



METHOD FOR THE HYDROCYANATION OF UNSATURATED COMPOUNDS

The present invention relates to a process for the hydrocyanation of unsaturated compounds to unsaturated
5 mononitrile compounds or to dinitrile compounds.

It relates more particularly to a process for the manufacture of dinitriles by double hydrocyanation of diolefins, such as butadiene, comprising a recovery and
10 separation of the catalyst system.

The hydrocyanation reaction is used industrially for the synthesis of compounds comprising nitrile functional groups from compounds comprising
15 unsaturations. Thus, adiponitrile, which is an important chemical intermediate, in particular in the manufacture of hexamethylene diamine, a monomer for a number of polymers, such as polyamide, is manufactured by hydrocyanation in two stages of butadiene or of a
20 hydrocarbon cut, known as C4 cut, comprising butadiene. In this manufacturing process, the two reactions are carried out with catalytic systems comprising essentially the same entities, namely an organometallic coordination complex and at least one organophosphorus
25 ligand of monodentate organophosphite type, such as tritolyl phosphite.

Numerous patents disclose this process for the manufacture of adiponitrile and processes for the
30 manufacture of the catalysts.

Furthermore, for the economics of the process, it is important to be able to recover the catalytic system and to recycle it in the hydrocyanation stages.

Thus, Patent US 4 539 302 discloses a process for the
35 recovery of the catalyst from the reaction medium obtained in the second stage of the process for the preparation of adiponitrile, namely the hydrocyanation of unsaturated nitriles to dinitriles.



This process for recovery by settling makes it possible to limit the losses of metal element and facilitates the control of the organophosphorus ligand/metal element ratio for the hydrocyanation of unsaturated nitriles. Thus, it is also possible to recover a catalytic system with a high ligand/metal element ratio which makes possible recycling and reuse of the catalytic system in the stages for the manufacture of catalyst and/or in the stages of hydrocyanation of butadiene or the isomerization of branched pentenenitriles.

Numerous other organophosphorus ligands have been provided for the catalysis of these hydrocyanation reactions.

Thus, bidentate ligands of organophosphite, organophosphinite, organophosphonite and organophosphine type have been disclosed in numerous patents, such as, for example, Patents WO 99/06355, WO 99/06356, WO 99/06357, WO 99/06358, WO 99/52632, WO 99/65506, WO 99/62855, US 5 693 843, WO 96/1182, WO 96/22968, US 5 981 772, WO 01/36429, WO 99/64155 or WO 02/13964.

Finally, provision has also been made, in patent WO 03/11457, to use a mixture of mono- and bidentate ligands for the catalysis of hydrocyanation reactions.

In the case of mixtures of ligands, it is also important to be able to recover the catalyst without losing ligands or metal element.

One of the aims of the present invention is to provide a process for the manufacture of dinitriles by hydrocyanation of unsaturated compounds using a catalytic system comprising a mixture of monodentate organophosphite ligands and of bidentate organophosphorus ligands which makes possible separation and recovery of the catalyst and of various

products with minimum loss of compounds forming the catalytic system.

To this end, the invention provides a process for the manufacture of dinitriles by hydrocyanation of unsaturated compounds comprising at least one stage of hydrocyanation in the presence of a catalytic system comprising an organometallic complex formed by one or more organophosphorus ligands of monodentate organophosphite type and one or more bidentate organophosphorus ligands and optionally a promoter of Lewis acid type and at least one stage of separation by distillation of a reactant used in the process or of a compound formed by the reaction from a medium comprising the said catalytic system, characterized in that the medium subjected to the stage of separation by distillation comprises a ratio of the number of moles of monodentate and bidentate organophosphorus ligands, expressed as phosphorus atoms, with respect to the number of metal element atoms of less than or equal to 15 and/or a concentration by weight of metal element forming the organometallic complex of less than or equal to 2%, preferably of less than 1.3%, and in that the distillation bottom temperature of the distillation stage is less than or equal to 180°C.

The term "distillation bottom temperature" is understood to mean the temperature of the medium present in the boiler of the distillation plant and the temperature of the walls of the boiler.

The distillation conditions and in particular the maximum temperature of the walls of the boiler make it possible to limit and even to eliminate the precipitation of the metal element forming the organometallic complex. This is because a higher temperature can bring about decomplexing of the catalyst, resulting in the precipitation of the metal element, during the separation or distillation stage.

The metal elements exhibiting a catalytic effect in a hydrocyanation reaction are, for example, nickel, cobalt, iron, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, silver, gold, zinc, cadmium or cerium. Nickel is the preferred catalytic element. For greater clarity, the metal element will be denoted by the term "nickel" in the continuation of the present text, without this having a limiting meaning.

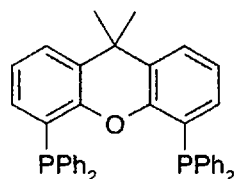
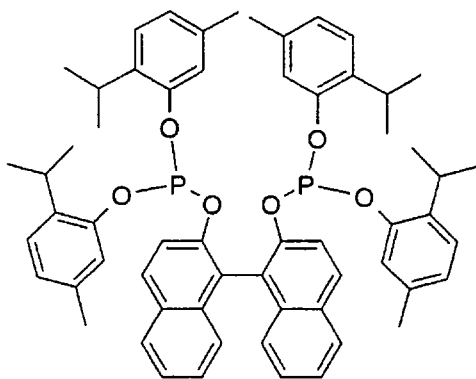
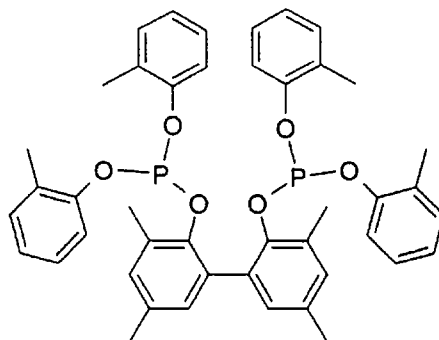
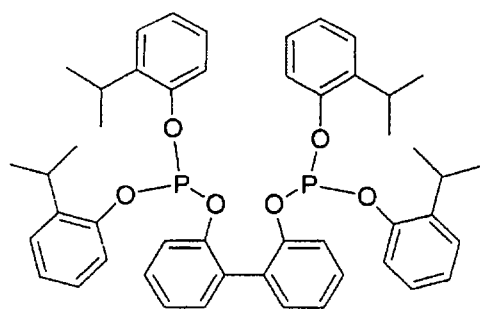
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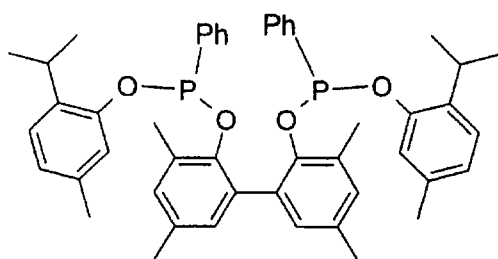
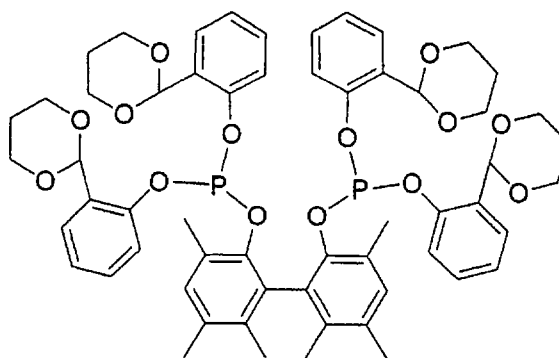
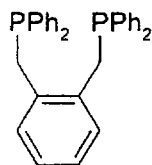
Mention may be made, as monodentate organophosphite ligands which are suitable for the invention, by way of examples, of triphenyl phosphite, tritolyl phosphite (TTP) or tricymenyl phosphite.

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Mention may be made, as bidentate ligands which are suitable for the invention, of organophosphite, organophosphonite, organophosphinite or organophosphine compounds and in particular of those with the following structures, in which Ph means phenyl:

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According to a preferred characteristic of the
 5 invention, the catalytic system present in the reaction
 medium generally comprises a number of moles of
 bidentate ligands, expressed as the number of
 phosphorus atoms with respect to a metal element atom,
 of between 1 and 4 (limits included), while that of
 10 monodentate ligands, expressed as the number of
 phosphorus atoms, is between 4 and 12 (limits
 included).

These ratios can be different according to the
 15 hydrocyanation reaction carried out. This is because
 the manufacture of dinitriles is generally carried out
 in two successive stages consisting, in a first stage,
 in hydrocyanating a diolefin, such as butadiene, with
 HCN to give unsaturated mononitriles and, in a second
 20 stage, in converting these mononitriles to dinitriles
 by reaction with HCN. Furthermore, the process
 generally comprises a stage of isomerization of the
 branched unsaturated mononitriles obtained from the
 first stage in order to convert them to linear

mononitriles which will be converted to linear dinitriles in the second stage.

Thus, the ligand/nickel ratio used in the first stage
5 is generally higher than that used in the second stage. Likewise, the concentration of nickel can be different in the two stages.

Furthermore, in the reaction for the hydrocyanation of the unsaturated nitriles or second stage, a promoter or
10 cocatalyst is generally used. Lewis acids are generally chosen as preferred promoters.

Use may in particular be made, by way of examples, of the Lewis acids mentioned in the work edited by
15 G.A. Olah "Friedel-Crafts and Related Reactions", volume I, pages 191 to 197 (1963).

The Lewis acids which can be employed as cocatalysts in the present process are advantageously chosen from
20 compounds of the elements from Groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the Elements. These compounds are generally salts, in particular halides, such as chlorides or bromides, sulphates, sulphonates,
25 haloalkylsulphonates, perhaloalkylsulphonates, in particular fluoroalkylsulphonates or perfluoroalkylsulphonates, haloacetates, perhaloacetates, carbonylates and phosphates.

30 Mention may be made, as nonlimiting examples of such Lewis acids, of zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium
35 chloride, indium trifluoromethylsulphonate, indium trifluoroacetate, chlorides or bromides of rare earth elements, such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thulium, ytterbium and

lutetium, cobalt chloride, ferrous chloride or yttrium chloride.

Use may also be made, as Lewis acid, of compounds such
5 as triphenylborane or titanium tetraisopropoxide.

It is, of course, possible to employ mixtures of several Lewis acids.

Preference is very particularly given, among Lewis
10 acids, to zinc chloride, zinc bromide, stannous chloride, stannous bromide, triphenylborane, indium trifluoromethylsulphonate, indium trifluoroacetate and zinc chloride/stannous chloride mixtures.

The Lewis acid cocatalyst employed generally represents
15 from 0.005 to 50 mol per mole of nickel.

In each of these stages, the reaction medium obtained after the hydrocyanation reaction is advantageously subjected to separation by distillation of the
20 unreacted reactant, namely butadiene or the unsaturated nitrile, in order to be recycled.

According to invention, these separation stages are carried out while observing a distillation bottom
25 temperature according to the conditions of ligand/nickel ratio and nickel concentration indicated above in order to avoid or limit decomplexing of the nickel and its precipitation.

30 According to preferred characteristics of the invention, the total ligand/nickel ratio, expressed as number of phosphorus atoms with respect to the number of nickel atoms, is preferably less than or equal to 15, advantageously between 5 and 15, the concentration
35 by weight of nickel advantageously being between 0.1% and 2%, preferably between 0.1% and 1.2% (limits included).

The term "total ligand" is understood to mean all the molecules of monodentate and bidentate ligands. In the present text, the expression "ligand/nickel" also relates to the ratio of all the molecules of mono- and bidentate ligands with respect to the number of nickel atoms, unless expressly indicated otherwise.

Thus, in the case of the separation of butadiene by distillation of the reaction medium resulting from the first hydrocyanation stage, the maximum temperature of the distillation bottoms is less than or equal to 180°C for a ratio of moles of bidentate ligand, expressed as phosphorus atoms, to the number of nickel atoms of between 1 and 4 (limits included) and that of the monodentate ligand of between 4 and 12 (limits included). In addition, according to a preferred characteristic of the invention, the concentration by weight of nickel is greater than or equal to 0.1%, advantageously greater than 0.2%.

Likewise, in the stage of separation of the unsaturated nitriles from the medium resulting from the second stage of hydrocyanation of the unsaturated nitriles, the distillation bottom temperature is advantageously less than or equal to 140°C for a ratio of moles of bidentate ligand, expressed as phosphorus atoms, to the number of nickel atoms of between 1 and 4 (limits included) and that of the monodentate ligand of between 4 and 7 (limits included). In addition, according to a preferred characteristic of the invention, the concentration by weight of nickel is greater than or equal to 0.2% by weight.

Furthermore, in one embodiment, the process of the invention can comprise a stage of extraction of the organometallic complex and of the organophosphorus ligands from the medium comprising the nitriles and in particular the dinitriles by liquid/liquid extraction using an extraction solvent. Mention may be made, as

suitable extraction solvent, by way of examples, of saturated, linear or cyclic, aliphatic hydrocarbons, such as hexane, heptane, octane, cyclohexane, cyclopentane, cycloheptane and more generally cycloparaffins or analogues. Cyclohexane is the preferred extraction solvent.

The solution of ligands and of organometallic complex in the extraction solvent is also subjected to distillation in order to separate the extraction solvent and to recycle the ligands and the organometallic complex thus recovered. In the present invention, the extraction solvent is a reactant used for the implementation of the process.

This separation is also carried out while observing the characteristics of the invention indicated above, such as ligand/nickel ratio, concentration of nickel and distillation bottom temperature.

According to a preferred embodiment of the invention, this separation of the cyclohexane is carried out with a distillation bottom temperature of less than or equal to 180°C for a concentration by weight of nickel of greater than or equal to 0.7%. In addition, according to a preferred characteristic of the invention, the ratio of moles of bidentate ligand, expressed as phosphorus atoms, to the number of nickel atoms is between 1 and 4 (limits included) and that of the monodentate ligand is greater than or equal to 8.

According to the invention, in the stages of separation by distillation starting from a medium comprising the catalytic system, the maximum temperature of the distillation bottoms is determined and is a function of the ligand/nickel ratio and of the concentration of nickel in the medium. Thus, this temperature increases as the ligand/nickel ratio increases and/or as the concentration of nickel increases.

In a preferred embodiment of the invention, the process comprises a stage of separation of the catalytic system and of the dinitriles carried out in a stage of settling into two dense and light phases. The medium fed to this settling stage is either the medium obtained after the second hydrocyanation stage or the distillation bottoms obtained in the stage of separation of the unreacted unsaturated nitriles.

10

Thus, the lower or dense phase comprises most of the nickel and of the bidentate ligand and a portion of the monodentate ligand, the upper or light phase being composed of the dinitriles and the remaining portion of the nickel and of the mono- and bidentate ligands.

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The medium fed to the settling stage is advantageously cooled to a temperature of between 25 and 75°C, preferably between 30 and 55°C.

20

According to another characteristic of the process of the invention, the upper phase recovered in the settling stage comprises a ligand/nickel molar ratio advantageously of greater than 8.

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According to the invention, the total recovery of the metal complex and of the ligands is carried out by liquid/liquid extraction of these using an extraction solvent which is immiscible with the dinitriles. This operation corresponds to that described above, the solvents being identical.

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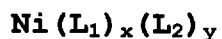
In this embodiment, it is advantageous, prior to the stage of distillation of the unreacted unsaturated nitriles, to adjust and to control the concentration of nickel in the medium by addition of a portion of the lower or dense phase recovered in the settling stage.

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This is because the concentration of nickel used in the hydrocyanation medium, when the nickel is used in combination with a bidentate ligand in accordance with the process of the invention, can be very low, such as, 5 for example, of the order of 100 to 2000 mg of nickel/kg of reaction medium. In order to obtain a concentration of nickel suitable for promoting the settling, it may be necessary to add a certain amount of catalytic system to the reaction medium exiting from 10 the hydrocyanation stage. This adjustment to the concentration of nickel can be made as indicated above.

The process of the invention thus makes possible recovery and separation of the catalyst with a loss of 15 metal element and thus of catalyst which is minimized.

The present invention preferably applies to the hydrocyanation of butadiene and of unsaturated nitriles comprising from 3 to 8 carbon atoms and more preferably 20 of 3-pentenitrile and/or 4-pentenitrile for the production of adiponitrile with use of a catalyst of the type represented by the following formula:



in which L_1 represents a monodentate ligand and L_2 a 25 bidentate ligand,

x and y represent decimal numbers ranging from 0 to 4, the sum $x + 2y$ being equal to 3 or 4.

The catalyst can be composed of a mixture of complexes corresponding to the above general formula.

30

The catalytic system or the reaction medium can also comprise an amount of mono- and/or bidentate organophosphorus ligand in the free form, that is to say not bonded to the nickel. The catalytic systems of 35 the invention can be obtained by formation, in a first stage, of an organometallic complex between the nickel and monodentate ligand. Processes for the formation of such complexes are, for example, disclosed in patents US 3 903 120 and US 4 416 825.

In a second stage, the bidentate ligand is added to the medium comprising the said organometallic complex.

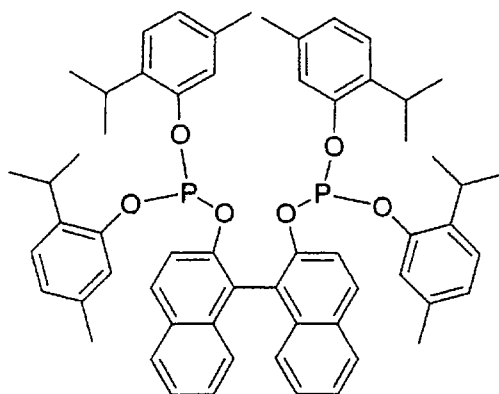
5 The first and second hydrocyanation stages are advantageously carried out in series. In this case, it is advantageous for at least a portion of the catalyst recovered, in particular that recovered in the liquid/liquid extraction, and more particularly the catalyst recovered in the upper phase of the settling
10 stage, to be recycled and used as catalyst in the first stage of hydrocyanation of butadiene and/or in the stage of isomerization of branched unsaturated nitriles to linear unsaturated nitriles. The use of an identical or similar catalytic system for the hydrocyanation of
15 butadiene and that of pentenenitriles is preferred.

However, it is also possible to use the catalytic system described above solely in the stage of hydrocyanation of unsaturated nitriles, the catalytic
20 system used in the first stage of hydrocyanation of butadiene and the isomerization stage being different, either in the nature of the compounds or in the ratio between the various compounds.

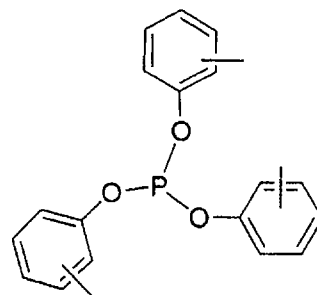
25 Other details and advantages of the invention will become more clearly apparent in the light of the examples given below solely by way of illustration.

Abbreviations used in the examples:

30 PN: pentenenitriles
DN: dinitriles (mixture of dinitriles AdN, MGN and ESN, predominantly comprising AdN)
AdN: adiponitrile
MGN: methylglutaronitrile
35 ESN: ethylsuccinonitrile
Ligands:



Ligand A



TTP

Example 1: Distillation of the pentenenitriles (PN)

5 A mixture with the following composition is prepared under an inert atmosphere (the percentages are expressed by weight; the ratios are molar ratios):

Ni = 1.2%

10 TTP/Ni = 5

Ligand A/Ni = 1

P/Ni = 7

DN = 38.5%

PN = 5%

15

This mixture is introduced into a tube, which is sealed and heated at a certain temperature (see Table) for 2 h, then the loss of complexed nickel is determined by chromatographic analysis:

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Temperature	Loss of Ni
130°C	0%
150°C	25%

Example 2: Stage of distillation of the solution obtained after liquid/liquid extraction

25 A mixture with the following composition is prepared under an inert atmosphere (the percentages are expressed by weight; the ratios are molar ratios):

Ni = 1.0%

TTP/Ni = 12

Ligand **A**/Ni = 1

5 P/Ni = 13

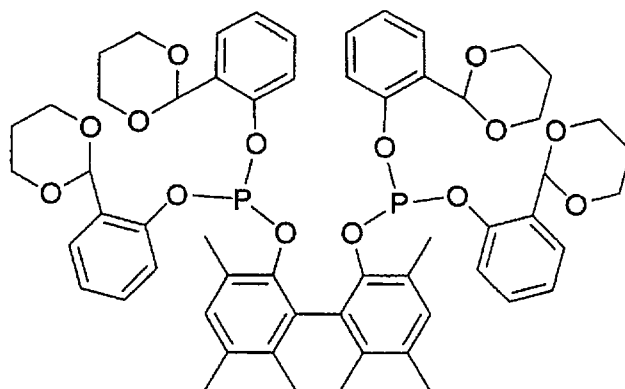
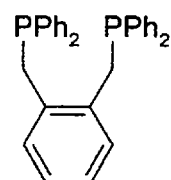
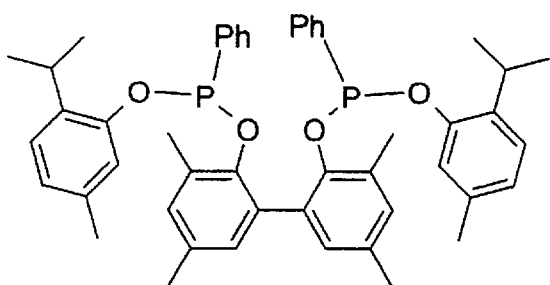
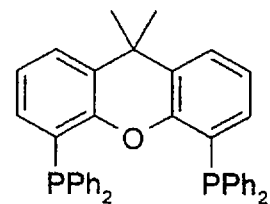
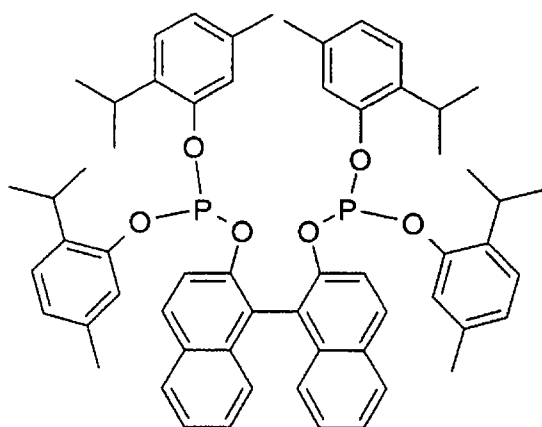
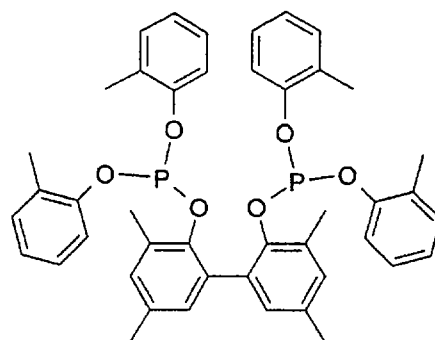
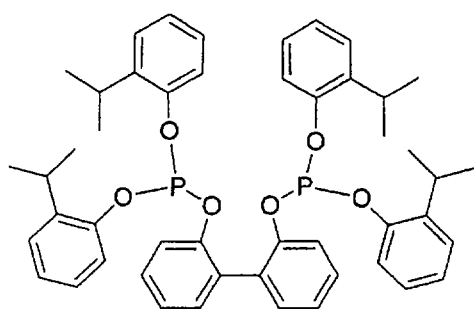
PN = 11%

10 This mixture is introduced into a tube, which is sealed and heated at a certain temperature (see Table) for 2 h, and the loss of complexed nickel is determined by chromatographic analysis:

Temperature	Loss of Ni
170°C	0%
190°C	45%

CLAIMS

1. Process for the hydrocyanation of unsaturated compounds comprising at least one stage of hydrocyanation in the presence of a catalytic system comprising an organometallic complex formed by one or more organophosphorus ligands of monodentate organophosphite type and one or more bidentate organophosphorus ligands and optionally a promoter of Lewis acid type and at least one stage of separation by distillation of a reactant used in the process or of a compound formed by the reaction of a medium comprising the said catalytic system, characterized in that the medium subjected to the stage of separation by distillation comprises a ratio of the number of moles of organophosphorus ligands, expressed as phosphorus atoms, with respect to the number of metal element atoms of less than or equal to 15 and/or a concentration by weight of metal element forming the organometallic complex of less than or equal to 1.3% and in that the distillation bottom temperature of the distillation stage is less than or equal to 180°C.
2. Process according to the preceding claim, characterized in that the monodentate ligand is a compound chosen from the group consisting of triphenyl phosphite, tritolyl phosphite and tricymenyl phosphite.
3. Process according to either of the preceding claims, characterized in that the bidentate organophosphorus ligand is chosen from the group consisting of organophosphites, organophosponites, organophosphinites and organophosphines.
4. Process according to Claim 3, characterized in that the bidentate organophosphorus ligand is chosen from the group consisting of the compounds with the following structures, in which Ph means phenyl:



5. Process according to one of the preceding claims, characterized in that the promoter is chosen from the group consisting of compounds of the elements from Groups Ib, IIb, IIIa, IIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Table of the Elements. These compounds are generally salts, in particular halides, such as chlorides or bromides, sulphates, sulphonates, haloalkylsulphonates, perhaloalkylsulphonates, in particular fluoroalkylsulphonates or perfluoroalkylsulphonates, haloacetates, perhaloacetates, carbonylates and phosphates, zinc chloride, arylboranes, fluoroacetates and perfluoroacetates, fluoroalkylsulphonates and perfluoroalkylsulphonates.
6. Process according to Claim 5, characterized in that the Lewis acid is chosen from the group consisting of zinc chloride, zinc bromide, zinc iodide, manganese chloride, manganese bromide, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, indium chloride, indium trifluoromethylsulphonate, indium trifluoroacetate, chlorides or bromides of rare earth elements, such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, hafnium, erbium, thulium, ytterbium and lutetium, cobalt chloride, ferrous chloride, yttrium chloride, triphenylborane, titanium tetraisopropoxide and their mixtures.
7. Process according to one of the preceding claims, characterized in that the unsaturated compound is butadiene and/or an unsaturated nitrile compound.
8. Process according to one of the preceding claims, characterized in that the unsaturated nitrile is a linear or branched aliphatic compound comprising from 3 to 8 carbon atoms.

9. Process according to Claim 7, characterized in that the unsaturated nitrile is a pentenenitrile.

10. Process according to one of the preceding claims, characterized in that the stage of separation by distillation is a stage of distillation of the medium resulting from a hydrocyanation stage in order to separate the unreacted unsaturated compound.

11. Process according to one of the preceding claims, characterized in that the recovery of the catalytic system from the dinitriles formed comprises a stage of settling the reaction medium resulting from the hydrocyanation of an unsaturated nitrile, optionally after separation by distillation of the unreacted unsaturated nitrile.

12. Process according to Claim 10 or 11, characterized in that the reaction medium resulting from the hydrocyanation of an unsaturated nitrile, optionally after separation of the said unreacted mononitrile, or the upper or light phase recovered in the settling stage is subjected to liquid/liquid extraction in order to extract the organophosphorus ligands and the organometallic complex present in the said media.

13. Process according to Claim 12, characterized in that the extraction solvent is chosen from the group consisting of hexane, heptane, octane, cyclohexane, cyclopentane and cycloheptane.

14. Process according to one of Claims 10 to 12, characterized in that the separation stage is a stage of distillation of the extraction solvent from the solution obtained after liquid/liquid extraction.

15. Process according to one of Claims 10 to 14, characterized in that a portion of the said lower phase is recycled in the reaction medium resulting from the

hydrocyanation, before the stage of distillation of the unsaturated nitriles.