

PROCESS FOR THE HYDROCYANATION OF ORGANIC COMPOUNDS
COMPRISING ETHYLENIC UNSATURATIONS

The present invention relates to a process
5 for the hydrocyanation of organic compounds comprising
ethylenic unsaturations for in particular the
preparation of nitriles and more particularly to the
hydrocyanation of diolefins or of substituted olefins
for the manufacture of dinitriles and/or to the
10 isomerization of nitriles obtained by hydrocyanation.

The invention relates more particularly to a
hydrocyanation catalysed by a nickel-base compound.

French Patent No. 1,599,761 discloses a
process for the preparation of nitriles by addition of
15 hydrocyanic acid to organic compounds having at least
one ethylenic double bond in the presence of a nickel
catalyst and of a triaryl phosphite. This reaction can
be carried out in the presence or in the absence of a
solvent.

20 When a solvent is used in this process of the
prior art, it is preferably a hydrocarbon, such as
benzene or xylenes, or a nitrile, such as acetonitrile.

The catalyst employed is an organic nickel
complex comprising ligands such as phosphines, arsines,
25 stilbines, phosphites, arsenites or antimonites.

The presence of a promoter to activate the
catalyst, such as a boron compound or a metal salt,

generally a Lewis acid, is also recommended in the said patent.

Provision has been made, in Patent FR-A-2,338,253, for carrying out the hydrocyanation of compounds having at least one ethylenic unsaturation in the presence of an aqueous solution of a compound of a transition metal, in particular nickel, palladium or iron, and of a sulphonated phosphine.

The sulphonated phosphines disclosed in this patent are sulphonated triarylphosphines and more particularly sulphonated triphenylphosphines.

This process makes possible satisfactory hydrocyanation, in particular of butadiene and pentene-nitriles, and an easy separation of the catalytic solution by a simple separation by settling and consequently avoids as far as possible the discharge of effluents or of waste comprising metals acting as catalyst.

However, in these processes, the overall lifetime of the catalyst is affected by a loss of nickel during each passage of the catalyst in the reactor. This loss is due in particular to a nickel hydroxide precipitate. This precipitate is also disadvantageous in the operation of the process as it contaminates the plants, requiring either periodic cleaning of the latter or a stage of separation and removal of the precipitate. In the latter embodiment, an environmentally harmful effluent is produced.

One of the objects of the present invention is to overcome these disadvantages by providing a process which makes it possible to treat the precipitate in order, on the one hand, to eliminate the risks of contamination of the plants or of the environment and, on the other hand, to decrease the losses of catalyst.

To this end, the invention provides a process for the hydrocyanation of organic compounds comprising at least one ethylenic bond by reaction with hydrogen cyanide in the presence of an aqueous solution of a catalyst comprising at least one nickel compound and at least one water-soluble phosphine and, after reaction, separation of the organic and aqueous phases.

The process of the invention consists in treating the recovered aqueous phase, which comprises a solid phase (colloids, gel or solid in suspension or precipitated) formed during the hydrocyanation reaction, with hydrogen cyanide in order to dissolve the said solid phase.

Thus, the aqueous phase can be recycled at least partially in the reactor without contaminating the plant.

In another embodiment of the invention, the recovered aqueous phase A comprising the solid phase formed is subjected to a separation stage in order to extract the solid phase, the purified or clarified aqueous phase A_1 subsequently being at least partially

recycled in the hydrocyanation reactor, the solid phase being dissolved by treatment with hydrogen cyanide.

According to a preferred characteristic of the invention, the treatment of the separated solid
5 phase with hydrogen cyanide is carried out in the presence of an aqueous solution comprising a water-soluble phosphine. The solution B thus recovered is, in a preferred embodiment, fed to a stage of regeneration of the catalyst which consists, in brief, of a
10 reduction of nickel in the (II) oxidation state to nickel in the (0) oxidation state. This reduction is carried out advantageously after addition of nickel in the (0) oxidation state to the solution obtained by dissolution of the solid phase.

15 According to a preferred characteristic of the invention, the solution B is mixed with at least a portion of the clarified aqueous solution A₁ before the reduction regeneration treatment. Thus, as this solution A₁ comprises nickel in the (0) oxidation state,
20 regeneration of all the catalyst is possible.

According to a characteristic of the invention, the treatment with hydrogen cyanide of the solid phase formed, either after clarification of the recovered liquid phase A or directly in this liquid
25 phase, is carried out by addition of hydrogen cyanide to the aqueous solution advantageously comprising a water-soluble phosphine or hydrocyanation catalyst and stirring the reaction mixture for the time necessary

for the, preferably complete, dissolution of the precipitate.

The temperature of the reaction mixture is advantageously less than 100°C, preferably between 20
5 and 80°C. The hydrogen cyanide is added in liquid form or in solution in water or in a solution of water-soluble phosphine.

The amount of hydrogen cyanide added is at least equal to the stoichiometric amount for converting
10 the precipitated or insoluble nickel to soluble nickel cyanide. This minimum amount can be determined as a function of the weight of precipitate to be dissolved and by assuming that this precipitated or insoluble Ni is nickel hydroxide.

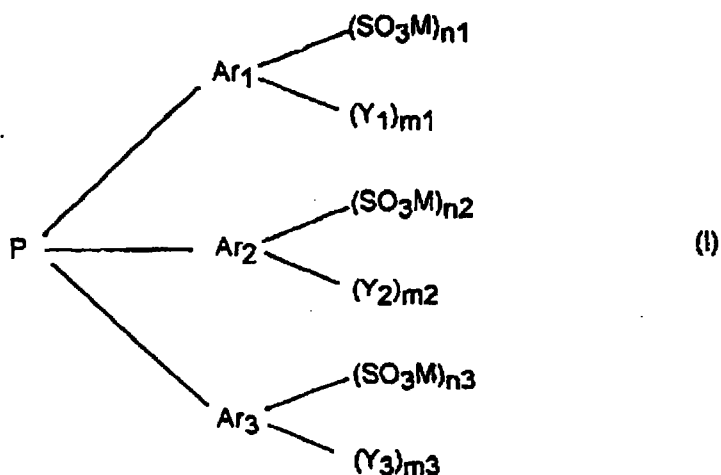
15 The amount of hydrogen cyanide added will advantageously be from 30% to 400% greater than the stoichiometric amount.

The stage of regeneration of the catalyst or, in other words, the reduction of the nickel to the 0
20 oxidation state can be carried out by several processes, such as reduction by gaseous hydrogen, by electrochemical reduction or addition of an organic or inorganic reducing agent. The reduction processes are known and are disclosed in particular in Patents
25 WO 97/24184, EP 0,715,890 and FR 2,338,253.

The water-soluble phosphine compounds suitable for implementing the invention can be one of the compounds belonging to the family of the phosphine

compounds which are disclosed in French Patent No. 2,338,253 or in Patent Applications WO 97.12857 and EP 0,650,959.

Thus, suitable phosphines for the invention
5 correspond to the following general formula (I):



in which:

- * Ar₁, Ar₂ and Ar₃, which are identical or different, represent aryl groups
- 10 * Y₁, Y₂ and Y₃, which are identical or different, represent
 - . an alkyl radical having 1 to 4 carbon atoms,
 - . an alkoxy radical having 1 to 4 carbon atoms,
 - . a halogen atom,
 - 15 . a CN radical,
 - . an NO₂ radical,
 - . an OH radical,
 - . an NR₁R₂ radical, in the formula of which R₁ and R₂, which are identical or different,

represent an alkyl radical having from 1 to 4 carbon atoms,

* M is an inorganic or organic cationic residue chosen, so that the compound of formula (I) is soluble in water, from the group comprising:

- . H^+ ,
- . cations derived from alkali metals or alkaline earth metals,
- . $N(R_3R_4R_5R_6)^+$, with R_3 , R_4 , R_5 and R_6 , which are identical or different, representing an alkyl radical having 1 to 4 carbon atoms or a hydrogen atom,
- . other cations derived from metals, the benzenesulphonic acid salts of which are soluble in water,

* m_1 , m_2 and m_3 are identical or different integers from 0 to 5,

* n_1 , n_2 and n_3 are identical or different integers from 0 to 3, at least one of them being equal to or greater than 1.

Mention may be made, as examples of metals, the benzenesulphonic acid salts of which are soluble in water, of lead, zinc and tin.

The expression "soluble in water" generally means, in the present text, a compound soluble to at least 0.01 g per litre of water.

Preference is given, among the phosphines of formula (I), to those in which:

- Ar_1 , Ar_2 and Ar_3 are phenyl groups,
- Y_1 , Y_2 and Y_3 represent groups chosen from
 - . alkyl radicals having from 1 to 2 carbon atoms,
 - 5 . alkoxy radicals having from 1 to 2 carbon atoms,
- M represents a cation chosen from the group comprising
 - . H^+
 - 10 . cations derived from Na, K, Ca and Ba
 - . NH_4^+
 - . tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium cations
- 15 - m_1 , m_2 and m_3 are integers from 0 to 3
- n_1 , n_2 and n_3 are integers from 0 to 3, at least one also being greater than 1.

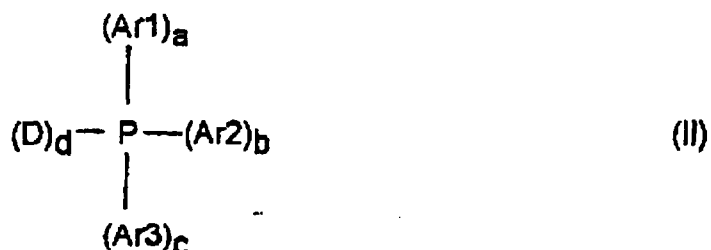
The more particularly preferred among these phosphines are the sodium, potassium, calcium, barium, ammonium, tetramethylammonium and tetraethylammonium salts of mono(sulphophenyl)diphenylphosphine, di(sulphophenyl)phenylphosphine and tri(sulphophenyl)phosphine, in the formulae of which the SO_3 groups are preferably in the meta position.

25 Mention may be made, as other examples of phosphines of formula (I) which can be employed in the process of the invention, of the alkali metal or alkaline earth metal salts, the ammonium salts or the

- quaternary ammonium salts of (3-sulpho-4-methylphenyl)di(4-methylphenyl)phosphine, (3-sulpho-4-methoxyphenyl)di(4-methoxyphenyl)phosphine, (3-sulpho-4-chlorophenyl)di(4-chlorophenyl)phosphine, di(3-sulphophenyl)phenylphosphine, di(4-sulphophenyl)phenylphosphine, di(3-sulpho-4-methylphenyl)(4-methylphenyl)phosphine, di(3-sulpho-4-methoxyphenyl)(4-methoxyphenyl)phosphine, di(3-sulpho-4-chlorophenyl)(4-chlorophenyl)phosphine, tri(3-sulphophenyl)phosphine, tri(4-sulphophenyl)phosphine, (tri(3-sulpho-4-methylphenyl)phosphine, tri(3-sulpho-4-methoxyphenyl)phosphine, tri(3-sulpho-4-chlorophenyl)phosphine, (2-sulpho-4-methylphenyl)(3-sulpho-4-methylphenyl)(3,5-disulpho-4-methylphenyl)phosphine or (3-sulphophenyl)(3-sulpho-4-chlorophenyl)(3,5-disulpho-4-chlorophenyl)phosphine.

It is very clearly possible to use a mixture of these phosphines. In particular, a mixture of mono-, di- and tri-meta-sulphonated phosphines can be used.

- Monodentate or bidentate phosphines of following general formulae (II) and (III) are also suitable for the invention:



in which:

- Ar1 and Ar2, which are identical or different ,
represent aryl groups or aryl groups comprising
one or more substituents, such as:

- alkyl or alkoxy radicals having 1 to 4 carbon
5 atoms,
- halogen atom,
- hydrophilic group, such as:

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

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

-OH

-Ar3 represents an aryl group comprising one or more
substituents, such as:

- 25 - alkyl or alkoxy radicals having 1 to 4 carbon
atoms,
- halogen atom,
- hydrophilic group, such as:

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

-N(R)₄, in the formula of which the R symbols, which are 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 hydrophilic group as defined above,

- a represents 0 or 1,
- b represents 0 or 1,
- c represents an integer from 0 to 3,
- D represents an alkyl group, a cycloalkyl group or an alkyl or cycloalkyl group comprising one or more substituents, such as:

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

-COOM, -SO₃M or -PO₃M, M representing an inorganic or organic cationic residue chosen from hydrogen, cations derived from alkali metals or

alkaline earth metals, ammonium cations $-N(R)_4$ in the formula of which the R symbols, which are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, or other cations derived from metals, the arylcarboxylic acid, arylsulphonic acid or phosphonic acid salts of which are soluble in water,

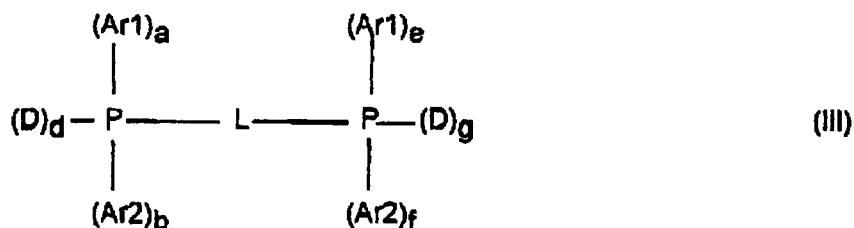
$-N(R)_4$, in the formula of which the R symbols, which are identical or different, represent a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms,

$-OH$

- d represents an integer from 0 to 3,

- the sum $(a+b+c+d)$ is equal to 3;

15



in which:

- Ar1, Ar2 and D have the meanings indicated above for the formula (II),

20

- a, b, e, and f each represent 0 or 1,

- d and g each represent an integer from 0 to 2,

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

- the sum $(e+f+g)$ is equal to 2,

- L represents a single valency bond or a divalent hydrocarbonaceous radical, such as an alkylene radical, a cycloalkylene radical, an arylene radical or a radical deriving from a heterocycle comprising one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to both phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which are optionally parts of the divalent radical L to comprise one or more substituents, such as [lacuna] alkyl group having 1 to 4 carbon atoms.

Mention may in particular be made, as nonlimiting examples of phosphines of general formula (II), of tris(hydroxymethyl)phosphine, tris(2-hydroxyethyl)phosphine, tris(3-hydroxypropyl)phosphine, tris(2-carboxymethyl)phosphine, the sodium salt of tris(3-carboxylatophenyl)phosphine, tris(3-carboxyethyl)phosphine, tris(4-trimethylammonium-phenyl)phosphine iodide, the sodium salt of tris(2-phosphonoethyl)phosphine, or bis(2-carboxyethyl)phenylphosphine.

Mention may in particular be made, as nonlimiting examples of phosphines of general formula (III), of the sodium salt of 2,2'-bis[di(sulphophenyl)phosphino]-1,1'-binaphthyl,

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

Some of the water-soluble phosphines of formulae (I) to (III) are commercially available.

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 literature, such as Houben-Weyl, Method der organischen Chemie, organische Phosphor Verbindungen [Methods of Organic Chemistry, Organic Phosphorus Compounds], part 1 (1963).

Finally, for the preparation of water-soluble derivatives which have not been described, it is possible, starting with phosphines not comprising water-soluble substituents defined above, to introduce one or more of these hydrophilic substituents. Thus, sulphonate groups, for example, can be introduced by the reaction of SO_3 in sulphuric acid. Carboxylate, phosphonate or quaternary ammonium groups can likewise be introduced by applying the chemical methods known for this type of synthesis.

The organic compounds comprising at least one ethylenic bond more particularly employed in the present process are diolefins, such as butadiene, isoprene, 1,5-hexadiene or 1,5-cyclooctadiene,

aliphatic nitriles comprising ethylenic unsaturation, particularly linear pentenenitriles, such as 3-pentenenitrile or 4-pentenenitrile, monoolefins, such as styrene, methylstyrene, vinyl naphthalene, 5 cyclohexene or methylcyclohexene, and mixtures of several of these compounds.

The pentenenitriles in particular can comprise amounts, generally minor amounts, of other compounds, such as 2-methyl-3-butenitrile, 2-methyl-10 2-butenitrile, 2-pentenenitrile, valeronitrile, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or butadiene, originating, for example, from the prior hydrocyanation reaction of butadiene.

15 Not insignificant amounts of 2-methyl-2-butenitrile and 2-methyl-2-butenitrile, which can be isomerized to linear nitriles, are formed with the linear pentenenitriles during the hydrocyanation of butadiene.

20 The catalytic solution used for the hydrocyanation according to the process of the invention can be prepared before it is introduced into the reaction region, for example by addition, to the aqueous solution of the water-soluble phosphine of 25 formulae (I) to (III), of the appropriate amount of chosen transition metal compound and optionally of the reducing agent. It is also possible to prepare the

catalytic solution "in situ" by simple mixing of these various constituents.

The amount of nickel compound used is chosen so that there is, per litre of reaction solution,
5 between 10^{-4} and 1 and preferably between 0.005 and 0.5 mol of nickel.

The amount of water-soluble phosphine of formulae (I) to (III) used to prepare the reaction solution is chosen so that the number of moles of this
10 compound with respect to 1 mol of nickel is from 0.5 to 2000 and preferably from 2 to 300.

Mention may be made, among suitable nickel compounds, as nonlimiting examples, of:

- compounds in which the nickel is in the zero
15 oxidation state, such as potassium tetracyanonickelate $K_4[Ni(CN)_4]$, bis(acrylonitrile)nickel(0), bis(1,5-cyclooctadiene)₂nickel and derivatives comprising ligands from group Va, such as tetrakis(triphenylphosphine)nickel(0) (in the latter
20 case, the compound can be dissolved in a water-immiscible solvent, such as toluene, and then an aqueous solution of sulphonated phosphine extracts part of the nickel, a red coloration developing in the aqueous solution which separates by settling);
- 25 - nickel compounds, such as carboxylates (in particular the acetate), carbonate, bicarbonate, borate, bromide, chloride, citrate, thiocyanate, cyanide, formate, hydroxide, hydrophosphite, phosphite,

phosphate and derivatives, iodide, nitrate, sulphate, sulphite, arylsulphonates and alkylsulphonates.

It is not necessary for the nickel compound itself to be soluble in water. For example, nickel
5 cyanide, one of the preferred compounds, which is sparingly soluble in water, can be dissolved in an aqueous solution of phosphine.

When the nickel compound used corresponds to a nickel oxidation state of greater than 0, the
10 catalyst is subjected to a chemical or electrochemical reduction stage as indicated above.

Although the reaction is generally carried out without a third solvent, it can be advantageous to add an inert water-immiscible organic solvent which can
15 be that of the subsequent extraction.

Mention may be made, as examples of such solvents, of aromatic, aliphatic or cycloaliphatic hydrocarbons which maintain the reaction mixture in the two-phase state.

20 Thus, once the reaction has ended, it is very easy to separate, on the one hand, an aqueous phase comprising water-soluble phosphines and the nickel compound and, on the other hand, an organic phase composed of the reactants involved in the reaction, the
25 reaction products and, if appropriate, the water-immiscible organic solvent.

The hydrocyanation reaction is generally carried out at a temperature of 10°C to 200°C and preferably of 30°C to 120°C.

The process of the invention can be carried
5 out continuously or batchwise.

The hydrogen cyanide employed can be prepared from metal cyanides, in particular sodium cyanide, or cyanohydrins.

The hydrogen cyanide is introduced into the
10 reactor in the gaseous form or in the liquid form. It can also be dissolved beforehand in an organic solvent.

Within the context of a batchwise implementation, it is possible, in practice, to charge to a reactor which has been purged beforehand using an
15 inert gas (such as nitrogen or argon) either an aqueous solution comprising all or part of the various constituents, such as the water-soluble phosphine, the transition metal compound, the optional reducing agent and the optional solvent, or the said constituents
20 separately. Generally, the reactor is then brought to the chosen temperature and then the compound to be hydrocyanated is introduced. The hydrogen cyanide is then itself introduced, preferably continuously and uniformly.

25 When the reaction (the progress of which can be monitored by quantitative determination of samples withdrawn) has finished, the reaction mixture is drawn off after cooling and the reaction products are

isolated by separation by settling, optionally followed by extraction of the aqueous layer using an appropriate solvent, such as, for example, the abovementioned water-immiscible solvents.

5 The aqueous catalytic solution can then be recycled in a fresh reaction for the hydrocyanation of organic compounds comprising at least one ethylenic double bond, after having been treated in accordance with the process of the invention.

10 It is also possible to use the catalyst in combination with a Lewis acid.

 The Lewis acid used as cocatalyst makes it possible in particular, in the case of the hydrocyanation of aliphatic nitriles comprising
15 ethylenic unsaturation, to improve the linearity of the dinitriles obtained, that is to say the percentage of linear dinitrile with respect to all the dinitriles formed, and/or to increase the lifetime of the catalyst.

20 The term "Lewis acid" means in the present text, according to the usual definition, compounds which are electron-pair acceptors.

 The Lewis acids cited in the work edited by G.A. Olah, "Friedel-Crafts and Related Reactions",
25 volume I, pages 191 to 197 (1963), can in particular be employed.

 The Lewis acids which can be employed as cocatalysts in the present process are chosen from

compounds of the elements from groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Classification of the Elements, in so far as the said compounds are at least partially soluble in water. These compounds are generally salts, in particular halides, preferably chlorides and bromides, sulphates, carboxylates and phosphates.

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, chlorides or bromides of rare earth metal 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.

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

It is also advantageous, if appropriate, to stabilize the Lewis acid in aqueous solution by the addition of an alkali metal or alkaline earth metal halide, such as lithium chloride, sodium chloride, calcium chloride or manganese chloride, in particular. The alkali metal or alkaline earth metal halide/Lewis acid molar ratio varies very widely, for example from 0 to 100, it being possible for the specific ratio to be

adjusted according to the stability of the Lewis acid in water.

Among the Lewis acids, zinc chloride, zinc bromide, stannous chloride, stannous bromide, stannous chloride stabilized with lithium chloride, stannous chloride stabilized with sodium chloride and zinc chloride/stannous chloride mixtures are very particularly preferred.

The Lewis acid cocatalyst employed generally represents from 0.01 to 50 mol per mole of nickel compound and preferably from 1 to 10 mol per mole.

As for the implementation of the process which forms the basis of the invention, the catalytic solution used for the hydrocyanation in the presence of a Lewis acid can be prepared before it is introduced into the reaction region, for example by addition, to the aqueous solution of the water-soluble phosphine of formulae (I) to (III), of the appropriate amount of nickel compound, of Lewis acid and optionally of the reducing agent. It is also possible to prepare the catalytic solution "in situ" by simple mixing of these various constituents.

It is also possible, under the conditions of the hydrocyanation process of the present invention, and in particular by carrying out the reaction in the presence of the catalyst described above comprising at least one water-soluble phosphine of formulae (I) to (III) and at least one nickel compound, to isomerize

2-methyl-3-butenenitrile to pentenenitriles in the absence of hydrogen cyanide.

The 2-methyl-3-butenenitrile subjected to the isomerization according to the invention can be
5 employed alone or as a mixture with other compounds.

Thus, it is possible to use 2-methyl-3-butenenitrile as a mixture with 2-methyl-2-butenenitrile, 4-pentenenitrile, 3-pentenenitrile, 2-pentenenitrile, butadiene, adiponitrile,
10 2-methylglutaronitrile, 2-ethylsuccinonitrile or valeronitrile.

Thus, it is particularly advantageous to treat the reaction mixture originating from the hydrocyanation of butadiene with HCN in the presence of
15 an aqueous solution of at least one water-soluble phosphine [lacuna] of at least one nickel compound, more preferably of a nickel compound in the 0 oxidation state, as defined above.

Within the context of this preferred
20 alternative form, as the catalytic system is already present for the hydrocyanation reaction of butadiene, it is sufficient to stop any introduction of hydrogen cyanide in order to allow the isomerization reaction to take place.

25 It is possible, if appropriate, in this alternative form, to gently flush the reactor using an inert gas, such as nitrogen or argon, for example, in

order to drive off the hydrocyanic acid which might still be present.

The isomerization reaction is generally carried out at a temperature from 10°C to 200°C and
5 preferably from 60°C to 120°C.

In the preferred case of an isomerization immediately following the hydrocyanation reaction of butadiene, it will be advantageous to carry out the isomerization at the temperature at which the
10 hydrocyanation has been carried out.

As for the process for the hydrocyanation of compounds comprising ethylenic unsaturation, the catalytic solution used for the isomerization can be prepared before it is introduced into the reaction
15 region, for example by addition, to the aqueous solution of a water-soluble phosphine, of the appropriate amount of nickel compound and optionally of the reducing agent. It is also possible to prepare the catalytic solution "in situ" by simple mixing of these
20 various constituents. The amount of nickel compound and the amount of water-soluble phosphine are the same as for the hydrocyanation reaction.

Although the isomerization reaction is generally carried out without a third solvent, it can
25 be advantageous to add an inert water-immiscible organic solvent which can be that of the subsequent extraction. This is in particular the case when such a solvent has been employed in the hydrocyanation

reaction of butadiene which has been used to prepare the mixture subjected to the isomerization reaction. Such solvents can be chosen from those which have been mentioned above for the hydrocyanation.

5 At the end of the reaction, it is very easy to separate the catalyst from the isomerization reaction products, as has been indicated for the hydrocyanation, and to recycle it, if appropriate, in one of the hydrocyanation reactions described above or
10 in a fresh isomerization reaction, after treatment of the aqueous phase and/or of the solid phase according to the process of the invention with hydrogen cyanide in order to dissolve the said solid phase.

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

EXAMPLE 1

1) Preparation of the Ni/TSTPP catalytic solution

20 500 cm³ of a solution of 350 mmol of sodium salt of trisulphonated triphenylphosphine (TSTPP) in water are charged to a 1 litre round-bottomed glass flask equipped with a magnetic bar and an ascending reflux condenser; this solution is degassed.
25 21.40 g (78 mmol) of Ni(cyclooctadiene)₂ and then 350 cm³ of ortho-xylene, degassed beforehand, are subsequently introduced with stirring and under a stream of argon.

The mixture is heated at 45°C for 15 h. After cooling, the two-phase system is separated by settling and the aqueous phase, which is highly coloured red, is withdrawn. Its Ni concentration, determined by

5 analysis, is 134 mmol/kg.

2) Isomerization of 2-methyl-3-butenitrile

The following are charged to a 2 litre glass reactor purged under argon and stirred using a turbine:

- 2-methyl-3-butenitrile (2M3BN): 770 g
10 (9.50 mol)
- the catalytic solution: 250 cm³ (39.5 mmol of Ni and 175.5 mmol of TSTPP)

The reaction mixture is stirred for 1.5 h at 90°C. After cooling and separation by settling, the
15 final organic phase is quantitatively determined by gas chromatography (GC).

The following results are obtained:

	Degree of conversion (DC) of the 2M3BN:	95%
	Yield (Yd) of 3-pentenitrile (3PN)	
20	with respect to the 2M3BN converted:	91.5%
	Yield (Yd) of 2-methyl-2-butenitrile (2M2BN)	
	with respect to the 2M3BN converted:	8%

The aqueous phase recovered after separation by settling exhibits a slight precipitate (finely
25 divided solid phase in suspension). On standing, the latter slowly settles out in the form of a brown-coloured film which readily redisperses with stirring. Quantitative determination of the Ni on a withdrawn

aqueous sample filtered by means of a Millipore Millex-HV® filter (Hydrophilic PVDF, 0.45 µm) gives the following Ni concentration: 110 mmol/kg.

3) Treatment of the aqueous suspension

5 35 cm³ of the aqueous suspension mentioned above (§ 2) are charged to a 150 cm³ glass reactor purged with argon and equipped with an auto-suction turbine. With stirring (1200 revolutions/minute) at room temperature, 0.265 ml of hydrocyanic acid is
10 injected into the reactor head space, with a constant flow rate and over a duration of an hour, via a syringe thermostatically controlled at -10°C. After injection of the HCN, the mixture is kept stirred for 1 hour at room temperature in a closed system and then the head
15 space of the reactor is flushed with a flow of argon for a further 1 hour approximately. By this treatment, a homogeneous aqueous solution is obtained: no noticeable precipitate in the solution on standing. Quantitative determination of the total Ni and of the
20 Ni(II), respectively by elemental analysis and polarographic analysis, on a withdrawn sample filtered by means of a Millipore Millex-HV® filter (Hydrophilic PVDF, 0.45 µm) gives the following results:
[Ni] = 122 mmol/kg and [Ni(II)] = 23 mmol/kg
25 ([Ni⁰] = 99 mmol/kg).

EXAMPLE 2

35 cm³ of the aqueous suspension mentioned in Example 1, § 2, are charged to a 150 cm³ glass reactor

purged with argon and equipped with an auto-suction turbine. With stirring (1200 revolutions/minute) and at a temperature of 50°C, 0.265 ml of hydrocyanic acid is injected into the reactor head space, with a constant
5 flow rate and over a duration of 1 hour, via a syringe thermostatically controlled at -10°C. After injection of the HCN and returning to room temperature, the mixture is kept stirred for 1 hour in a closed system and then the head space of the reactor is flushed with
10 a flow of argon for a further 1 hour approximately. By this treatment, a homogeneous aqueous solution is obtained: no noticeable precipitate in the solution on standing. Quantitative determination of the total Ni and of the Ni(II), respectively by elemental analysis
15 and polarographic analysis, on a withdrawn sample filtered by means of a Millipore Millex-HV® filter (Hydrophilic PVDF, 0.45 µm) gives the following results: [Ni] = 129 mmol/kg and [Ni(II)] = 38 mmol/kg ([Ni⁰] = 91 mmol/kg).

20 **EXAMPLE 3**

35 cm³ of the aqueous solution mentioned in Example 1, § 2, are charged to a 150 cm³ glass reactor purged with argon and equipped with an auto-suction turbine. With stirring (1200 revolutions/minute) and at
25 a temperature of 70°C, 0.265 ml of hydrocyanic acid is injected into the reactor head space, with a constant flow rate and over a duration of 1 hour, via a syringe thermostatically controlled at -10°C. After injection

of the HCN and returning to room temperature, the mixture is kept stirred for 1 hour in a closed system and then the head space of the reactor is flushed with a flow of argon for a further 1 hour approximately. By 5 this treatment, a homogeneous aqueous solution is obtained: no noticeable precipitate in the solution on standing. Quantitative determination of the total Ni and of the Ni(II), respectively by elemental analysis and polarographic analysis, on a withdrawn sample 10 filtered by means of a Millipore Millex-HV® filter (Hydrophilic PVDF, 0.45 μ m) gives the following results: [Ni] = 122 mmol/kg and [Ni(II)] = 30 mmol/kg ([Ni⁰] = 92 mmol/kg).

EXAMPLE 4

15 35 cm³ of the aqueous suspension mentioned in Example 1, § 2, are charged to a 150 cm³ glass reactor purged with argon and equipped with an auto-suction turbine. With stirring (1200 revolutions/minute) and at a temperature of 50°C, 0.295 ml of hydrocyanic acid is 20 injected into the reactor head space, with a constant flow rate and over a duration of 1 hour, via a syringe thermostatically controlled at -10°C. After injection of the HCN and returning to room temperature, the mixture is kept stirred for 1 hour in a closed system 25 and then the head space of the reactor is flushed with a flow of argon for a further 1 hour approximately. By this treatment, a homogeneous aqueous solution is obtained: no noticeable precipitate in the solution on

standing. Quantitative determination of the total Ni and of the Ni(II), respectively by elemental analysis and polarographic analysis, on a withdrawn sample filtered by means of a Millipore Millex-HV® filter
 5 (Hydrophilic PVDF, 0.45 μm) gives the following results: $[\text{Ni}] = 132 \text{ mmol/kg}$ and $[\text{Ni(II)}] = 40 \text{ mmol/kg}$ ($[\text{Ni}^0] = 92 \text{ mmol/kg}$).

EXAMPLE 5

1) Separation of the solid phase

10 The aqueous phase recovered after separation by settling is filtered under an argon atmosphere through a sintered glass of porosity 4. The filtrate, stored under argon, has the form of a dark red homogeneous solution. A green paste is recovered on the
 15 sintered glass, which paste, dried under vacuum at room temperature for 12 h, results in a powder with a light green colouring. The X-ray diffraction diagram of the latter exhibits diffraction lines characteristic of crystalline Ni(OH)_2 and of the crystalline sodium salt
 20 of TSTPP. Elemental analysis of the powder in question gives the following composition: Ni: 11.7 wgt %; P: 3.7 wgt %; C: 27.6 wgt %; Na: 6.0 wgt %; N: < 1 wgt %.

2) Treatment of the solid phase

25 35 cm^3 of a solution of 24.6 mmol of sodium salt of trisulphonated triphenylphosphine (TSTPP) in water are charged to a 150 cm^3 glass reactor purged with argon and equipped with an auto-suction turbine. This solution is degassed. 2.75 g of the light-green powder

obtained above are subsequently introduced. With stirring (1200 revolutions/minute) and at room temperature, 0.540 ml of hydrocyanic acid is injected into the reactor head space, with a constant flow rate and over a duration of 1 hour, via a syringe thermostatically controlled at -10°C . During the injection of the HCN, the solution rapidly becomes orangey and then bright red. After injection, the mixture is kept stirred for 3 hours at 80°C and then cooled to room temperature, where it is kept stirred for a further 12 hours. After flushing the head space of the reactor with argon for approximately 1 hour, a clear and homogeneous solution with a dark red colouring is recovered. Quantitative determination of the Ni on a withdrawn sample filtered by means of a Millipore Millex-HV® filter (Hydrophilic PVDF, $0.45\text{ }\mu\text{m}$) gives the following result: $[\text{Ni}] = 123\text{ mmol/kg}$.

The solution thus recovered can be used as catalytic solution after having been subjected to a reduction regeneration stage after addition of nickel in the (0) oxidation state.

CLAIMS

1. Process for the hydrocyanation of organic compounds comprising at least one ethylenic bond by reaction with hydrogen cyanide in the presence
5 of an aqueous solution of a catalyst comprising at least one nickel compound and at least one water-soluble phosphine and in separating, after reaction, organic phase from the aqueous phase, characterized in that it consists in treating the separated aqueous
10 phase, comprising a solid phase formed during the hydrocyanation reaction, with hydrogen cyanide in order to at least partially dissolve the solid phase.

2. Process according to claim 1, characterized in that the separated aqueous phase is
15 subjected to a stage of separation of the solid phase formed, the treatment with hydrogen cyanide being carried out on the said separated solid phase.

3. Process according to claim 1 or 2, characterized in that the separated aqueous phase is
20 partially recycled, after dissolution of the solid phase formed, in the hydrocyanation reaction of ethylenically unsaturated organic compounds.

4. Process according to either of claims 2 and 3, characterized in that the portion of the
25 separated aqueous phase which is not recycled in the hydrocyanation reaction is subjected to a stage of regeneration of the catalyst.



5. Process according to claim 2 or 3, characterized in that the aqueous solution obtained by treatment of the solid phase formed with hydrogen cyanide is subjected to a stage of at least partial
5 reduction of nickel in the (II) state to nickel in the (0) oxidation state.

6. Process according to claim 5, characterized in that the aqueous solution obtained by treatment of the solid phase formed with hydrogen
10 cyanide is mixed, prior to the reduction stage, with at least a portion of the separated aqueous phase.

7. Process according to one of the preceding claims, characterized in that the reduction is carried out by treatment with gaseous hydrogen.

15 8. Process according to one of claims 1 to 7, characterized in that the reduction is carried out by a chemical reduction process with a reducing agent chosen from the group consisting of borohydrides, magnesium and zinc.

20 9. Process according to one of claims 1 to 7, characterized in that the reduction is carried out according to an electrochemical process.

10. Process according to one of the preceding claims, characterized in that the
25 hydrocyanation reaction comprises the isomerization reaction of the nitrile compounds formed.



* C L M S *