Convention Application for a Patent

11 035/76

We hereby apply for the grant of a Patent for an invention entitled

"REACTION SOLUTIONS FOR HYDRATION OF ACRYLONITRILE"

which is described in the accompanying complete specification. This application is a Convention Application and is based on the application numbered 558,999 for a patent or similar protection made in United States of America on March 17, 1975

My address for service is:

Care: SPRUSON & FERGUSON
PATENT ATTORNEYS
ESSO
GASTON HOUSE, 127 KENT STREET
SYDNEY, NEW SOUTH WALES,
AUSTRALIA.

Dated this 11 January 1976
The Common Seal of
AMERICAN CYANAMID
COMPANY was hereto
affixed in the presence of:

day of January 1976
AMERICAN CYANAMID COMPANY
BY: John J. Hagan, Manager
Patent Law Department
Signature of Applicant.

To:
The Commissioner of Patents
Commonwealth of Australia
DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT OR PATENT
OF ADDITION

In support of the Convention Application made for a

patent for an invention entitled

"REACTANT SOLUTIONS FOR HYDRATION OF ACRYLONITRILE"

Full name and address of Declarant.

1. JOHN J. HAGAN
63 Westcott Road, Stamford, State of Connecticut, of United States of America

do solemnly and sincerely declare as follows:—

1. I am the applicant for the patent of addition
(or, in the case of an application by a body corporate)

1. I am authorised by AMERICAN CYANAMID COMPANY
the applicant for the patent of addition to make this declaration on its behalf.

The basic application as defined by Section 141 of the Act was made in
United States of America on the 17th day of March 1975 by KEN MATSUDA
and KIN HSUEH-YUAN TSU,

3. I am the actual inventor of the invention referred to in the basic application
(or where a person other than the inventor is the applicant)

5. KEN MATSUDA and KIN HSUEH-YUAN TSU, citizens of the
United States of America,
of 29 Lancer Lane, Stamford; and 120 Perry Avenue, Norwalk, State of Connecticut, United States of America respectively

are the actual inventors of the invention and the facts upon which the Company is entitled to make the application are as follows: an Assignment dated May 13, 1975 assigning said invention from said inventors to the said Company.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

Declared at Stamford, this 13 day of January 1976
AMERICAN CYANAMID COMPANY

By: John J. Hagan, Manager
Patent Law Department

To: The Commissioner of Patents,
Commonwealth of Australia.

SPRUON & FERGUSON, SYDNEY
CLAIM 1. In the catalytic hydration of acrylonitrile to produce acrylamide wherein an aqueous feed solution of acrylonitrile is contacted in a reactor with a solid heterogeneous catalyst for the hydration reaction, the improvement wherein the solubility of acrylonitrile in said aqueous feed solution is increased by addition of acrylamide as a cosolvent in said feed solution and acrylonitrile is dissolved in said feed solution containing the acrylamide cosolvent in an amount to make an enriched feed solution having acrylonitrile concentration higher than the saturation concentration of acrylonitrile in water without a cosolvent.
The following statement is a full description of this invention, including the best method of performing it known to me/us:
The invention relates to catalytic hydration of acrylonitrile to produce acrylamide.

It is known that acrylonitrile will react with water in contact with any of several solid heterogeneous catalysts to produce acrylamide in very good yield. The selectivity of conversion to acrylamide is near 100% when certain catalysts are used. A variety of solid heterogeneous catalysts for hydration of nitriles have been described, such as manganese dioxide, copper oxide, copper chromium oxide, copper catalysts prepared by reduction of several copper compounds, Raney copper, copper metal in combination with cupric or cuprous ion, and the like.

The present invention relates particularly to continuous acrylonitrile hydration reactions in which a solution of acrylonitrile in water is contacted with a
1 solid heterogeneous catalyst in a continuous catalytic reactor. The catalyst is preferably situated in the reactor as a fixed bed but may be in a fluidized bed, or may be dispersed as a slurry in a stirred continuous reactor. The reactant mixture of water and acrylonitrile is usually fed to the reactor in a single feed stream and it is much preferred to feed the reactants as a homogeneous solution of acrylonitrile in water. A disadvantage is that acrylonitrile is only sparingly soluble in water, e.g. 7-1/2% at 25°C., 9% at 60°C., and 12-1/2% at 90°C. Consequently, the product stream from the reactor is a dilute acrylamide aqueous solution.

It was noticed that acrylamide present in the aqueous acrylamide solution acts as a cosolvent which increases the solubility of acrylonitrile. According to the invention the feed solution to a catalytic reactor for hydration of acrylonitrile contains acrylonitrile dissolved to a concentration that is higher than the saturation concentration of acrylonitrile in water alone, by means of acrylamide cosolvent in the solution.

As the acrylamide concentration is increased, in the solvent, the solubility of acrylonitrile is also increased. However, because the presence of acrylamide in the reactor inhibits the conversion of acrylonitrile to acrylamide, there is a practical limit to the advantage that is gained by increasing the acrylonitrile concentration by use of the acrylamide cosolvent. It is preferred to keep the acrylonitrile concentration in the feed solution higher, on a weight percent basis, than the concentration of acrylamide in the feed solution.
The practical upper limit of acrylamide concentration in the aqueous product solutions obtained with the invention is found to be in the range from about 20 to about 35% acrylamide.

In the examples which follow, the invention is illustrated by employing product acrylamide to increase the solubility of acrylonitrile in feed streams. The examples describe the invention using staged reactors and using a single reactor. In the latter instance recycled product mixed with the fresh feed provides the acrylamide cosolvent for the feed solution. The catalyst used for the examples are typical preferred catalysts but the invention can be used with any catalyst that is suitable for the hydration reaction.

Example 1

Three reactors constructed of one inch diameter stainless steel pipe were placed in series such that a 7% acrylonitrile solution in water is fed to the first reactor. Additional fresh acrylonitrile is mixed with the product of the first reactor and fed to the second reactor. Likewise, additional fresh acrylonitrile is mixed with the product of the second reactor and fed to the third reactor.

A commercially prepared catalyst containing 80% CuO and 17% Cr2O3 sold under the trade name Harshaw 0203T was crushed and sieved to obtain particles of 40 - 60 mesh size. 30 Grams of the sized catalyst was charged to the first reactor, 46 grams to the second and 100 grams to the third reactor. The catalyst in each reactor was reduced by passing a 3% H2 in N2 mixture at 20 liters
1. per minute and 200°C. over the catalyst for 8 hours.

After reduction, the three reactors together with the associated piping were immersed in a temperature bath maintained at 90°C. Reservoirs of deaerated 7% acrylonitrile solution in water as well as deaerated acrylonitrile were provided and connected to the reactor train through suitable pumps. All liquid streams were maintained under a back pressure of 35 psig.

7% Acrylonitrile solution was fed to the first reactor at a rate of 100 grams/hour. The product from the first reactor contained approximately 0.7% residual acrylonitrile and 8.4% acrylamide. 20 Grams/hour of acrylonitrile was mixed thoroughly at the bath temperature into the product of reactor 1 and fed to reactor 2. The product from the second reactor contained approximately 5.2% of acrylonitrile and 23.2% acrylamide. 30 Grams/hour of acrylonitrile was mixed into the product of reactor 2 and fed to reactor 3. The product from reactor 3 contained 14.5% acrylonitrile and 31.5% acrylamide. In each case, the mixed feed to each reactor at the bath temperature was homogeneous and of a single phase. Overall, 62% of the total acrylonitrile fed was converted with greater than 98% selectivity to acrylamide.

Example 2

A catalyst commercially available under the trade name BASF R3-11 was crushed and sieved to obtain particles of 40-60 mesh size. BASF R3-11 contains 28 - 30% copper combined in copper compounds and dispersed in magnesium silicate.
The reactor system of Example 1 was used. 35, 44 and 96 Grams of the sized catalyst were charged to the first, second and third reactors respectively. The catalyst was reduced as in Example 1.

The temperature bath was maintained at 70°C.

7% Acrylonitrile solution was fed to the first reactor at a rate of 100 grams/hour. The product from the first reactor contained approximately 0.3% residual acrylonitrile and 8.9% acrylamide. 15 Grams/hour of acrylonitrile was mixed in with the product of reactor 1 and fed to reactor 2. The product from the second reactor contained approximately 3.1% acrylonitrile and 21.4% acrylamide. 30 Grams/hour of acrylonitrile was mixed in with the product of reactor 2 and fed to reactor 3. The final product from reactor 3 contained 11.4% acrylonitrile and 32.4% acrylamide. As in Example 1, the mixed feed to each reactor was of a single phase at the bath temperature. Overall, 68% conversion of the total acrylonitrile feed was converted with greater than 98% selectivity to acrylamide.

Example 3

An apparatus was constructed such that a portion of the product from a continuous reactor could be collected and mixed with fresh make up acrylonitrile and water and fed back into the reactor. The apparatus consisted of a feed reservoir, feed pump, reactor maintained in a temperature bath, a product reservoir and transfer lines. The feed and product reservoirs are maintained under a nitrogen atmosphere to exclude air.

123 Grams of Harshaw 0203T catalyst in the form
of 1/8" x 1/8" cylinders was charged as received to a packed bed reactor and reduced. The reactor was maintained at 75°C. In the first pass, deaerated 7% acrylonitrile solution in water was charged to the feed reservoir and fed to the reactor at a rate of 73 grams/hour. The product collected under nitrogen in the product reservoir contained approximately 0.7% residual acrylonitrile and 8.4% acrylamide. A portion of the product was discharged; the remaining portion of the product was transferred to the empty feed reservoir. For each 100 grams of product transferred back to the feed reservoir, 97 grams of deaerated acrylonitrile and 70 grams of deaerated distilled water was charged also to the feed reservoir. This new feed for the second pass through the reactor contained approximately 8.9% acrylonitrile and 7.2% acrylamide and was fed to the reactor at a rate of 99 grams/hour. The product collected in the second pass contained approximately 4% residual acrylonitrile and 13.5% acrylamide. In a similar manner, a third pass through the reactor was carried out. For the third pass, the feed contained 8.1% acrylonitrile and 11% acrylamide and was fed to the reactor at a rate of 41 grams/hour. The product from the third pass contained 2.1% residual acrylonitrile and 19% acrylamide.

Although the recycle of product acrylamide was carried out in a batchwise manner for more precise control and therefore a more precise laboratory study, the product could have been recycled and mixed with fresh acrylonitrile feed continuously by the installation of additional metering pumps.
In the foregoing examples the concentration of acrylonitrile in the feed solutions was not the saturation concentration at the solution temperature in every instance, but the actual concentrations of acrylonitrile in the feed solutions were higher in every instance than the maximum concentration of acrylonitrile that could have been dissolved in water without the acrylamide cosolvent.
The claims defining the invention are as follows:

1. In the catalytic hydration of acrylonitrile to produce acrylamide wherein an aqueous feed solution of acrylonitrile is contacted in a reactor with a solid heterogeneous catalyst for the hydration reaction, the improvement wherein the solubility of acrylonitrile in said aqueous feed solution is increased by addition of acrylamide as a cosolvent in said feed solution and acrylonitrile is dissolved in said feed solution containing the acrylamide cosolvent in an amount to make an enriched feed solution having acrylonitrile concentration higher than the saturation concentration of acrylonitrile in water without a cosolvent.

2. A process defined by Claim 1 wherein acrylonitrile is added to and dissolved in the aqueous acrylamide product stream taken from a first continuous catalytic acrylonitrile hydration reactor and the enriched product solution with added acrylonitrile is fed as the reactant feed to a second continuous catalytic acrylonitrile hydration reactor.

3. A process defined by Claim 1 wherein a portion of the aqueous acrylamide product stream taken from a continuous catalytic acrylonitrile hydration reactor is recycled to the reactant feed stream of the same reactor to provide the defined acrylamide cosolvent in said feed stream.

4. A process defined by Claim 1 wherein said enriched feed solution has acrylonitrile dissolved to the saturation concentration in the enriched solution.

5. A process defined by Claim 2 wherein the
enriched feed solution has acrylonitrile dissolved to the saturation concentration in the enriched solution.

6. A process defined by Claim 3 wherein said enriched feed solution has acrylonitrile dissolved to the saturation concentration in the enriched feed stream.

DATED this ELEVENTH day of FEBRUARY, 1976

AMERICAN CYANAMID COMPANY

Patent Attorneys for the Applicant
SPRUSON & FERGUSON