



## (51) International Patent Classification:

*C01C 3/00* (2006.01) *B01J 31/10* (2006.01)  
*B01J 31/08* (2006.01)

## (21) International Application Number:

PCT/CZ2012/00013 1

## (22) International Filing Date:

11 December 2012 (11.12.2012)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

PV 201 1-816 13 December 2011 (13.12.2011)

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Na Belidle 3, 150 00 Praha 5 (CZ).(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,  
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,  
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP,  
KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,  
ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,  
NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU,  
RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ,  
TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA,  
ZM, ZW.

(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,  
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,  
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,  
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,  
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
ML, MR, NE, SN, TD, TG).

## Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a  
patent (Rule 4.17(h))

## Published:

— with international search report (Art. 21(3))  
— before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments (Rule 48.2(h))

## (54) Title: METHOD OF PRODUCTION OF ETHANE DINITRILE BY OXIDATION OF HYDROGEN CYANIDE

(57) Abstract: The present invention provides a method of production of ethane dinitrile (CN)<sub>2</sub> by oxidation of hydrogen cyanide HCN, wherein hydrogen cyanide is oxidized on a catalytic system Fem<sup>+</sup>/Cun<sup>+</sup>, wherein m has the value of 2 or 3, n has the value of 1 or 2, wherein the catalytic system is supported on a polymeric organic cation exchanger, wherein the oxidation reaction is carried out in an organic solvent, or in a homogeneous or heterogeneous mixture of an organic solvent with water, at the temperature in the range of 5 °C to 65 °C, using an oxygen-containing oxidizing agent selected from the group containing oxygen, air, hydrogen peroxide or its mono- or di-substituted alkyl or acyl derivatives selected from the group including tert-butyl hydroperoxide, benzoyl hydroperoxide, dibenzoyl peroxide, di-tert-butyl peroxide, di-(2-ethylhexyl) peroxydicarbonate.



## Method of production of ethane dinitrile by oxidation of hydrogen cyanide

### Field of Art

- 5 The invention relates to a production method of ethane dinitrile  $(\text{CN})_2$  from hydrogen cyanide HCN by oxidation thereof on a  $\text{Fe}^{\text{ra}+}/\text{Cu}^{\text{n}+}$  catalytic system supported on a polymeric organic cation exchanger, in which  $\text{m}^+$  has the value of 2 or 3,  $\text{n}^+$  has the value of 1 or 2.

### 10 Background Ail

Ethane dinitrile  $(\text{CN})_2$  (Herbert E. Williams, H. E.: The Chemistry of Cyanogen Compounds and Their Manufacture and Estimation, General Books, 2009.), termed also dicyan, (di)cyanogene, oxalyl (di)nitrile or oxalyl cyanide, is a chemical compound with  
15 a very small difference between the boiling point ( $-21\text{ }^\circ\text{C}$ ) and melting point ( $-28\text{ }^\circ\text{C}$ ), showing the second highest known combustion temperature ( $4640\text{ }^\circ\text{C}$ ) (Thomas, N., Gaydon, A. G., Brewer, L., A. G., Brewer, L.: Journal of Chemical Physics 1952, 20, 369.), for which it is used as a welding medium, and it has recently acquired a very wide range of application. It is used in organic synthesis for production of intermediates of  
20 pharmaceutical and agrochemical industry, it is applied as a rocket fuel, and in highly pure condition for preparation of polymers of ethane dinitrile (paracyanogen) used in nanotechnologies for polymer semiconductor layers. Due to its toxicological properties and the capability of effective degradation to ammonia and carbonate anion in the environment, it is used in a mixture with hydrogen cyanide or with carbon dioxide as a  
25 fumigant (replacement for carcinogenic methyl bromide) for the protection of cereals, including rice, timber, fruits and vegetables against animal parasites, fungi, and other microorganisms, and for the same reasons also as a sterilization agent for soil, etc. (O'Brien, I. G., Desmarchelier, F. J. M., Younglin, R. (Commonwealth scientific and industrial research organization): WO 9601051 A1 (1996)). In view of the wide  
30 application spectrum of ethane dinitrile, a wide range of methods for its preparation, or production, was previously described and patented. A review article (Brotherton, T. K., Lynn, J.W.: Chem. Rev. 1959, 59, 841) presents a number of methods of its preparation

with references to primary literature. Industrially significant methods based on hydrogen cyanide and its oxidation by air or oxygen are described in numerous patents (Eubanks, L. (Monsanto Chem. Company): US 2955022 (1960); Moje, W. (E. I. Du Pont de Nemours and Company): US 2712493 (1955); Gruber, W. (Rohm & Hass GmbH): US 3183060 (1965); Zima, H., Gruber, W. (Rohm & Hass GmbH): US 3239309 (1966); (Gruber, W., Zima, H. (Rohm & Hass GmbH): DE 1116641 (1961); Geerts, M. J., O'Malley, Ch. T. (The Pure Oil Company): US 3065057 (1962); Pfeil, E., Schaefer K.-H., Nebeling, R. (Dr. Emanuel Pfeil): DE 1 163302 (1964); Dreh, C, Kautter, T., Zima, H. (Rohm & Hass GmbH): DE 1040521 (1958); Fierce, W. L., Sandner, W. J. (The Pure Oil Company): US 2884308 (1959); Geerts, M. J., Sandner, W. J., Fierce, W. L. (The Pure Oil Company): US 3135582 (1964); Riemenschneider, W., Wegener, P. (Hoechst AG): US 3997653 (1976); Takeshi, Y., Tooru, I., Sueo, K., Takao, K. (Asahi Kasei Kogyo Kabushiki Kaisha): US 3949061 (1976).).

Previously known methods for preparation and production of ethane dinitrile which are closest to the present invention are based on the fact that the compound consisting of cyanide anion with cupric cation is meta-stable and is subject to immediate disproportionation reaction to ethane dinitrile and insoluble cuprous cyanide. It is insoluble in water and in organic solvents, as well, but the copper in the oxidation degree Cu(I) can be reoxidized to Cu(II) and thus the process can be performed as catalytic. The patent US 4003983 (Johannes, H., Werner, H., Lussling T., Weigert, W. (Deutsche Gold- und Silber—Scheideanstalt vormals Roessler), 1977) describes a homogenous catalytic continual system containing iron bromide and copper bromide dissolved in the mixture of water and sulfolane (tetramethylene sulfone). According to said solution, liquid hydrogen cyanide and 35% hydrogen peroxide are concurrently dosed in the molar ratio of 2:1 into a cooled through-flow reactor; the temperature of the reaction is maintained at about 35 °C and the pressure is 0.03 atm. After the completion of the reaction, the products are removed from the reactor for purification using fractional distillation. The yield of the raw ethane dinitrile is stated as 97.6 %; the product contains 98.1 % of ethane dinitrile, 0.2 % of oxygen, and 1.7 % of nitrogen. The salts were used in the reaction mixture in the concentrations from 10 % by weight to 20 % by weight with the equimolar ratio of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ ; the concentration of sulfolane in the reaction mixture is shown according to this patent as 0 to 80 % by volume. According to said solution, the sulfolane acts as a stabilizer for

the salts of iron and copper and the bromide form of both salts suppresses undesirable side reactions, such as the formation of a mixture of oxides of both metals, elimination of elementary metals, and formation of halocyanogen. When using the metal bromides, in comparison with chlorides, sulfates and nitrates, these provided the highest  
5 conversion of hydrogen cyanide and the yield of ethane dinitrile. The disadvantage of said solution is the use of relatively expensive metal bromides, their corrosiveness in the technological equipment, toxicity including environmental toxicity, and further the fact that the long-term stability of the system is relatively low. Another disadvantage is the necessity of cooling the reactor because of the high exothermicity of the process. A  
10 significant disadvantage of said solution is the fact that the addition of 35 % of hydrogen peroxide increases the volume of the aqueous reaction mixture hence it reduces the concentration of both salts and of sulfolane, which leads to reduction of the efficiency of the process and to reduction of stability of the system. It is then necessary to discontinue the process to remove water by distillation, which further increases the operating costs.

15

#### Disclosure of the Invention

The invention provides a method of production of ethane dinitrile  $(CN)_2$  by oxidation of hydrogen cyanide HCN, wherein hydrogen cyanide is oxidized on a catalytic system  
20  $Fe^{m+}/Cu^{n+}$ , wherein  $m$  has the value of 2 or 3,  $n$  has the value of 1 or 2, optionally in the presence of bidentate oxygen or nitrogen ligand, wherein the catalytic system is supported on a polymeric organic cation exchanger, wherein the oxidation reaction is carried out in an organic solvent, which is preferably methanol, or in a homogeneous or heterogeneous mixture of an organic solvent with water, at the temperature of 5 °C to  
25 65 °C, using an oxygen-containing oxidizing agent selected from the group containing oxygen, air, hydrogen peroxide or its mono- or di-substituted alkyl or acyl derivatives selected from the group including *ter*-butyl hydroperoxide, benzoyl hydroperoxide, dibenzoyl peroxide, di-*tert*-butyl peroxide, di-(2-ethylhexyl) peroxydicarbonate.

In a preferred embodiment, the oxygen-containing oxidizing agent is hydrogen peroxide.

30 More preferably, the oxidizing agent is hydrogen peroxide in the concentration in the range of 3 to 40 % by weight. In a preferred embodiment of the invention, hydrogen peroxide and liquid hydrogen cyanide are dosed in the molar ratio in the range of 1 : 3 to

3 : 1, the dosage rate is controlled by the conversion of hydrogen cyanide to ethane dinitrile and further by the concentration of carbon dioxide, an undesired by-product, in the mixture with the product and the unreacted hydrogen cyanide. The products, which are the desired ethane dinitrile, undesired carbon dioxide, which is formed by its  
5 oxidative hydrolysis, and the unreacted hydrogen cyanide are then removed from the reaction zone to further processing, that is to the separation of the components of the gaseous mixture by fractional distillation, to the adjustment of the ethane dinitrile, and to the recycling of hydrogen cyanide.

In a preferred embodiment of the invention, hydrogen cyanide is used in liquid form.

- 10 Preferably, the molar ratio of the ions  $\text{Fe}^{m+} : \text{Cu}^{n+}$  supported on the cation exchanger is in the range of 1 : 4 to 4 : 1.

The polymeric organic cation exchanger used for the support of the catalytic system  $\text{Fe}^{m+}/\text{Cu}^{n+}$  is preferably an organic synthetic polymer, co-polymer, or an organic polycondensate bearing strongly acidic, that is  $-\text{SO}_3\text{H}$ ,  $-\text{O}-\text{SO}_3\text{H}$ , or medium acidic, that  
15 is  $-\text{P}(\text{O})(\text{OH})_2$ ,  $-\text{P}(\text{O})\text{H}(\text{OH})$ ,  $-\text{O}-\text{P}(\text{O})(\text{OH})_2$ , or weakly acidic, that is  $-\text{COOH}$ ,  $-\text{alkyl}-\text{COOH}$ ,  $-\text{aryl}-\text{COOH}$ ,  $-\text{aryl}-\text{OH}$ , functional groups.

More preferably, the polymeric organic cation exchanger used for the support of the catalytic system  $\text{Fe}^{m+}/\text{Cu}^{n+}$  is a polyacrylate or polymethacrylate weakly acidic cation exchanger, or a strongly acidic cation exchanger on the basis of sulfonated copolymer of  
20 styrene and divinylbenzene, which are synthetic resins commonly used for example for industrial purification of water. These polymeric organic cation exchangers can be used in a gel or macroporous form.

The catalytic system is prepared by chemisorption of both iron and copper cations in the form of a salt or complex to the polymeric organic cation exchanger. The chemisorption  
25 can be performed for example by washing an aqueous solution of a metal salt or metal complex through a column filled with the cation exchanger or by mixing an aqueous solution of a metal salt or metal complex with the cation exchanger until the desired saturation of the cation exchanger is achieved. The salt or complex used for the chemisorption may be any soluble salt or complex of copper or iron. Preferably, it is  
30 selected from chloride, bromide, sulfate, nitrate and acetate.

The organic solvent is preferably an aliphatic alcohol containing 1 to 3 carbon atoms, preferably methanol, or optionally its mixture with water.

The bidentate oxygen ligand is preferably a 1,3-dicarbonyl compound of a general formula  $R-C(=O)CH_2C(=O)R'$ , wherein R and R' are independently selected from the group containing methyl, ethyl, isopropyl, *tert*-butyl, phenyl, methoxy, ethoxy, and *tert*-butoxy.

- 5 The bidentate nitrogen ligand is preferably selected from the group containing 2,2'-bipyridine, 1,10-phenanthroline, *N,N,N',N'*-tetramethyl-1,2-ethylenediamine, 1,2-ethylenediamine, 1,3-propylenediamine, *N,N,N',N'*-tetramethyl-1,3-propylenediamine.

The content of the bidentate ligand in the supported catalyst is preferably 0 to 10 % by weight.

- 10 An advantage of the invention is the substitution of a homogenous catalyst with a supported heterogeneous catalytic system. Water with the addition of sulfolane used in the state-of-the-art process as the solvent was replaced in one preferred embodiment of the invention with methanol. The reaction using the supported heterogeneous catalyst is slower and it does not need cooling; the optimum temperature mode is about 50 °C.
- 15 Methanol is separated from the reaction environment after the reactor shutdown by distillation; the advantage is that it does not form an azeotrope with water, and further the fact that its boiling temperature is approximately two thirds of the boiling temperature of water, which is energetically advantageous.

- The catalyst is significantly more stable in methanol or in its mixture with water than in  
 20 water alone. Stability of the catalyst can be further supported by addition of free cation exchanger, used for the support of the catalytic system  $Fe^{m+}/Cu^{n+}$ . The bidentate ligand present helps to stabilize  $Fe^{2+}$  and  $Cu^+$  against the reduction to elementary metals during the process, which deteriorates the catalytic system, and it suppresses the possible hydrolytic oxidation of ethane dinitrile to carbon dioxide, which decreases the selectivity  
 25 of the process. The process according to the present invention does not have to use the expensive and toxic copper and iron bromides. More available and cheaper salts of copper and iron than bromides can be used for preparation of the catalyst. Cation exchanger is an industrial resin used for treatment of water, it is easily available and cheap, and it forms a highly stable complex with the copper and iron cations. Further  
 30 advantages of the solution according to the present invention are easier modification of the reaction mixture during the process, especially elimination of waste solvent from the heterogeneous system of catalyst, absence of metal ions from the catalyst in the waste

solvent, and lower energy demands on processing of the liquid mixture; see the above-mentioned advantages of methanol versus water. The reaction medium has minimum corrosive effects on the technological equipment, in particular because water is not contaminated with copper and iron ions. The system according to the invention shows a  
5 higher efficiency than the known systems used in the industry, which leads to lower consumption of the hydrogen peroxide used. Further, there is no more need for cooling the reaction mixture with an easier control of the entire process, with the possibility of regulation and automation of the process in the reactor, which on the contrary runs under a slightly increased temperature, which brings further decrease of operating and  
10 production costs. The catalytic system by its concept and the method of production of ethane dinitrile according to the present invention meets the criteria of "green chemistry" and "sustainable chemistry".

The subject-matter of the present invention is further explained using the following examples, which should not be construed as limiting the scope of the invention.

15

#### Examples of carrying out the Invention

##### Example 1

The catalyst was prepared in the following manner: 75 g of weakly acidic polyacrylate  
20 cation exchanger of macroporous type in ionized  $\text{Na}^+$  form, with the minimum total capacity of 4.5 mol / liter and powder density of 750 g / liter, was mixed in 300 ml of water, 42.5 g (250 mmol) of copper(II) chloride dihydrate and 32.4 g (120 mmol) of iron(III) chloride hexahydrate were added and the mixture was stirred for 30 min. After that, 2.5 g (25 mmol) of acetyl-acetone was added to the solution, and the mixture was  
25 stirred for further 1 h. Then the aqueous phase was removed and the solid phase was washed twice by 100 ml of water, then subsequently twice by 150 ml of methanol, and the catalyst was used into the following reaction.

In a stirred three-necked round flask provided by a condenser with a cooling medium at the temperature of approximately 15 °C and with an outlet to cryoscopic distillation,  
30 50 g of hybrid catalyst Cu(II)-Fe(III) doped with acetyl-acetone was added to 500 ml methanol. Liquid hydrogen cyanide was added to the reaction mixture with the rate of 3.5 g (130 mmol) / min for the period of 5 minutes. After that, the reaction rate of

hydrogen cyanide dosage was increased to 7 g (260 mmol) / min and 30% hydrogen peroxide started to be added dropwise at the same time with the rate of 30 g (265 mmol) / min. The entire process was running at the temperature of 50 °C for the period of 3 hours, the gaseous products, that is the ethane dinitrile, carbon dioxide and the unreacted  
5 hydrogen cyanide were led off through the condenser to the apparatus for cryoscopic fractional distillation; ethane dinitrile was purified and adjusted, hydrogen cyanide was recycled backward into the process. The composition of gases at the output from the equipment in their total volume conveyed out from the reaction vessel for the period of three hours (as monitored by the gas chromatography using the area ratio of the peaks)  
10 was: 0.7 rel % of carbon dioxide, 48.2 rel % ethane dinitrile, 37.4 rel % of unreacted hydrogen cyanide and methanol to 100 rel %.

After three hours of oxidation process, the addition of reactants and the stirring of the reaction mixture were stopped, the reaction vessel was replaced with a new one containing methanol and catalyst in the above-given amount and the entire process was  
15 repeated. The catalyst was separated by decantation and used again in the process, methanol was distilled from the mixture and recycled backward into the process, and water was processed in the wastewater sewage plant.

### Example 2

20 The catalyst was prepared in the following manner: 78 g of strongly acidic sulfonated poly(styrene-divinylbenzene) cation exchanger of macroporous type in ionized Na<sup>+</sup> form, with the minimum total capacity of 1.8 mol / liter and with the powder density 780 g / liter, was mixed in 300 ml of water, 34.0 g (200 mmol) of copper(II) chloride dihydrate and 48.6 g (180 mmol) of iron(III) chloride hexahydrate were added and the  
25 mixture was stirred for 30 min. Then the aqueous phase was poured off and the solid phase was washed twice by 100 ml of water, then subsequently twice by 150 ml of methanol, and the catalyst was used into the following reaction.

In a stirred three-necked round flask provided with a condenser with a cooling medium at the temperature of approximately 15 °C and with an outlet to cryoscopic distillation,  
30 50 g of hybrid catalyst Cu(II)-Fe(III) was added to 500 ml of methanol. Liquid hydrogen cyanide was added dropwise to the reaction compound with the rate of 3.5 g (130 mmol) / min for the period of 5 minutes. After that, the rate of hydrogen cyanide dosage was



increased to 7 g (260 mmol) / min and 30% hydrogen peroxide started to be added dropwise at the same time with the rate of 15 g (133 mmol) / min. The entire process was running at the temperature of 40 °C for the period of 5 hours, the gaseous products, that is ethane dinitrile, carbon dioxide and unreacted hydrogen cyanide, and the methanol vapors were led off through the condenser to the apparatus for cryoscopic fractional distillation; ethane dinitrile was purified and adjusted, hydrogen cyanide was recycled backward into the process. The composition of gases at the output from the equipment in their total volume conveyed out from the reaction vessel for the period of five hours (as monitored by the gas chromatography using the ratio of areas of peaks) was: 2.2 rel % of carbon dioxide, 36.9 rel % ethane dinitrile, 50.1 rel % of unreacted hydrogen cyanide and methanol to 100 rel %.

### Example 3

The catalyst was prepared in the following manner: 84 g of strongly acidic sulfonated poly(styrene-divinylbenzene) cation exchanger of a gel type in ionized Na<sup>+</sup> form, with the minimum total capacity of 2.2 mol / liter and with the powder density of 840 g / liter, was stirred with 300 ml of water, 17.0 g (100 mmol) of copper(II) chloride dihydrate and 67.5 g (250 mmol) of iron(III) chloride hexahydrate were added and the mixture was stirred for 30 min. Then the aqueous phase was poured off and the solid phase was washed twice by 100 ml of water, then subsequently twice by 150 ml of methanol, and the catalyst was used into the following reaction.

In a stirred three-necked round flask provided with a condenser with a cooling medium at the temperature of approximately 15 °C and with the outlet to cryoscopic distillation, 50 g of hybrid catalyst Cu(II)-Fe(III) was added to 500 ml of methanol. Liquid hydrogen cyanide was added dropwise to the reaction mixture with the rate of 3.5 g (130 mmol) / min for the period of 5 minutes. After that, the reaction rate of hydrogen cyanide dosage was increased to 7 g (260 mmol) / min and gaseous oxygen started to be added at the same time with the rate of 8 g (250 mmol) / min. The entire process was running at the temperature of 55 °C for the period of 24 hours, its constant volume was maintained using methanol, the gaseous products, that is the ethane dinitrile, carbon dioxide and unreacted hydrogen cyanide, and the methanol vapors were conveyed through the condenser to the apparatus for cryoscopic fractional distillation; ethane dinitrile was

purified and adjusted, hydrogen cyanide was recycled backward into the process. The composition of gases at the output from the equipment in their total volume conveyed out from the reaction vessel for the period of 24 hours (as monitored by the gas chromatography using the ratio of areas of peaks) was: 2.9 rel % of carbon dioxide, 40.2  
5 rel % ethane dinitrile, 40.8 rel % of non-reacted hydrogen cyanide and methanol to 100 rel %.

#### Example 4

The catalyst was prepared in the following manner: 84 g of strongly acidic sulfonated  
10 poly(styrene-divinylbenzene) cation exchanger of a gel type in ionized Na<sup>+</sup> form, with the minimum total capacity of 2.2 mol / liter and with the powder density of 840 g / liter, was stirred in 300 ml of water, 17.0 g (100 mmol) of copper(II) chloride dihydrate and 27.8 g (100 mmol) of iron(II) sulfate heptahydrate were added, and the mixture was stirred for 30 min. Then 1.56 g (10 mmol) of 2,2-bipyridine was added to the compound,  
15 and the compound was mixed for the period of 60 min. Then the aqueous phase was poured off and the solid phase was washed twice by 100 ml of water, then subsequently twice by 150 ml of methanol, and the catalyst was used into the following reaction.

In a stirred three-necked round flask provided by a condenser with a cooling medium at the temperature of approximately 15 °C and with the outlet to cryoscopic distillation, 50  
20 g of hybrid catalyst Cu(II)-Fe(II) doped with 2,2-dipyridine was added to 500 ml of methanol. Liquid hydrogen cyanide was added dropwise to the reaction compound with the rate of 3.5 g (130 mmol) / min for the period of 5 minutes. After that, the reaction rate of hydrogen cyanide dosage was increased to 14 g (520 mmol) / min and 30% hydrogen peroxide started to be added dropwise at the same time with the rate of 25 g  
25 (222 mmol) / min. The entire process was running at the temperature of 60 °C for the period of 4 hours, the gaseous products, that is ethane dinitrile, carbon dioxide and unreacted hydrogen cyanide, and the methanol vapors were led off through the condenser to the apparatus for cryoscopic fractional distillation; ethane dinitrile was purified and adjusted, hydrogen cyanide was recycled backward into the process. The  
30 composition of gases at the output from the equipment in their total volume conveyed out from the reaction vessel for the period of four hours (as monitored by the gas chromatography using the areas of the peaks) was: 1.1 rel % of carbon dioxide, 59.8 rel

% ethane dinitrile, 29.2 rel % of unreacted hydrogen cyanide and methanol to 100 rel % .

#### Example 5

The catalyst was prepared in the following manner: 84 g of strongly acidic sulfonated  
5 poly(styrene-divinylbenzene) cation exchanger of a gel type in ionized Na<sup>+</sup> form, with  
the minimum total capacity of 2.2 mol / liter and with powder density of 840 g / liter,  
was mixed in 300 ml of water, 25.5 g (150 mmol) of copper(II) chloride dihydrate and  
21.6 g (80 mmol) of iron(III) chloride hexahydrate were added, and the mixture was  
stirred for 30 min, then dipivaloylmethane (1.84 g, 10 mmol) was added to the mixture,  
10 and the mixture was stirred for another 60 min. Then the aqueous phase was poured off  
and the solid phase was washed twice by 100 ml of water, then subsequently twice by  
150 ml of methanol, and the catalyst was used into the following reaction.

In a stirred three-necked round flask provided by a condenser with a cooling medium at  
the temperature of approximately 15 °C and with the outlet to cryoscopic distillation, 50  
15 g of hybrid catalyst Cu(II)-Fe(III) was added into 500 ml of methanol. Liquid hydrogen  
cyanide was added dropwise to the reaction compound with the rate of 3.5 g (130 mmol)  
/ min for the period of 5 minutes. After that, the rate of hydrogen cyanide dosage was  
increased to 7 g (260 mmol) / min and 30% hydrogen peroxide started to be added  
dropwise at the same time with the rate of 15.0 g (222 mmol) / min. The entire process  
20 was running at the temperature of 50 °C for the period of 5 hours, the gaseous products,  
that is ethane dinitrile, carbon dioxide and unreacted hydrogen cyanide, and methanol  
vapors were conveyed through the condenser to the apparatus for cryoscopic fractional  
distillation; ethane dinitrile was purified and adjusted, hydrogen cyanide was recycled  
backward into the process. The composition of gases at the output from the equipment in  
25 their total volume conveyed out from the reaction vessel for the period of five hours (as  
monitored by the gas chromatography using the ratio of areas of peaks) was: 0.7 rel % of  
carbon dioxide, 75.8 rel % ethane dinitrile, 10.8 rel % of unreacted hydrogen cyanide  
and methanol to 100 rel % .

## CLAIMS

1. A method of production of ethane dinitrile  $(\text{CN})_2$  by oxidation of hydrogen cyanide HCN, wherein hydrogen cyanide is oxidized on a catalytic system  $\text{Fe}^{m+}/\text{Cu}^{n+}$ , wherein  $m$  has the value of 2 or 3,  $n$  has the value of 1 or 2, **characterized in that** the catalytic system is supported on a polymeric organic cation exchanger, **and in that** the oxidation reaction is carried out in an organic solvent, or in a homogeneous or heterogeneous mixture of an organic solvent with water, at the temperature in the range of 5 °C to 65 °C, using an oxygen-containing oxidizing agent selected from the group containing oxygen, air, hydrogen peroxide or its mono- or di-substituted alkyl or acyl derivatives selected from the group including *tert*-butyl hydroperoxide, benzoyl hydroperoxide, dibenzoyl peroxide, di-*ter*/-butyl peroxide, di-(2-ethylhexyl) peroxydicarbonate.
2. The method according to claim 1, wherein the oxidizing agent is hydrogen peroxide in the concentration in the range of 3 to 40 % by weight, preferably in the molar ratio of hydrogen peroxide to hydrogen cyanide in the range of 1 : 3 to 3 : 1.
3. The method according to claim 2, wherein hydrogen peroxide to hydrogen cyanide in the molar ratio in the range of 1 : 3 to 3 : 1 are continuously added to the catalytic system in the reaction mixture, the products are then conveyed from the reaction zone to further processing, and the unreacted hydrogen cyanide is recycled.
4. The method according to any of the preceding claims, wherein liquid hydrogen cyanide is used.
5. The method according to any of the preceding claims, wherein the molar ratio of the ions  $\text{Fe}^{m+} : \text{Cu}^{n+}$  supported on the cation exchanger is in the range of 1 : 4 to 4 : 1.
6. The method according to any of the preceding claims, wherein the polymeric organic cation exchanger used for the support of the catalytic system  $\text{Fe}^{m+}/\text{Cu}^{n+}$  is an organic synthetic polymer, co-polymer, or an organic polycondensate bearing functional groups

selected from the group comprising  $-SO_3H$ ,  $-O-SO_3H$ ,  $-P(O)(OH)_2$ ,  $-P(O)H(OH)$ ,  $-O-P(O)(OH)_2$ ,  $-COOH$ ,  $-alkyl-COOH$ ,  $-aryl-COOH$ ,  $-aryl-OH$ .

7. The method according to any of the preceding claims, wherein the polymeric organic  
5 cation exchanger used for the support of the catalytic system  $Fe^{m+}/Cu^{n+}$  is a polyacrylate or polymethacrylate weakly acidic cation exchanger, or a strongly acidic cation exchanger on the basis of sulfonated copolymer of styrene and divinylbenzene, in a gel or macroporous form.

10 8. The method according to any of the preceding claims, wherein the organic solvent is an aliphatic alcohol containing 1 to 3 carbon atoms, preferably methanol, or optionally its mixture with water.

9. The method according to any of the preceding claims, wherein in the catalyst, a  
15 bidentate oxygen or nitrogen ligand is comprised, preferably in an amount of up to 10 % by weight.

10. The method according to claim 9, wherein the bidentate nitrogen or oxygen ligand is  
selected from a group comprising 2,2'-bipyridine, 1,10-phenanthroline,  $N,N,N',N'$ -  
20 tetramethyl-1,2-ethylenediamine, 1,2-ethylenediamine, 1,3-propylenediamine,  $N,N,N',N'$ -tetramethyl-1,3-propylenediamine, and a 1,3-dicarbonyl compound of a general formula  $R-C(=O)CH_2C(=O)R'$ , wherein R and R' are independently selected from the group containing methyl, ethyl, isopropyl, *tert*-butyl, phenyl, methoxy, ethoxy, and *ter*-butyloxy.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/CZ2012/000131

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C01C3/00 B01J31/08 B01J31/10  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C01C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal , WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 003 983 A (HEILOS JOHANNES ET AL) 18 January 1977 (1977-01-18) cited in the application the whole document -----	1-10
A	US 2008/041794 AI (SHAH VISHAL [US]) 21 February 2008 (2008-02-21) paragraphs [0019] , [0022] -----	1,6,7
A	US 4 046 862 A (HEIMBERGER WERNER ET AL) 6 September 1977 (1977-09-06) claims 1, 11, 12, 20, 21 -----	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

26 April 2013

Date of mailing of the international search report

08/05/2013

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/CZ2012/000131

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4003983	A	18-01-1977	NONE	
-----				
US 2008041794	AI	21-02-2008	AU 2007284367 AI	21-02-2008
			CA 2660982 AI	21-02-2008
			EP 2059483 A2	20-05-2009
			US 2008041794 AI	21-02-2008
			WO 2008021562 A2	21-02-2008
-----				
US 4046862	A	06-09-1977	AR 215438 AI	15-10-1979
			CH 602487 A5	31-07-1978
			DD 124591 A5	02-03-1977
			GB 1525343 A	20-09-1978
			IL 49545 A	31-01-1979
			SE 415175 B	15-09-1980
			SE 7605427 A	13-11-1976
			US 4046862 A	06-09-1977
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