

Chemical process

The subject of the present invention is a new process for the removal of azide ions from aqueous liquids, first of all from waste waters.

- 5 Azides, *e.g.* sodium azide, potassium azide are frequently used in chemical syntheses. A synthesis of this type is for example described in patent US-5629331 and patent application WO-2006/023889, where a tetrazole ring is built by applying sodium azide in aqueous alkaline solution.

The azide ions remain in the aqueous phase of the reaction mixtures in considerable
10 concentration. When these aqueous phases are treated as waste waters, it is of major importance that the azide ion concentration is decreased to very low level, since the azide ions in aqueous solutions are toxic, even at a concentration of 50 mg/l.

Consequently, there is a considerable need for processes suitable to remove the azide ions from aqueous alkaline solutions, first of all from waste waters.

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We have found that by treating the azide ion-containing aqueous liquids at alkaline pH with one or more metals soluble under alkaline conditions in the presence of nickel catalyst, or with hydrogen in the presence of nickel catalyst, then the azide ions present in the solution are reduced by the resulting hydrogen, giving rise to
20 ammonia and nitrogen during the formation of hydroxide ions.

The equation is the following:



In this way the toxic azide ions can be removed from aqueous liquids, first of all from waste waters.

In the process according to the invention as for alkali-soluble metal we use *e.g.* aluminium or zinc, and as catalyst we use nickel. Preferably the alloy or the mixture of these metals is used, their ratio and the particle distribution is deliberate. In general, metal powders with fine particles are favorable (*e.g.* Raney-nickel). If the
5 pH of the azide-containing liquid is not alkaline, it has to be set to alkaline with bases, preferably with inorganic bases, *e.g.* sodium hydroxide or potassium hydroxide.

The process is performed at a temperature lower than the boiling point of the liquid to be purified, preferably between +5 °C and +40 °C. A preferred embodiment of
10 the process is the catalytic reaction under hydrogen atmosphere in the presence of nickel. The applied pressure is preferably between the atmospheric pressure and 60 bar.

The process according to the invention can be used very efficiently for the removal of azide-ions from alkaline or alkalinized waste-waters, ensuring an environment-
15 friendly purification process, since it results only well-recoverable metal ions, nitrogen gas and ammonia, which are easily treatable products. The process can be used in large scale. The applied metals can also be wastes or by-products of metal processing or metallurgy (powders, chip or cast scrap).

By the process according to the invention the azide-ion concentration can be
20 decreased to below 5 ppm. When implementing the process according to the invention, the azide-ion concentration was determined by the ion-chromatographic analytical method described here below. By this method we were able to follow the decrease of the azide-ion concentration in various waste waters.

Sample preparation

Before the measurement the sample to be investigated was diluted with 0.1 N sodium hydroxide solution to 50-fold of its volume, because of the expected high organic material concentration and high azide level.

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Conditions of the measurement

Investigated component: azide content

Instrument: DIONEX 600-type ion-chromatographic system with conductometric detector

10 Column: IONPAC AS 10. 250 mm long, 4 mm inner diameter, ethyl-vinyl-benzene / divinyl-benzene anion exchanger

Pre-column: IONPAC AG 10 DIONEX

Eluent: 0.1 N sodium hydroxide solution

Flow rate: 1.0 ml / min

15 Neutralization of the eluent: with self-regenerating „Anion Self Regenerating Suppressor”

Injected volume: 25 µl

By this method we were able to determine the azide ion concentration from a level of 5 ppm.

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Further details of the invention are demonstrated by the examples below, without limiting the claims to the examples.

Examples

Example 1

15 g of the alloy powder containing 50 mass % of nickel and 50 mass % of aluminium (particle size less than 100 micrometer) were weighed. 600 g of 27 mass % of aqueous sodium hydroxide solution containing azide-ions in 9000 ppm concentration (obtained in the reaction described in Example 1., step a.) of patent description US 5629331) were weighed into an Erlenmeyer flask and placed in cold water bath. To this solution 15 g of alloy powder were added in small portions, during 4 h, under continuous stirring, while keeping the temperature of the mixture at 20 °C. After the addition the mixture was stirred at 20 °C for an additional 5 h. By the end of this reaction time the gas evolution ceased.

The azide-ion concentration of the resulting aqueous solution was < 5 ppm, as determined by the above ion-chromatographic method.

15 Example 2

10 g of aluminium powder and 0.2 g of nickel-aluminium alloy powder (with 50 mass % of nickel and 50 mass % of aluminium content, particle size less than 100 micrometer) were weighed. 600 g of 27 mass % of aqueous sodium hydroxide solution containing azide-ions in 9000 ppm concentration (US Patent US-5629331, Example 1) were weighed into an Erlenmeyer flask and placed in cold water bath and stirred. To this solution under continuous stirring mixture of the metal powders was added in small portions during 4 h, while keeping the temperature of the mixture at 20 °C. After the addition the mixture was stirred at 20 °C for additional 2 hours. Then 3 g of the 50 mass % of nickel - 50 mass % of aluminium alloy powder

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were added to the alkaline solution, during 4 hours, and after the addition stirring was continued for 3 hours.

The azide-ion concentration of the resulting aqueous solution was < 5 ppm, as determined by the above ion-chromatographic method.

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Example 3

Into a 250 cm³ acid-resistant steel autoclave, equipped with magnetic stirrer, 0.5 g of Raney-nickel catalyst and 40 g of aqueous-alkaline solution of 7000 ppm azide-ion concentration (Patent US-5629331, Example 1.) (NaOH content 20 mass %) were placed. The container was flushed with nitrogen, then 3-times with hydrogen, filled with hydrogen to 50 bar pressure and stirred for 5 hours. After stopping the stirrer and release of the pressure, the reaction mixture was sedimented and decanted. The azide-ion concentration of the resulting aqueous solution was < 10 ppm, as determined by the above ion-chromatographic method.

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Example 4

Into a 850 cm³ acid-resistant steel autoclave, equipped with magnetic stirrer, 4 g of Raney-nickel catalyst and 100 g of aqueous NaOH solution of 20 mass % were placed. The container was flushed with nitrogen, then 3-times with hydrogen. The autoclave was closed, filled with hydrogen to 10 bar pressure. With the help of a feeding pump a solution containing 1500 ppm azide ion and 25 mass % of sodium hydroxide (Patent US-5629331, Example 1.) was added with a speed of 250 g/h.

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Samples were taken from the reaction mixture hourly, and the azide ion content was determined. After 3 hours the azide-ion concentration of the sample was < 10 ppm, as determined by the above ion-chromatographic method.

Claims

1. A process for the removal of azide ions from aqueous liquids, characterized in that, the azide ion containing liquid is treated at alkaline pH a.) with one or
5 more alkali-soluble metals and catalyst, or b.) with hydrogen and catalyst.
2. A process as defined in Claim 1, characterized in that, for alkali-soluble metals aluminium and zinc are applied.
- 10 3. A process as defined in Claim 1, characterized in that, nickel is applied as alkali-soluble metal.
4. A process as defined in Claim 1, characterized in that, the azide ion containing liquid is alkalized by addition of an inorganic base.
- 15 5. A process as defined in Claim 1, characterized in that, the applied azide-ion containing liquid has alkaline pH.
6. A process as defined in Claim 1, characterized in that, for a mixture of the
20 alkali-soluble metal catalysts, aluminium-nickel mixture or aluminium-nickel alloy is applied.
7. A process as defined in Claim 1, characterized in that, the reaction is carried out at a temperature between +5 °C and +40 °C.

8. A process as defined in Claim 1, characterized in that, the azide-ion containing liquid is an aqueous solution.
- 5 9. A process as defined in Claim 4, characterized in that, sodium hydroxide is applied as inorganic base.
- 10 10. A process as defined in Claim 1, characterized in that, the reaction is carried out under hydrogen atmosphere where hydrogen is formed during the dissolution of a metal.
11. A process as defined in Claim 1, characterized in that, the reaction is carried out at a pressure between atmospheric pressure and 60 bar, under hydrogen atmosphere.
- 15 12. A process as defined in Claim 1, characterized in that, a liquid containing more than 90 mass % of water is treated at alkaline pH with one or more alkali-soluble metals and catalysts.

INTERNATIONAL SEARCH REPORT

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International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

INV. C02F1/70

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)

C02F

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 024 860 A (CASH PETER PHILIP [US] ET AL) 15 February 2000 (2000-02-15) column 1, lines 7-11,15-32 column 2, line 64 - column 3, line 15 column 3, lines 40-44,60,61,66,67 column 4, lines 1,2,15-21,26-28,39-43 column 5, lines 10-31 claims 1,11,14	1-12
A	US 5 073 273 A (GUPTA RAJ K [US] ET AL) 17 December 1991 (1991-12-17) column 1, lines 6-9,33-45 column 2, lines 5-15,47-52 column 3, lines 28-37,46-52 column 3, line 64 - column 4, line 6 column 4, lines 21-29 claims 1,7	1-12
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

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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

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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* & * document member of the same patent family

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rozanska, Agnieszka

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 457 265 A (HEUBNER ARNULF [DE] ET AL) 10 October 1995 (1995-10-10) column 1, lines 4-8, 34-37, 61-65 claim 1 -----	1-12
A	US 4 004 994 A (ANDRUS JOSEPH M) 25 January 1977 (1977-01-25) the whole document -----	1-12
A	US 4 236 982 A (POLSON JACK R) 2 December 1980 (1980-12-02) the whole document -----	1-12
A	GB 2 332 210 A (TOKYO SHIBAURA ELECTRIC CO [JP]) 16 June 1999 (1999-06-16) the whole document -----	1-12