

PROCESS FOR FILTERING A THREE-PHASE REACTION MIXTURE

The present invention relates to a process for filtering a three-phase reaction mixture comprising a liquid phase, a non-dissolved solid catalytic phase
5 and a gaseous phase.

In processes using a compound comprising at least one nitrile function and a non-dissolved catalyst of Raney nickel or cobalt type, it has been observed that in the absence of gas, and more particularly in
10 the absence of hydrogen, the nitrile functions of the medium have a harmful influence on the activity of the catalyst.

Thus, in particular in the processes for the hydrogenation of nitriles into amines, and even more
15 particularly in processes for the partial hydrogenation of a dinitrile into aminonitrile, the Applicant has demonstrated that the catalyst of Raney nickel or cobalt type has a tendency to become deactivated in the presence of nitrile functions, when the medium no
20 longer or only sparingly contains hydrogen.

Moreover, it turns out that metal catalysts deposited on a support, which are also used, in particular in hydrogenation processes, separate out poorly by settling and are difficult to filter.

25 The present invention proposes a solution to these problems, which consists in tangentially filtering, on a membrane filter, at least some of a three-phase reaction mixture comprising a liquid phase

in which nitrile functions are found, a gaseous phase comprising hydrogen and a catalytic solid phase comprising Raney nickel and/or cobalt or a supported metal catalyst, and in recycling the catalyst while at the same time recovering at least some of the filtrate containing the reaction products.

The tangential circulation, relative to the membrane and at high speed, of the mixture to be filtered minimizes the amount of solid retained on the filter. It is thus possible to minimize the risks of deactivation of the catalyst. It allows continuous filtration while at the same time keeping the catalyst in its reaction medium.

Generally, the circulation speed of the reaction mixture through the membrane is between 0.5 metre/second and 20 metres/second and preferably between 1 metre/second and 10 metres/second.

The membrane filters used for the tangential filtration generally consist of a flat or tubular support and an inorganic or organic membrane, often referred to as the active layer, which is a few micrometres in thickness.

For the process of the invention, the membranes used will preferably be inorganic membranes which generally behave better chemically and thermally with respect to the reaction mixture used.

The support and the active layer can be made of the same material or of different materials. The

active layer of the filter can be made, for example, of α -alumina, zirconium oxide, titanium dioxide or graphite fibres. The support can also be made of alumina, graphite, zirconium oxide or titanium dioxide.

5 The membrane is also characterized by its mean pore diameter. Generally, this mean pore diameter ranges between 1 nanometre and one micrometre.

 For reasons of lifetime and regenerability of the membrane, it is preferred in the present process to
10 use ultrafiltration membranes which have a mean pore diameter of from 10 nanometres to 100 nanometres and a cutoff threshold (which is defined by the molecular mass of the compounds stopped by the membrane and is expressed in grams/mole or daltons) of greater than or
15 equal to 5 kilodaltons (kD) and preferably greater than or equal to 100 kilodaltons.

 The liquid phase of the reaction mixture to be filtered essentially comprises at least one compound containing nitrile functions, such as the unconverted
20 starting dinitrile or nitrile, the aminonitrile and/or the amine and/or the diamine formed, and an optional solvent which can be, in particular, water and/or an amide and/or an alcohol and/or an amine and/or ammonia. The alcohols usually used are alkanols such as
25 methanol, ethanol, 1-propanol, 2-propanol and 1-butanol, diols such as ethylene glycol and propylene glycol, polyols or mixtures of the said alcohols. When the solvent is an amide, use may be made in particular

of dimethylformamide and dimethylacetamide. Among the amines which can be used as solvent, mention may be made, for example, of the amine, the diamine or the aminonitrile corresponding to the nitrile or the dinitrile which is hydrogenated. The liquid phase also generally comprises a strong inorganic base derived from an alkali metal or alkaline-earth metal.

When water is present with another solvent, the said solvent represents, on a weight basis, from two to four times the weight of water.

The solid catalytic phase generally consists of a catalyst based on Raney nickel and/or Raney cobalt, optionally, but preferably, comprising a doping element chosen from the elements from Groups IVb, VIb, VIIb and VIII of the Periodic Table of the Elements as published in the Handbook of Chemistry and Physics, 51st edition (1970-1971).

The catalyst based on Raney nickel and/or Raney cobalt used in the process can thus comprise, besides nickel or cobalt and the residual amounts of the metal eliminated from the original alloy during the preparation of the catalyst, i.e., generally, aluminium, one or more other doping elements, such as, for example, chromium, titanium, molybdenum, tungsten, iron or zinc.

Among these doping elements, chromium and/or iron and/or titanium are considered as the most advantageous. These doping elements usually represent,

on a weight basis relative to the weight of nickel, from 0% to 15% and preferably from 0% to 10%.

The catalytic phase can also consist of a metal, which is generally a metal from Group VIII of the Periodic Table of the Elements, such as ruthenium, rhodium, nickel or cobalt, deposited on a support which is generally a metal oxide, such as aluminas, silicas, aluminosilicates, titanium dioxide, zirconium oxide or magnesium oxide.

In the supported metal catalysts, the metal generally represents from 0.1 to 80% of the weight of the support, and preferably from 0.5 to 50%.

The solid phase generally represents from 1% to 50% by weight relative to the weight of the liquid phase, without these values being critical.

The gaseous phase consists essentially of hydrogen.

The tangential filtration can be carried out at a temperature which is advantageously that at which the hydrogenation reaction is carried out. This temperature is usually less than or equal to 150°C, preferably less than or equal to 120°C and even more preferably less than or equal to 100°C.

In concrete terms, this temperature is usually between room temperature (about 20°C) and 100°C. The process can be performed, without any technical difficulties, at a temperature below 20°C, but there is no advantage in doing so on account of the

lower production efficiency of the hydrogenation reaction.

The pressure difference between the filter inlet and outlet, which is required for the filtration, can be provided in part by the pressure at which the hydrogenation reaction is carried out. However, it is necessary to create a pressure greater than atmospheric pressure. Generally, this pressure is between 1 bar (0.10 MPa) and 20 bar (1 MPa) and preferably between 2 bar (0.5 MPa) and 10 bar (5 MPa). In practice, the pressure is created by a pump which feeds the membrane filter from the reactor.

The flow feeding the membrane filter obviously depends on the amount of reaction mixture present in the reactor, as well as the capacity of the filter. It is also determined according to the reaction progress, such that the liquid filtrate or permeate, which will be at least partially recovered and treated elsewhere, contains sufficient amounts of the intended product(s) of the hydrogenation reaction.

The catalyst filtered in the presence of hydrogen remains active and is recycled into the hydrogenation reaction.

The example which follows illustrates the invention.

EXAMPLE

A reactor fitted with a stirrer, means for heating and cooling, means for introducing reagents at

its top part and removal means at its bottom part, contains about 20 litres of a mixture composed, on a weight basis, of:

- 20.1% adiponitrile
- 5 - 51.4% aminocapronitrile
- 9.1% hexamethylenediamine
- 14.2% water
- 5.2% Raney nickel with a mean particle size of about 10 micrometres.

10 This solution is at a hydrogen pressure of 2 bar and at a temperature of 55°C.

A volumetric pump with a flow rate of 2 m³/h is placed at the removal outlet located at the bottom of the reactor, followed by an electromagnetic flow meter and a manometer. The solution removed from the reactor feeds a membrane filter consisting of a graphite support and an inorganic active layer of zirconium oxide with a cutoff threshold of 300 kD and a mean pore diameter of between 25 and 50 nm (trade name Carbosep M9 from the company Tech-Sep).

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The filter-feed flow is placed under a hydrogen pressure of 2 bar and the circulation speed of the reaction mixture through the membrane is about 5 m/s.

25 The flow of permeate is 67 kg/h.m². The permeate is at atmospheric pressure.

No Raney nickel is found in the permeate.

The retentate containing the catalyst is

recycled into the reactor.

Under these conditions, the concentration of catalyst in the retentate is constant and also at its initial value.



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CLAIMS

1. Filtration process, characterized in that a tangential filtration is carried out, on a membrane filter, of at least some of a three-phase
5 reaction mixture comprising a liquid phase in which nitrile functions are found, a gaseous phase comprising hydrogen and a catalytic solid phase comprising Raney nickel and/or cobalt or a supported metal catalyst, and
10 process for recycling the catalyst while at the same time recovering at least some of the filtrate containing the reaction products.

2. Process according to Claim 1, characterized in that the membrane filter used for the tangential filtration consists of a flat or tubular
15 support and of an inorganic or organic membrane (or active layer) which is a few micrometres in thickness.

3. Process according to Claim 2, characterized in that the active layer of the filter is made of α -alumina, zirconium oxide, titanium dioxide or
20 graphite fibres and the support is made of graphite, alumina, zirconium oxide or titanium dioxide.

4. Process according to either of Claims 2 and 3, characterized in that the membrane has a mean pore diameter ranging between 1 nanometre and one
25 micrometre and preferably a mean pore diameter of from 10 nanometres to 100 nanometres.

5. Process according to one of Claims 1 to 4, characterized in that the liquid phase of the

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reaction mixture to be filtered essentially comprises
at least one compound containing nitrile functions,
such as the unconverted starting dinitrile or nitrile,
the aminonitrile and/or the amine and/or the diamine
5 formed, and an optional solvent.

6. Process according to Claim 5,
characterized in that the solvent is chosen from water
and/or an amide and/or an alcohol and/or an amine
and/or ammonia.

10 7. Process according to one of Claims 1 to
6, characterized in that the solid catalytic phase
consists of a catalyst based on Raney nickel and/or
Raney cobalt, preferably comprising a doping element
chosen from the elements from Groups IVb, VIb, VIIb and
15 VIII of the Periodic Table of the Elements as published
in the Handbook of Chemistry and Physics, 51st edition
(1970-1971).

8. Process according to one of Claims 1 to
6, characterized in that the solid catalytic phase
20 consists of a metal, which is a metal from Group VIII
of the Periodic Table of the Elements, such as
ruthenium, rhodium, nickel or cobalt, deposited on a
support which is a metal oxide, such as aluminas,
silicas, aluminosilicates, titanium dioxide, zirconium
25 oxide or magnesium oxide.

9. Process according to one of Claims 1 to
8, characterized in that the tangential filtration is
carried out at a temperature which is less than or





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equal to 150°C, preferably less than or equal to 120°C
and even more preferably less than or equal to 100°C.

10. Process according to one of Claims 1 to
9, characterized in that the pressure difference
5 between the filter inlet and outlet is between 1 bar
(0.10 MPa) and 20 bar (1 MPa) and preferably between
2 bar (0.5 MPa) and 10 bar (5 MPa).

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<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(21) International application number: PCT/FR97/00937</p> <p>(22) International filing date: 29 May 1997 (29.05.97)</p> <p>(30) Data relating to the priority: 96/07,169 4 June 1996 (04.06.96) FR</p> <p>(71) Applicant (for all designated States except US): RHÔNE-POULENC FIBER AND RESIN INTERMEDIATES <i>retu</i> [FR/FR]: 25, quai Paul Doumer, F-92408 Courbevoie Cedex (FR). <i>Lyon X</i></p> <p>(72) Inventors: and</p> <p>(75) Inventors/Applicants (US only): Philippe PERRONA [FR/FR]: 275, rue de la Fabrique, F-01120 Montluel (FR). Lionel SEVER [FR/FR]: 113, rue Jean Vallier, F-69007 Lyon (FR).</p> <p>(74) Representative: Noël VIGNALLY; Rhône-Poulenc Chimie, Industrial Property Directorate, C.R.I.T. - Carrières, P.O. Box 62, F-69192 Saint-Fons Cedex (FR).</p> </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(81) Designated States: BR, BY, CA, CN, CZ, JP, KR, MX, PL, RO, RU, <u>SG</u>, SK, UA, US, VN, European Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With the International Search Report.</p> <p><i>PC/18/306</i></p> </td> </tr> </table>			<p>(21) International application number: PCT/FR97/00937</p> <p>(22) International filing date: 29 May 1997 (29.05.97)</p> <p>(30) Data relating to the priority: 96/07,169 4 June 1996 (04.06.96) FR</p> <p>(71) Applicant (for all designated States except US): RHÔNE-POULENC FIBER AND RESIN INTERMEDIATES <i>retu</i> [FR/FR]: 25, quai Paul Doumer, F-92408 Courbevoie Cedex (FR). <i>Lyon X</i></p> <p>(72) Inventors: and</p> <p>(75) Inventors/Applicants (US only): Philippe PERRONA [FR/FR]: 275, rue de la Fabrique, F-01120 Montluel (FR). Lionel SEVER [FR/FR]: 113, rue Jean Vallier, F-69007 Lyon (FR).</p> <p>(74) Representative: Noël VIGNALLY; Rhône-Poulenc Chimie, Industrial Property Directorate, C.R.I.T. - Carrières, P.O. Box 62, F-69192 Saint-Fons Cedex (FR).</p>	<p>(81) Designated States: BR, BY, CA, CN, CZ, JP, KR, MX, PL, RO, RU, <u>SG</u>, SK, UA, US, VN, European Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With the International Search Report.</p> <p><i>PC/18/306</i></p>
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As printed

(54) Title: METHOD FOR ~~FILTERING A THREE-PHASED REACTION MIXTURE~~

(54) Titre: PROCEDE DE FILTRATION D'UN MELANGE REACTIONNEL TRIPHASIQUE

(57) Abstract

The invention discloses a method for filtering a three-phased reaction mixture, comprising a liquid phase, an undissolved solid catalytic phase and a gas phase. More precisely it consists tangentially in filtering on one membrane filter at least one part of a three-phased reaction mixture comprising one liquid phase in which are found nitrile functions, one gas phase comprising hydrogen and one solid catalytic phase comprising nickel and/or Raney cobalt, or a supported metal catalyst, in recycling the catalyst while recuperating at least one part of the filtrate comprising the reaction products.

(57) Abrégé

La présente invention concerne un procédé de filtration d'un mélange réactionnel triphasique, comportant une phase liquide, une phase catalytique solide non dissoute et une phase gazeuse. Plus précisément elle consiste à filtrer tangentiellement sur un filtre à membrane au moins une partie d'un mélange réactionnel triphasique comportant une phase liquide dans laquelle se trouvent des fonctions nitrile, une phase gazeuse comprenant de l'hydrogène et une phase solide catalytique comprenant du nickel et/ou du cobalt de Raney, ou un catalyseur métallique supporté, à recycler le catalyseur tout en récupérant au moins une partie du filtrat contenant les produits de la réaction.

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CLAIMS

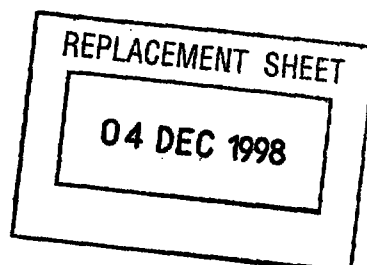
1. Filtration process, characterized in that a tangential filtration is carried out, on a membrane filter, of at least some of a three-phase
5 reaction mixture comprising a liquid phase in which nitrile functions are found, a gaseous phase comprising hydrogen and a catalytic solid phase comprising Raney nickel and/or cobalt or a supported metal catalyst, and process for recycling the catalyst while at the same
10 time recovering at least some of the filtrate containing the reaction products.

2. Process according to Claim 1, characterized in that the membrane filter used for the tangential filtration consists of a flat or tubular
15 support and of an inorganic or organic membrane (or active layer) which is a few micrometres in thickness.

3. Process according to Claim 2, characterized in that the active layer of the filter is made of α -alumina, zirconium oxide, titanium dioxide or
20 graphite fibres and the support is made of graphite, alumina, zirconium oxide or titanium dioxide.

4. Process according to either of Claims 2 and 3, characterized in that the membrane has a mean pore diameter ranging between 1 nanometre and one
25 micrometre and preferably a mean pore diameter of from 10 nanometres to 100 nanometres.

5. Process according to one of Claims 1 to



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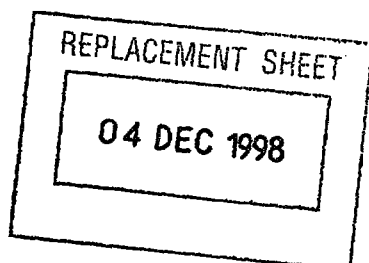
4, characterized in that the liquid phase of the reaction mixture to be filtered essentially comprises at least one compound containing nitrile functions, such as the unconverted starting dinitrile or nitrile, the aminonitrile and/or the amine and/or the diamine formed, and an optional solvent.

6. Process according to Claim 5, characterized in that the solvent is chosen from water and/or an amide and/or an alcohol and/or an amine and/or ammonia.

7. Process according to one of Claims 1 to 6, characterized in that the solid catalytic phase consists of a catalyst based on Raney nickel and/or Raney cobalt, preferably comprising a doping element chosen from the elements from Groups IVb, VIb, VIIb and VIII of the Periodic Table of the Elements as published in the Handbook of Chemistry and Physics, 51st edition (1970-1971).

8. Process according to one of Claims 1 to 6, characterized in that the solid catalytic phase consists of a metal, which is a metal from Group VIII of the Periodic Table of the Elements, such as ruthenium, rhodium, nickel or cobalt, deposited on a support which is a metal oxide, such as aluminas, silicas, aluminosilicates, titanium dioxide, zirconium oxide or magnesium oxide.

9. Process according to one of Claims 1 to

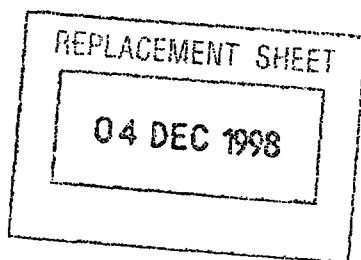


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8, characterized in that the tangential filtration is carried out at a temperature which is less than or equal to 150°C, preferably less than or equal to 120°C and even more preferably less than or equal to 100°C.

- 5 10. Process according to one of Claims 1 to 9, characterized in that the pressure difference between the filter inlet and outlet is between 1 bar (0.10 MPa) and 20 bar (1 MPa) and preferably between 2 bar (0.5 MPa) and 10 bar (5 MPa).



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