the cathode compartment of an electrolysis cell of an electrolyser, the monodentate phosphine corresponding to the general formula (I):



in which:

15 - Ar1 and Ar2, which may be identical or different, represent aryl groups or aryl groups containing one or more substituents such as:

- alkyl or alkoxy radical having 1 to 4 carbon atoms,

20 - halogen atom,
- nitrile group,
- nitro group,

- hydrophilic group such as:

-COOM, -SO₃M, -PO₃M, M representing an

25 inorganic or organic cationic residue chosen from a proton, cations derived from alkali metals or alkaline-earth metals, ammonium cations -N(R)₄ in which formula the symbols R, which may be identical or different,



represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, the other cations derived from metals whose arylcarboxylic acid, arylsulphonic acid or arylphosphonic acid salts are water-soluble,

5 $-N(R)_3$ in which formula the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms,

 -OH

10 - Ar_3 represents an aryl group containing one or more substituents such as:

 - alkyl or alkoxy radical having 1 to 4 carbon atoms,

 - halogen atom,

15 - nitrile group,

 - nitro group,

 - hydrophilic group such as:

$-COOM$, $-PO_3M$, M representing an inorganic or organic cationic residue chosen from a proton, cations
20 derived from alkali metals or alkaline-earth metals, ammonium cations $-N(R)_4$ in which formula the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, the other cations derived from metals
25 whose arylcarboxylic acid or arylphosphonic acid salts are water-soluble,

$-N(R)_3$ in which formula the symbols R, which may be identical or different, represent a hydrogen



atom or an alkyl radical having from 1 to 4 carbon atoms,

-OH

at least one of the said substituents of Ar₃ being a
5 hydrophilic group as defined above,

- a represents 0 or 1,
- b represents 0 or 1,
- c represents 0 or 1,
- D₁, D₂ and D₃, which may be identical or different,
10 represent an alkyl group, a cycloalkyl group or an
alkyl or cycloalkyl group containing one or more
substituents such as:

- alkoxy radical having 1 to 4 carbon atoms,
- halogen atom,
- 15 - nitrile group,
- nitro group,
- hydrophilic group such as:

-COOM, -SO₃M, -PO₃M, M representing an
inorganic or organic cationic residue chosen from a
20 proton, cations derived from alkali metals or alkaline-
earth metals, ammonium cations -N(R)₄ in which formula
the symbols R, which may be identical or different,
represent a hydrogen atom or an alkyl radical having
from 1 to 4 carbon atoms, the other cations derived
25 from metals whose carboxylic acid, sulphonic acid or
phosphonic acid salts are water-soluble,

-N(R)₃ in which formula the symbols R, which
may be identical or different, represent a hydrogen



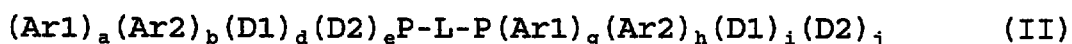
atom or an alkyl radical having from 1 to 4 carbon atoms,

-OH

- d, e and f represent 0 or 1,

5 - the sum (a+b+c+d+e+f) is equal to 3

or a bidentate phosphine corresponding to the general formula (II):



in which:

10 - Ar1, Ar2, D1 and D2 have the meanings given above for formula (I),

- a, b, d, e, g, h, i and j each represent 0 or 1,

- the sum (a+b+d+e) is equal to 2,

- the sum (g+h+i+j) is equal to 2,

15 - L represents a single valency bond or a divalent hydrocarbon-based radical such as an alkylene radical, a cycloalkylene radical, an arylene radical, a radical derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these
20 various cyclic radicals being directly attached to one of the phosphorus atoms or to the two phosphorus atoms or being attached to one of the phosphorus atoms or to the two via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for
25 the ring(s) which may form part of the divalent radical L to contain one or more substituents as defined for Ar1, Ar2, D1 and D2.

2. Process according to claim 1,



characterized in that the electrolysis cell of the electrolyser contains a cathode compartment and an anode compartment separated by a separating member consisting of an ion-exchange membrane or a porous
5 diaphragm.

3. Process according to either of claims 1 and 2, characterized in that the cathode of the electrolysis cell is made of a material such as platinum, gold, iridium, ruthenium, palladium, nickel,
10 graphite, vitreous carbon, iron, a stainless steel, a special steel, lead, zinc, cadmium, mercury or an amalgam, or consists of titanium, tantalum, nickel or a stainless steel, coated with a layer of platinum, gold, iridium or ruthenium, with a mixture of several of
15 these metals, with platinum oxide, palladium oxide, iridium oxide, rhodium oxide, ruthenium oxide, osmium oxide or tantalum oxide, or with a mixture of several of these oxides.

4. Process according to one of claims 1 to
20 3, characterized in that the cathode and the anode of the electrolysis cell have a flat structure such as a plate or grille or a voluminous structure, and in that they are perforated or unfolded.

5. Process according to one of claims 1 to
25 4, characterized in that the cathode or the anode has a voluminous structure chosen from granular piles of the materials constituting it, felts or foams of these said materials.



6. Process according to one of claims 1 to 5, characterized in that the anode is a material such as platinum, gold, iridium, ruthenium, palladium, nickel, graphite, vitreous carbon, a stainless steel, a special steel or lead, or consists of titanium or tantalum coated with a layer of platinum, gold, iridium, ruthenium, with a mixture of several of these metals, with platinum oxide, palladium oxide, iridium oxide, rhodium oxide, ruthenium oxide, osmium oxide or tantalum oxide, or with a mixture of several of these oxides.

7. Process according to one of claims 1 to 6, characterized in that the separating member is chosen from membranes of cationic type, prepared from cation-exchange resins containing acidic groups, such as sulphonic groups or carboxylic groups, and preferably from membranes prepared with sulphonic resins.

8. Process according to one of claims 1 to 6, characterized in that the separating member is chosen from diaphragms made of porous ceramic, diaphragms made of woven or nonwoven synthetic fibres, and deposited diaphragms based on asbestos fibres or synthetic fibres.

9. Process according to one of claims 1 to 8, characterized in that the preferred water-soluble phosphines are the phosphines of formula (I) or of formula (II) in which Ar1 and Ar2 are phenyl groups or



phenyl groups containing one or two substituents as defined in claim 1, Ar₃ is a phenyl group containing one or two substituents as defined above in claim 1, D₁, D₂ and D₃, which may be identical or different, represent an alkyl group having from 1 to 6 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkyl group having from 1 to 6 carbon atoms or cycloalkyl group having 5 to 8 carbon atoms containing one or more substituents as defined above in claim 1, L is a single valency bond, an alkylene radical having from 1 to 6 carbon atoms, a monocyclic or bicyclic cycloalkylene radical having from 4 to 12 carbon atoms, a phenylene radical, a diphenylene radical, a naphthylene radical, a dinaphthylene radical, a radical derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being directly attached to one of the phosphorus atoms or to the two phosphorus atoms or being attached to one of the phosphorus atoms or to the two via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring(s) which may form part of the divalent radical L to contain one or more substituents such as an alkyl group having 1 to 4 carbon atoms.

10. Process according to one of claims 1 to 9, characterized in that the preferred water-soluble phosphines are the phosphines of formula (I) or of formula (II) in which:



- the substituent(s) of Ar₁ and Ar₂, which may be identical or different, represent(s) groups such as:

- alkyl or alkoxy radical having 1 to 2 carbon atoms,

5 - chlorine atom,

- hydrophilic group such as:

-COOM, -SO₃M, -PO₃M, M representing an inorganic or organic cationic residue chosen from a proton, cations derived from sodium, potassium, calcium
10 or barium, ammonium, tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium cations, cations derived from zinc, lead or tin,

-N(R)₃ in which formula the symbols R, which may be identical or different, represent a hydrogen
15 atom or an alkyl radical having from 1 to 4 carbon atoms,

-OH

- the substituent(s) of Ar₃, which may be identical or different, represent(s) groups such as:

20 - alkyl or alkoxy radical having 1 to 2 carbon atoms,

- chlorine atom,

- hydrophilic group such as:

-COOM, -PO₃M, M representing an inorganic or
25 organic cationic residue chosen from a proton, cations derived from sodium, potassium, calcium or barium, ammonium, tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium cations,



cations derived from zinc, lead or tin,

-N(R)₃ in which formula the symbols R, which may be identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms,

-OH

overall, at least two of the said substituents of Ar₁, Ar₂, Ar₃, D₁, D₂ and D₃ for the phosphines of formula (I) and of Ar₁, Ar₂, D₁ and D₂ for the phosphines of formula (II) being a hydrophilic group as defined above.

11. Process according to one of claims 1 to 10, characterized in that the monodentate water-soluble phosphine of general formula (I) is chosen from tris-(hydroxymethyl)phosphine, tris(2-hydroxyethyl)-phosphine, tris(3-hydroxypropyl)phosphine, tris-(2-carboxymethyl)phosphine, the sodium salt of tris-(3-carboxyphenyl)phosphine, tris(3-carboxyethyl)-phosphine, tris(4-trimethylammonio-phenyl)phosphine iodide, the sodium salt of tris(2-phosphoethyl)-phosphine, bis(2-carboxyethyl)phenylphosphine, hydroxymethylbis(2-hydroxyethyl)phosphine, the sodium salt of tris(para-phosphophenyl)phosphine, the sodium salt of bis(meta-sulphophenyl)-para-carboxyphenyl-phosphine and the sodium salt of bis(meta-sulphophenyl)-2-sulphoethylphosphine, and the bidentate phosphine of general formula (II) is chosen from the sodium salt of 2,2'-bis[di(sulphonatophenyl)phosphino]-



1,1'-binaphthyl, the sodium salt of 1,2-bis[di-(sulphonatophenyl)phosphinomethyl]cyclobutane (CBDTS), 1,2-bis(dihydroxymethylphosphino)ethane, 1,3-bis-(dihydroxymethylphosphino)propane and the sodium salt
5 of 2,2'-bis[di(sulphonatophenyl)phosphinomethyl]-1,1'-binaphthyl.

12. Process according to one of claims 1 to 11, characterized in that the transition metal compound is chosen from nickel, cobalt, iron, palladium,
10 platinum, rhodium and iridium compounds which are water-soluble or capable of dissolving under the reaction conditions.

13. Process according to one of claims 1 to 12, characterized in that the transition metal compound
15 is chosen from nickel compounds such as nickel carboxylates, in particular nickel acetate, nickel formate and nickel citrate, nickel carbonate, nickel bicarbonate, nickel borate, nickel bromide, nickel chloride, nickel iodide, nickel thiocyanate, nickel
20 cyanide, nickel hydroxide, nickel hydrophosphite, nickel phosphite, nickel phosphate and its derivatives, nickel nitrate, nickel sulphate, nickel sulphite, nickel arylsulphonates and nickel alkylsulphonates.

14. Process according to one of claims 1 to
25 13, characterized in that, in the cathode compartment, the initial concentration of sulphone-containing phosphine is between 10^{-3} mol/litre and 1 mol/litre and the initial concentration of transition metal compound,



in particular of nickel compound, is between 10^{-5} mol/litre and 1 mol/litre.

15. Process according to one of claims 1 to 14, characterized in that the cathode compartment
5 contains other compounds which allow the electrolyte conductivity to be increased, such as soluble salts and complexing agents capable of modifying the potential at which the reduction of the transition metal is carried out, such as cyanides or chlorides and Lewis acids.

10 16. Process according to claim 15, characterized in that the Lewis acid used in the cathode compartment is chosen from compounds of the elements from groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the
15 Elements, as published in the Handbook of Chemistry and Physics, 51st edition (1970-1971) of The Chemical Rubber Co., provided that the said compounds are at least partially soluble and stable in water or more generally in the aqueous solution to be treated by
20 electrolysis, preferably from salts, in particular halides, preferably chlorides and bromides, sulphates, nitrates, sulphonates, in particular trifluoromethanesulphonates, carboxylates, acetylacetonates, tetrafluoroborates and phosphates.

25 17. Process according to either of claims 15 and 16, characterized in that the Lewis acid is chosen from zinc chloride, zinc bromide, zinc iodide, zinc trifluoromethanesulphonate, zinc acetate, zinc nitrate,



zinc tetrafluoroborate, manganese chloride, manganese
bromide, nickel chloride, nickel bromide, nickel
cyanide, nickel acetylacetonate, cadmium chloride,
cadmium bromide, stannous chloride, stannous bromide,
5 stannous sulphate, stannous tartrate, chlorides,
bromides, sulphates, nitrates, carboxylates or
trifluoromethanesulphonates of rare-earth elements such
as lanthanum, cerium, praseodymium, neodymium,
samarium, europium, gadolinium, terbium, dysprosium,
10 holmium, erbium, thulium, ytterbium and lutetium,
cobalt chloride, ferrous chloride or yttrium chloride.

18. Process according to one of claims 15 to
17, characterized in that the Lewis acid is chosen from
zinc chloride, zinc bromide, zinc sulphate, zinc
15 tetrafluoroborate, stannous chloride, stannous bromide,
zinc chloride/stannous chloride mixtures, nickel
chloride, nickel bromide and nickel acetylacetonate.

19. Process according to one of claims 1 to
18, characterized in that the Lewis acid represents
20 from 0 to 50 mol per mole of transition metal compound,
more particularly of nickel compound, and preferably
from 0 to 10 mol per mole.

20. Process according to one of claims 1 to
19, characterized in that the anode compartment
25 contains an aqueous solution of an anolyte consisting
of an acid such as, in particular, sulphuric acid,
nitric acid, water-soluble carboxylic acids such as
acetic acid, of the corresponding salts, such as the



sodium, potassium, ammonium or quaternary ammonium salts, or of a base such as sodium hydroxide or potassium hydroxide, the anolyte preferably being chosen from sulphuric acid and its salts.

5 21. Process according to one of claims 1 to 19, characterized in that the anode compartment contains an aqueous solution of an anolyte consisting of one or more monodentate or bidentate water-soluble phosphines.

10 22. Process according to one of claims 1 to 21, characterized in that the initial concentration of the anolyte in the solution in the anode compartment is from 10^{-3} mol/litre to 3 mol/litre.

 23. Process according to one of claims 1 to 15 22, characterized in that it consists in using, in the cathode compartment, an aqueous solution of a spent catalyst, based on monodentate or bidentate water-soluble phosphine and on a transition metal, and more particularly nickel, converted at least partly into 20 cyanide, the said spent catalyst also optionally containing one or more Lewis acids, and it being possible for the said solution to contain relatively low amounts of compounds such as butadiene and/or pentenenitriles or such as adiponitrile, methyl- 25 glutaronitrile, ethylsuccinonitrile or methylbutene-nitriles.

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(54) Title: **PROCESS FOR THE ELECTROCHEMICAL PREPARATION OF CATALYSTS BASED ON TRANSITION METAL AND PHOSPHINE** ✓

(54) Titre: **PROCEDE DE PREPARATION ELECTROCHIMIQUE DE CATALYSEURS A BASE DE METAL DE TRANSITION ET DE PHOSPHINE**

(57) Abstract

The present invention relates to an electrochemical process for the preparation of compounds which can be used as catalysts. The disclosed compounds comprise more specifically a transition metal with an oxidation degree of 0 or 1 associated to at least one monodentate or bidentate hydrosoluble phosphine. The process for the electrochemical synthesis of catalysts comprises the treatment by electrolysis of an aqueous solution containing at least a compound of a transition metal and a monodentate or bidentate hydrosoluble phosphine placed within the cathode compartment of an electrolysis cell of an electrolyser.

(57) Abrégé

La présente invention concerne un procédé électrochimique de préparation de composés pouvant être utilisés comme catalyseurs. Les composés visés comportent plus spécifiquement au moins un métal de transition au degré d'oxydation 0 ou 1 associé à au moins une phosphine hydrosoluble monodentate ou bidentate. Le procédé de synthèse électrochimique des catalyseurs consiste à traiter par électrolyse une solution aqueuse contenant au moins un composé d'un métal de transition et une phosphine hydrosoluble monodentate ou bidentate, placée dans le compartiment cathodique d'une cellule d'électrolyse d'un électrolyseur.