

PROCESS FOR THE HYDROCYANATION OF  
UNSATURATED NITRILES TO DINITRILES

The present invention relates to a process for the hydrocyanation of nitriles containing ethylenic unsaturation to saturated dinitriles, in particular the  
5 hydrocyanation of pentenenitriles to adiponitrile, one of the basic compounds for the production of nylon 66.

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

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

The catalyst used is an organonickel complex containing ligands such as phosphines, arsines, stilbenes, phosphites, arsenites or antimonites.

20 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.

In this process, the medium is entirely  
25 organic and one of its major disadvantages lies in the difficulty of separating, at the end of the reaction, the hydrocyanation products from the catalytic solution containing several constituents (nickel complex,

triaryl phosphite, promoter), with a view in particular to recycling the latter solution in a new hydrocyanation reaction. Such a separation is difficult and imperfect, and a substantial loss of catalyst is  
5 observed, as well as the presence of the said catalyst in the hydrocyanation products.

It has been proposed in Patent FR-A-2,338,253 to perform the hydrocyanation of compounds having at least one ethylenic unsaturation in the presence of an  
10 aqueous solution of a compound of a transition metal, in particular nickel, palladium or iron, and a sulphonated phosphine.

The latter process permits good hydrocyanation, in particular of pentenenitriles, and  
15 an easy separation from the catalytic solution by simple decantation.

The results obtained during the hydrocyanation reaction are relatively good with various substrates and in particular with  
20 functionalized olefins such as pentenenitriles. However, it turns out that the percentage of linear dinitrile compound formed relative to all of the isomers obtained generally does not exceed 65 % to 70 %.

25 Furthermore, it is observed that the catalyst becomes rapidly deactivated.

The present invention proposes to overcome these disadvantages, in particular to improve the

degree of linearity of the products formed and/or to increase the lifetime of the catalyst.

It consists of a process for the hydrocyanation of an aliphatic nitrile containing ethylenic unsaturation, by reaction with hydrogen cyanide in the presence of an aqueous solution of a catalyst comprising a transition metal compound and a sulphonated phosphine, characterized in that the said solution also contains a cocatalyst consisting of at least one Lewis acid.

The nitriles containing ethylenic unsaturation more particularly used in the present process are linear pentenenitriles such as 3-pentenenitrile, 4-pentenenitrile and their mixtures.

These pentenenitriles may contain amounts, generally minor, of other compounds such as 2-methyl-3-butenitrile, 2-methyl-2-butenitrile, 2-pentenenitrile, valeronitrile, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or butadiene, obtained from the previous hydrocyanation reaction of butadiene and/or from the isomerization of 2-methyl-3-butene-nitrile to pentenenitriles.

Compounds of nickel, of palladium and of iron are preferably used as transition metal compounds.

Compounds which are water-soluble or capable of dissolving under the reaction conditions are used. The residue bonded to the metal is not critical, as long as it satisfies these conditions.

Among the abovementioned compounds, the compounds most preferred are those of nickel, and there may be mentioned by way of non-limiting examples:

- compounds in which the nickel is in oxidation state zero, for instance potassium tetracyanonickelate  $K_4(NiCN_4)$ , bis(acrylonitrile)nickel zero, bis(1,5-cyclooctadiene)<sub>2</sub> nickel and derivatives containing ligands of group Va, for instance tetrakis(triphenylphosphine)nickel zero (in the latter case the compound may be dissolved in a water-immiscible solvent such as toluene, and an aqueous solution of sulphonated phosphine then extracts some of the nickel, a red colour developing in the aqueous solution which separates out by settling);
- nickel compounds such as carboxylates (in particular 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 water-soluble. For example, nickel cyanide, which is sparingly soluble in water, is very soluble in an aqueous solution of phosphine.

- When the nickel compound used corresponds to a nickel oxidation state greater than 0, a nickel-reducing agent which reacts preferentially with nickel under the reaction conditions is added to the reaction

medium. This reducing agent may be organic or inorganic. By way of non-limiting examples there may be mentioned  $\text{NaBH}_4$ , Zn powder, magnesium,  $\text{KBH}_4$ , and borohydrides which are preferably water-soluble.

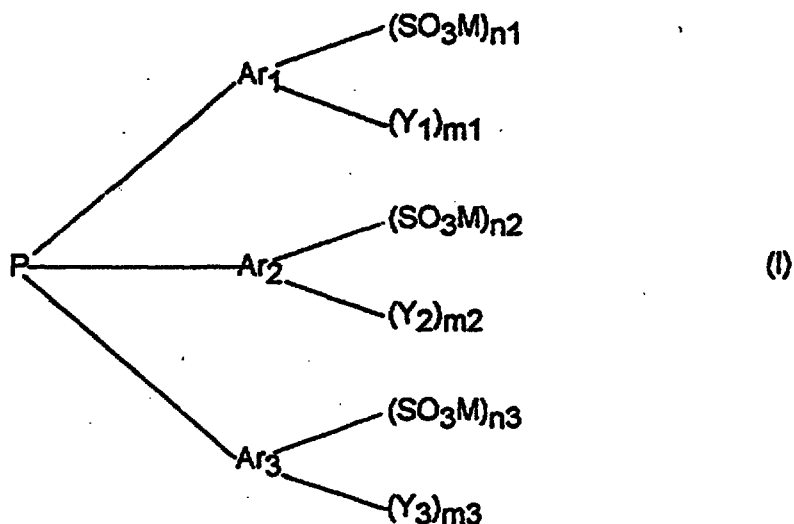
5                This reducing agent is added in an amount such that the number of redox equivalents is between 1 and 10. However, values of less than 1 and greater than 10 are not excluded.

              When the nickel compound used corresponds to  
10 a nickel oxidation state of 0, it is also possible to add a reducing agent of the type of those mentioned above, but this addition is not essential.

              When an iron compound is used, the same reducing agents are suitable.

15                In the case of palladium, the reducing agents may additionally be components of the reaction medium (phosphine, solvent, olefin).

              The sulphonated phosphines used in the present process are more particularly sulphonated  
20 phosphines of general formula (I):



in which:

\*  $Ar_1$ ,  $Ar_2$  and  $Ar_3$ , which may be identical or different, represent aryl groups,

\*  $Y_1$ ,  $Y_2$  and  $Y_3$ , which may be 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,

• a CN radical,

• an  $NO_2$  radical

• an OH radical,

• a radical  $NR_1R_2$  in the formula for which

$R_1$  and  $R_2$ , which may be identical or different, represent an alkyl radical having 1 to 4 carbon atoms,

\* M is an inorganic or organic cationic residue

chosen, so that the compound of formula (I) is water-soluble, 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 may be identical or different, representing an alkyl radical having 1 to 4 carbon atoms or a hydrogen atom,
- other cations derived from metals for which the benzenesulphonic acid salts have water-soluble,
- $m_1$ ,  $m_2$  and  $m_3$  are integers, which may be identical or different, from 0 to 5,
- $n_1$ ,  $n_2$  and  $n_3$  are integers, which may be identical or different, from 0 to 3, at least one of these being greater than or equal to 1.

Lead, zinc and tin may be mentioned as examples of metals for which the benzenesulphonic acid salts are water-soluble.

The expression water-soluble is understood, in the present text, to refer to a compound with a solubility of at least 0.01 g per litre of water.

Among the phosphines of formula (I), those are preferred for 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,
  - alkoxy radicals having from 1 to 2 C-C<sub>1</sub> atoms,
- 5        - M represents a cation chosen from the group comprising
- H<sup>+</sup>
  - cations derived from Na, K, Ca and Ba
  - NH<sub>4</sub><sup>+</sup>
- 10        • tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium cations
- m<sub>1</sub>, m<sub>2</sub> and m<sub>3</sub> are integers from 0 to 3
  - n<sub>1</sub>, n<sub>2</sub> and n<sub>3</sub> are integers from 0 to 3, at
- 15        least one also being greater than 1.
- Among these phosphines, the sodium, potassium, calcium, barium, ammonium, tetramethylammonium and tetraethylammonium salts of mono(sulphophenyl)diphenylphosphine, di(sulphophenyl)-
- 20        phenylphosphine and tri(sulphophenyl)phosphine in the formulae for which the SO<sub>2</sub> groups are preferably in the meta-position are the most particularly preferred.
- There may be mentioned, as other examples of phosphines of formula (I) which may be used according
- 25        to the process of the invention, alkali metal or alkaline-earth metal salts, ammonium salts, quaternary ammonium salts of (3-sulpho-4-methylphenyl)di(4-methylphenyl)phosphine; (3-sulpho-4-methoxyphenyl)di(4-methoxy-

phenyl)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; (3-sulphophenyl)(3-sulpho-4-chlorophenyl)(3,5-disulpho-4-chlorophenyl)phosphine.

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

The sulphonated phosphines used in the process according to the present invention may be prepared by employing known processes. Thus, in accordance with the teaching of H. Schindlbauer, Monatsch. Chem. 96, pages 2051-2057 (1965), the sodium salt of (p-sulphophenyl)diphenylphosphine may be prepared by reacting sodium p-chlorobenzenesulphonate with diphenylchlorophosphine, in the presence of sodium or potassium. According to the method described in J. Chem. Soc., pages 276-288 (1958) and in English Patent No. 1,066,261, phenylphosphines of formula (I) may be prepared by employing the reaction for the sulphonation

of aromatic ring-systems using oleum, followed by neutralization of the sulfonic groups formed using a suitable basic derivative of one of the metals represented by M in the formula (I). The crude  
5 sulphonated phosphine obtained may contain, as a mixture, the corresponding sulphonated phosphine oxide, whose presence does not, however, interfere with the carrying out of the hydrocyanation process according to the present invention.

10 The hydrocyanation reaction is generally performed at a temperature of 10°C to 150°C and preferably of 30°C to 120°C.

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

The amount of phosphine of formula (I) used in order to prepare the reaction solution is chosen such that the number of moles of this compound relative  
20 to 1 mol of elemental metal is from 0.5 to 2000 and preferably from 2 to 300.

The Lewis acid used as cocatalyst allows the linearity of the dinitriles obtained to be improved, that is to say the percentage of linear dinitrile  
25 relative to all of the dinitriles formed, and/or to increase the lifetime of the catalyst.

Lewis acid is understood, in the present text and according to the usual definition, to refer to

compounds which are electron-pair acceptors.

The Lewis acids cited in the work edited by G.A. Olah "Friedel-Crafts and related Reactions", volume I, pages 191 to 197 (1963) may in particular be  
5 used.

The Lewis acids which may be used as cocatalysts in the present process as chosen from compounds of the elements of groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the  
10 Periodic Classification of the Elements, insofar as the said compounds are at least partially soluble and stable in water or, more generally, in the aqueous phase of the reaction mixture. These compounds are most often, but non-limitingly, salts, in particular  
15 halides, preferably chlorides and bromides, sulphates, nitrates, sulphonates, in particular trifluoromethane-sulphonates, carboxylates, acetylacetonates, tetrafluoroborates and phosphates.

By way of non-limiting examples of such Lewis  
20 acids, there may be mentioned 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,  
25 cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, chlorides, bromides, sulphates, nitrates, carboxylates or trifluoromethanesulphonates of rare-earth metal

elements, for instance lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium, cobalt chloride, ferrous chloride and yttrium chloride.

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

It is also advantageous, where necessary, to stabilize the Lewis acid in aqueous solution by addition of an alkali metal chloride, for instance lithium chloride or sodium chloride in particular. The lithium chloride or sodium chloride/Lewis acid molar ratio varies very widely, for example from 0 to 100, it being possible for the specific ratio to be adjusted depending on the stability of the Lewis acid in water.

Among the Lewis acids, zinc chloride, zinc bromide, zinc sulphate, zinc tetrafluoroborate, stannous chloride, stannous bromide, stannous chloride stabilized with lithium chloride, stannous chloride stabilized with sodium chloride, zinc chloride/stannous chloride mixtures, nickel chloride, nickel bromide and nickel acetylacetonate, are most particularly preferred.

The Lewis acid cocatalyst used generally represents from 0.01 to 50 mol per mole of transition metal compound, more particularly of nickel compound, and preferably from 1 to 10 mol per mole.

The catalytic solution used for the

hydrocyanation according to the invention may be prepared before its introduction into the reaction zone, for example by addition of the appropriate amount of chosen transition metal compound, of Lewis acid and possibly of reducing agent to the aqueous solution of the phosphine of formula (I). It is also possible to prepare the catalytic solution "in situ" simply by mixing these various constituents.

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

By way of examples of such solvents, there may be mentioned aromatic, aliphatic or cycloaliphatic hydrocarbons which maintain the reaction medium in the two-phase state.

Thus, once the reaction has ended, it is very simple to separate out, on the one hand, an aqueous phase containing the sulphonated phosphine of formula (I), the transition metal compound and the Lewis acid and, on the other hand, an organic phase consisting of the reactants employed in the reaction, the reaction products and, where appropriate, the water-immiscible organic solvent.

Among the organic solvents which may be used in the hydrocyanation process, there may be mentioned benzene, toluene, xylenes, hexane and cyclohexane.

The process of the invention may be carried

out continuously or discontinuously.

The hydrogen cyanide used may be prepared from metal cyanides, in particular sodium cyanide, or from cyanohydrins.

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

          Within the context of a discontinuous implementation, it is possible, in practice, to charge  
10 to a reactor which has been flushed beforehand using an inert gas (such as nitrogen or argon) either an aqueous solution containing all or some of the various constituents such as the sulphonated phosphine, the transition metal compound, the optional reducing agent  
15 and solvent, and the Lewis acid, or to charge the said constituents thereto separately. Generally, the reactor is then brought to the chosen temperature, followed by introduction of the pentenenitrile. Hydrogen cyanide is itself then introduced, preferably in a continuous and  
20 regular manner.

          When the reaction (whose progress may be followed by assaying withdrawn samples) has finished, the reaction mixture is removed after cooling and the reaction products are isolated by separation of the  
25 phases after settling has taken place, optionally followed by extraction of the aqueous layer using a suitable solvent, such as for example the abovementioned water-immiscible solvents.

The aqueous catalytic solution may then be recycled to a new hydrocyanation reaction.

Within the context of a continuous implementation of the process, only the organic phase  
5 may be removed, while the aqueous catalytic phase remains in the reactor.

The examples which follow illustrate the invention.

#### EXAMPLE 1

10 a) Preparation of the Ni/TSTPP catalytic solution.

500 cm<sup>3</sup> of a solution of 300 mmol of the sodium salt of trisulphonated triphenylphosphine (TSTPP) in water are charged to a 1 litre glass round-  
15 bottomed flask fitted with a magnetic stirring bar and an ascending condenser; this solution is degassed. Next, with stirring and under a stream of argon, 20 g (73 mmol) of Ni(cyclooctadiene)<sub>2</sub> are introduced, followed by 350 cm<sup>3</sup> of previously degassed ortho-xylene.

20 The mixture is heated at 45°C for 15 h. After cooling, the two-phase system separates out after settling has taken place and the strongly red-coloured aqueous phase is withdrawn.

2) Hydrocyanation of 3-pentenitrile.

25 34.8 cm<sup>3</sup> of an aqueous solution of Ni/TSTPP catalyst, containing 5 mmol of Ni and 20 mmol of TSTPP, are charged to a 150 cm<sup>3</sup> glass reactor. The mixture is

heated to 60°C with stirring, and the following are successively injected while maintaining this temperature:

- 5                   -     3.2 cm<sup>3</sup> of an aqueous solution containing  
                      20 mmol of Zn chloride
- 8 g (105 mmol) of 3-pentenitrile  
                      (3PN).

Next, hydrogen cyanide is injected at a rate of 1.8 g/h (67 mmol/h) for 2 h.

- 10                   At the end of the test, the reaction mixture obtained is cooled, the possible excess hydrogen cyanide injected is neutralized using concentrated sodium hydroxide solution and the various constituents are assayed by gas chromatography (GC).

15                   The following results are obtained:

- Extent of conversion (EC) of 3PN                   89 %
- Yield (Yd) of adiponitrile (ADN)  
          relative to the 3PN converted                   66 %
- Yd of 2-methylglutaronitrile (MGN)  
20           relative to the 3PN converted                   26 %
- Yd of 2-ethylsuccinonitrile (ESN)  
          relative to the 3PN converted                   5 %
- Yd of valeronitrile (VN) relative  
          to the 3PN converted                            3 %
- 25           -     Linearity (\*)                           68 %
- Activity of the catalyst (\*\*)                   20
- Production efficiency for ADN (relative  
          to the volume of the aqueous phase)   90 g/h.l

(\*) ADN formed/ADN + MGN + ESN formed

(\*\*) number of moles of 3PN converted per  
mole of Ni employed

EXAMPLES 2 to 5 and Comparative Test 1

5                    Example 1 is repeated with the following  
charges and operating conditions:

- Ni: 5 mmol
- TSTPP: 20 mmol
- ZnCl<sub>2</sub>: see Table 1
- 10                    - water: qs 38 ml
- 3PN: 320 mmol
- HCN injection flow rate: 67 mmol/h
- Temperature: 65°C

The results obtained are collated in Table 1

15                    (Yd of DN = yield of ADN + MGN + ESN relative to the  
3PN converted).

| Test                            | ZnCl <sub>2</sub><br>(in<br>mmol) | Activity<br>of the<br>catalyst | % Yd of<br>DN | Linear-<br>ity |
|---------------------------------|-----------------------------------|--------------------------------|---------------|----------------|
| Example 2                       | 1                                 | 5                              | 88            | 73             |
| Example 3                       | 5                                 | 14                             | 97            | 74             |
| 20                    Example 4 | 20                                | 30                             | 97            | 63             |
| Example 5                       | 40                                | 30                             | 97            | 57             |
| Comparative<br>test             | 0                                 | 3                              | 76            | 62             |

Table 1

**EXAMPLE 6**

Example 1 is repeated with the following charges and operating conditions:

- |    |                            |           |
|----|----------------------------|-----------|
| 5  | - Ni:                      | 10 mmol   |
|    | - TSTPP:                   | 20 mmol   |
|    | - ZnCl <sub>2</sub> :      | 20 mmol   |
|    | - water:                   | qs 38 ml  |
|    | - 3PN:                     | 320 mmol  |
|    | - HCN injection flow rate: | 67 mmol/h |
| 10 | - Temperature:             | 65°C      |

The following results are obtained:

- |                             |      |
|-----------------------------|------|
| - Yd of DN:                 | 98 % |
| - Activity of the catalyst: | 15   |
| - Linearity:                | 71 % |

15 **EXAMPLES 7 and 8**

Example 1 is repeated with the following charges and operating conditions:

- |    |                            |             |
|----|----------------------------|-------------|
|    | - Ni:                      | 5 mmol      |
|    | - TSTPP:                   | see Table 2 |
| 20 | - ZnCl <sub>2</sub> :      | 20 mmol     |
|    | - water:                   | qs 38 ml    |
|    | - 3PN:                     | 320 mmol    |
|    | - HCN injection flow rate: | 67 mmol/h   |
|    | - Temperature:             | 65°C        |

25 The results obtained are collated in Table 2.

| Example   | TSTPP<br>(in<br>mmol) | Activity<br>of the<br>catalyst | % Yd of<br>DN | Linear-<br>ity |
|-----------|-----------------------|--------------------------------|---------------|----------------|
| Example 7 | 6                     | 6                              | 98            | 60             |
| Example 8 | 32                    | 17                             | 98            | 73             |

Table 25 EXAMPLES 9 and 10

Example 1 is repeated with the following  
charges and operating conditions:

- Ni: 5 mmol
- TSTPP: 20 mmol
- 10 - ZnCl<sub>2</sub>: 20 mmol
- water: qs 38 ml
- 3PN: 320 mmol
- HCN injection flow rate: see Table 3
- Temperature: see Table 3

15 The results obtained are collated in Table 3  
(Example 4 has also been given in the table).

| Examples      | Temper-<br>ature | HCN<br>injec-<br>tion<br>flow<br>rate | Acti-<br>vity<br>of<br>the<br>cata-<br>lyst | % Yd<br>of<br>DN | Line-<br>arity |
|---------------|------------------|---------------------------------------|---------------------------------------------|------------------|----------------|
| Example 9     | 45°C             | 17 mmol/h                             | 35                                          | 99               | 68             |
| Example 4     | 65°C             | 67 mmol/h                             | 30                                          | 97               | 63             |
| 20 Example 10 | 85°C             | 135 mmol/h                            | 10                                          | 99               | 63             |

Table 3

**EXAMPLES 11 to 23**

Example 1 is repeated with the following charges and operating conditions:

- |    |   |                          |           |
|----|---|--------------------------|-----------|
|    | - | Ni:                      | 5 mmol    |
| 5  | - | TSTPP:                   | 20 mmol   |
|    | - | Lewis acid (nature       |           |
|    |   | indicated in Table 4):   | 20 mmol   |
|    | - | water:                   | qs 35 ml  |
|    | - | 3PN:                     | 200 mmol  |
| 10 | - | HCN injection flow rate: | 67 mmol/h |
|    | - | Temperature:             | 65°C      |
|    | - | Duration:                | 1 h       |

The results obtained are collated in Table 4.

**EXAMPLES 24 to 49**

Example 1 is repeated with the following charges and operating conditions:

- |    |   |                          |           |
|----|---|--------------------------|-----------|
|    | - | Ni:                      | 5 mmol    |
|    | - | TSTPP:                   | 20 mmol   |
|    | - | Lewis acid (nature       |           |
| 20 |   | indicated in Table 5):   | 20 mmol   |
|    | - | water:                   | qs 35 ml  |
|    | - | 3PN:                     | 200 mmol  |
|    | - | HCN injection flow rate: | 67 mmol/h |
|    | - | Temperature:             | 65°C      |
| 25 | - | Duration:                | 1 h       |

The results obtained are collated in Table 5.

| Example       | Lewis Acid                               | Activity<br>of the<br>catalyst | Linearity |
|---------------|------------------------------------------|--------------------------------|-----------|
| Example 11    | MnBr <sub>2</sub>                        | 8                              | 64        |
| Example 12    | MnCl <sub>2</sub>                        | 8                              | 66        |
| Example 13    | FeCl <sub>2</sub>                        | 6                              | 68        |
| 5 Example 14  | CoCl <sub>2</sub> /ZnCl <sub>2</sub> (*) | 19                             | 72        |
| Example 15    | ZnBr <sub>2</sub>                        | 25                             | 68        |
| Example 16    | ZnI <sub>2</sub>                         | 23                             | 66        |
| Example 17    | YCl <sub>3</sub>                         | 8                              | 75        |
| Example 18    | CdBr <sub>2</sub>                        | 20                             | 69        |
| 10 Example 19 | SnBr <sub>2</sub>                        | 10                             | 88        |
| Example 20    | SnCl <sub>2</sub>                        | 12                             | 88        |
| Example 21    | SnCl <sub>2</sub> /LiCl(**)              | 15                             | 87        |
| Example 22    | SnCl <sub>2</sub> /ZnCl <sub>2</sub> (*) | 15                             | 83        |
| Example 23    | CeBr <sub>3</sub>                        | 6                              | 64        |

15

Table 4

(\*) equimolar mixture of 2 Lewis acids

(\*\*) supplementary addition of 200 mmol of LiCl

| Example       | Lewis Acid      | Activity<br>of the<br>catalyst | Linearity |
|---------------|-----------------|--------------------------------|-----------|
| Example 24    | $\text{CoCl}_2$ | 3                              | 84        |
| Example 25    | $\text{CdCl}_2$ | 5                              | 72        |
| Example 26    | $\text{SnSO}_4$ | 5                              | 89        |
| 5 Example 27  | Sn tartrate     | 4                              | 87        |
| Example 28    | $\text{LaCl}_3$ | 3                              | 70        |
| Example 29    | $\text{CeCl}_3$ | 3                              | 73        |
| Example 30    | $\text{PrCl}_3$ | 4                              | 73        |
| Example 31    | $\text{NdCl}_3$ | 4                              | 75        |
| 10 Example 32 | $\text{SmCl}_3$ | 3                              | 77        |
| Example 33    | $\text{EuCl}_3$ | 5                              | 87        |
| Example 34    | $\text{GdCl}_3$ | 3                              | 78        |
| Example 35    | $\text{DyCl}_3$ | 4                              | 78        |
| Example 36    | $\text{HoCl}_3$ | 3                              | 81        |
| 15 Example 37 | $\text{ErCl}_3$ | 3                              | 80        |
| Example 38    | $\text{TmCl}_3$ | 6                              | 77        |
| Example 39    | $\text{YbCl}_3$ | 4                              | 81        |
| Example 40    | $\text{LuCl}_3$ | 4                              | 81        |

Table 5 (start)

| Example       | Lewis Acid                                        | Activity of<br>the catalyst | Linearity |
|---------------|---------------------------------------------------|-----------------------------|-----------|
| Example 41    | NiBr <sub>2</sub>                                 | 2.2                         | 83        |
| Example 42    | Ni(acac) <sub>2</sub> (*)                         | 3.2                         | 77        |
| Example 43    | Mg(OTf) <sub>2</sub> (**)                         | 3.3                         | 71        |
| 5 Example 44  | Zn(OTf) <sub>2</sub> (**)                         | 14                          | 57        |
| Example 45    | Sn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> | 3                           | 87        |
| Example 46    | NiCl <sub>2</sub>                                 | 2                           | 91        |
| Example 47    | La(CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> | 2                           | 77        |
| Example 48    | ZnSO <sub>4</sub>                                 | 7                           | 77        |
| 10 Example 49 | Zn)BF <sub>4</sub> ) <sub>2</sub>                 | 11                          | 77        |

Table 5 (end)

(\*) acac = acetylacetonate

(\*\*) OTf = trifluoromethanesulphonate

CLAIMS

1) Process for the hydrocyanation of an aliphatic nitrile containing ethylenic unsaturation, by reaction with hydrogen cyanide in the presence of an aqueous solution of a catalyst comprising a transition metal compound and a sulphonated phosphine, characterized in that the said solution also contains a cocatalyst consisting of at least one Lewis acid.

2) Process according to Claim 1, characterized in that the nitrile containing ethylenic unsaturation is chosen from linear pentenenitriles, for instance 3-pentenenitrile, 4-pentenenitrile and their mixtures.

3) Process according to either of Claims 1 and 2, characterized in that compounds of nickel, of palladium and of iron, which are water-soluble or capable of dissolving under the reaction conditions, and preferably nickel compounds, are used as transition metal compounds.

4) Process according to Claim 3, characterized in that the nickel compound used is a nickel zero compound.

5) Process according to Claim 3, characterized in that the nickel compound used is a compound of nickel with an oxidation state greater than zero.

6) Process according to Claim 5, characterized in that an organic or inorganic nickel-



reducing agent which reacts preferentially with nickel under the reaction conditions is added to the reaction medium.

7) Process according to Claim 6,  
5 characterized in that the reducing agent is added in an amount such that the number of redox equivalents is between 1 and 10.

8) Process according to one of Claims 1 to 7, characterized in that the amount of nickel compound  
10 used is chosen such that there is between  $10^{-4}$  and 1 and preferably between 0.005 and 0.5 mol of nickel per litre of reaction solution.

9) Process according to one of Claims 1 to 8, characterized in that the Lewis acid used as  
15 cocatalyst is chosen from compounds of the elements of groups Ib, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII of the Periodic Classification of the Elements, insofar as the said compounds are at least partially soluble and stable in water or, more  
20 generally, in the aqueous phase of the reaction mixture.

10) Process according to Claim 9,  
characterized in that the compounds are salts, such as halides, preferably chlorides and bromides, sulphates,  
25 nitrates, sulphonates, in particular trifluoromethanesulphonates, carboxylates, acetylacetonates, tetrafluoroborates and phosphates.

11) Process according to one of Claims 1 to

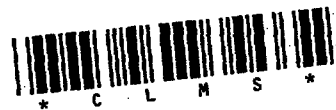


10, characterized in that the Lewis acid is chosen from zinc chloride, zinc bromide, zinc iodide, zinc trifluoromethane sulphonate, zinc acetate, zinc nitrate, zinc tetrafluoroborate, manganese chloride, manganese bromide, nickel chloride, nickel bromide, nickel cyanide, nickel acetylacetonate, cadmium chloride, cadmium bromide, stannous chloride, stannous bromide, stannous sulphate, stannous tartrate, chlorides, bromides, sulphates, nitrates, carboxylates or trifluoromethane sulphonates of rare-earth metal elements, for instance lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium, cobalt chloride, ferrous chloride and yttrium chloride and mixtures of several of these compounds.

12) Process according to one of Claims 1 to 11, characterized in that the Lewis acid is stabilized in aqueous solution by addition of an alkali metal chloride, for instance lithium chloride or sodium chloride.

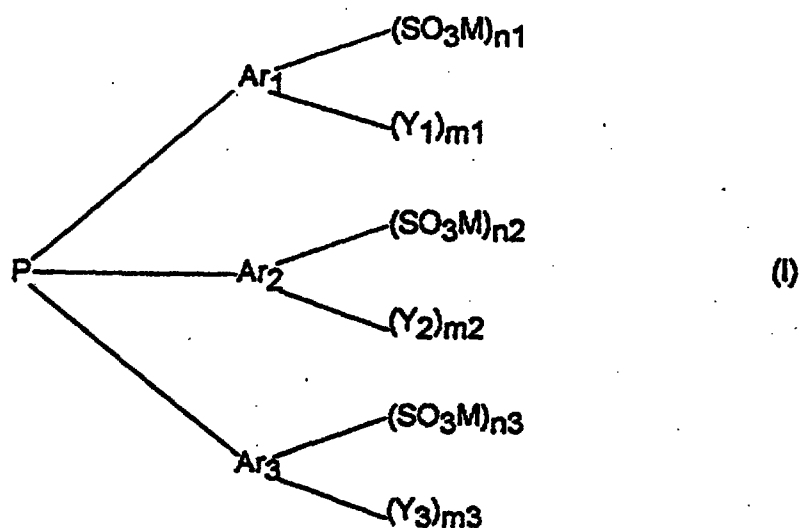
13) Process according to one of Claims 1 to 12, characterized in that the lithium chloride or sodium chloride/Lewis acid molar ratio varies from 0 to 100, it being possible for the specific ratio to be adjusted depending on the stability in water of the Lewis acid.

14) Process according to one of Claims 1 to 13, characterized in that the Lewis acid cocatalyst



used represents from 0.01 to 50 mol per mole of transition metal compound, more particularly of nickel compound, and preferably from 1 to 10 mol per mole.

15) Process according to one of Claims 1 to 14, characterized in that the sulphonated phosphines used are chosen from the sulphonated phosphines of general formula (I):



in which:

- \*  $\text{Ar}_1$ ,  $\text{Ar}_2$  and  $\text{Ar}_3$ , which may be identical or different, represent aryl groups,
- \*  $\text{Y}_1$ ,  $\text{Y}_2$  and  $\text{Y}_3$ , which may be 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,
  - a CN radical,



- an NO<sub>2</sub> radical
- an OH radical,
- a radical NR<sub>1</sub>R<sub>2</sub> in the formula for which R<sub>1</sub> and R<sub>2</sub>, which may be identical or different, represent an alkyl radical having 1 to 4 carbon atoms,

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

- H<sup>+</sup>,
- cations derived from alkali metals or alkaline-earth metals,
- N(R<sub>3</sub>R<sub>4</sub>R<sub>5</sub>R<sub>6</sub>)<sup>+</sup> with R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub>, which may be identical or different, representing an alkyl radical having 1 to 4 carbon atoms or a hydrogen atom,
- other cations derived from metals for which the benzenesulphonic acid salts have water-soluble,

\* m<sub>1</sub>, m<sub>2</sub> and m<sub>3</sub> are integers, which may be identical or different, from 0 to 5,

\* n<sub>1</sub>, n<sub>2</sub> and n<sub>3</sub> are integers, which may be identical or different, from 0 to 3, at least one of these being greater than or equal to 1.

16) Process according to Claim 15, characterized in that the sulphonated phosphines used are chosen from the sulphonated phosphines of formula



(I), 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,
    - alkoxy radicals having from 1 to 2 C-C<sub>1</sub> atoms,
  - M represents a cation chosen from the group comprising
    - $H^+$
    - cations derived from Na, K, Ca and Ba
    - $NH_4^+$
    - tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium cations
  - $m_1$ ,  $m_2$  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.
- 17) Process according to one of Claims 1 to 16, characterized in that the sulphonated phosphines used are chosen from the sodium, potassium, calcium, barium, ammonium, tetramethylammonium and tetraethylammonium salts of mono(sulphophenyl)-diphenylphosphine, di(sulphophenyl)phenylphosphine and tri(sulphophenyl)phosphine in the formulae for which  $SO_3$  groups are preferably in the meta-position.
- 18) Process according to one of Claims 1 to 17, characterized in that the amount of sulphonated



phosphine used is chosen such that the number of moles of this compound relative to 1 mol of transition metal is from 0.5 to 2000 and preferably from 2 to 300.

- 19) Process according to one of Claims 1 to 5 18, characterized in that the hydrocyanation reaction is performed at a temperature of 10°C to 150°C and preferably of 30°C to 120°C.