COMMONWEALTH of AUSTRALIA
Patents Act 1952

APPLICATION FOR A STANDARD PATENT

I/We
Mitsui Toatsu Chemicals, Inc.
of
2-5, Kasumigaseki 3-chome, Chiyoda-ku, Tokyo, 100, Japan

hereby apply for the grant of a Standard Patent for an invention entitled:

Preparation process of xylylene diisocyanate

which is described in the accompanying complete specification.

Details of basic application(s):

<table>
<thead>
<tr>
<th>Number</th>
<th>Convention Country</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-041495</td>
<td>Japan</td>
<td>23 February 1989</td>
</tr>
<tr>
<td>1-046410</td>
<td>Japan</td>
<td>1 March 1989</td>
</tr>
</tbody>
</table>

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

DATED this TWENTY FIRST day of FEBRUARY 1990

To: THE COMMISSIONER OF PATENTS

[Signature]

a member of the firm of DAVIES & COLLISON for and on behalf of the applicant(s)

Davies & Collison, Melbourne

016082 210290
COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF CONVENTION OR
NON—CONVENTION APPLICATION FOR A PATENT

In support of the Application made for a patent for an invention
entitled: PREPARATION PROCESS OF XYLLENE DIISOCYANATE

1. Masayoshi MISHIMA, Executive managing and
Representative Director of MITSUI TOATSU CHEMICALS,
INC. having its head office at No. 2-5 Kasumigaseki
3-chome, Chiyoda-Ku, Tokyo, 100 JAPAN

do solemnly and sincerely declare as follows:—
1. (a) I am the applicant for the patent

we are

or (b) I am authorized by

the applicant............. for the patent to make this declaration on its behalf.

2. (a) I am the actual inventor of the invention

we are

or (b)

(1) Teruyuki NAGATA of 154 Shiragane-Nachi, Omata-Shi, Fukuoka-Ken, 836 JAPAN
(2) Masaru WADA of 1807-159 Ooaza Kunugi, Omata-Shi, Fukuoka-Ken, 837 JAPAN
(3) Hideki MIZUHA of 219 Ooaza Miike, Omata-Shi, Fukuoka-Ken, 837 JAPAN

are the actual inventors of the invention and the facts upon which

is the actual inventor............ of the invention and the facts upon which

the applicant.................... is entitled to make the application are as follows:—

The contract of employment, whereby the applicant
would if a patent were granted on an application
made by the said actual inventors be entitled to
have the patent assigned to it.

3. The basic application... as defined by Section 141 of the Act were

made in JAPAN

on February 23th, 1989

by MITSUI TOATSU CHEMICALS, INC.

in JAPAN

on March 1st, 1989

by MITSUI TOATSU CHEMICALS, INC.

by


4. The basic application... referred to in paragraph 3 of this Declaration

were the first application... made in a Convention country in respect of the invention the subject
of the application.

Declared at Tokyo this Feb. 1st, day of 1990

Masayoshi MISHIMA

DAVIES & COLLISON, MELBOURNE and CANBERRA.
1. A process for the preparation of xyylene diisocyanate in the presence of an ester as a reaction solvent as to inhibit the formation of chloromethylbenzyl isocyanate which comprises reacting xyylene diamine with hydrogen chloride gas in a first step at a temperature of 30°C or less, and in a second step reacting the resultant xyylene diamine hydrochloride with phosgene at a temperature of from 120 to 170°C.
NAME & ADDRESS
OF APPLICANT:
Mitsui Toatsu Chemicals, Inc.
2-5, Kasumigaseki 3-chome
Chiyoda-ku
Tokyo 100
Japan

NAME(S) OF INVENTOR(S):
Teruyuki NAGATA
Masaru WADA
Hideki MIZUTA

ADDRESS FOR SERVICE:
DAVIES & COLLISON
Patent Attorneys
1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:
Preparation process of xylylene diisocyanate

The following statement is a full description of this invention, including the best method of performing it known to me/us:-
Background of the Invention

1. Field of the Invention

The present invention relates to a process for the preparation of xylylene diisocyanate by reacting xylylene diamine or its salt with phosgene.

Xylylene diisocyanate is a very useful compound as a raw material for polyurethane-based materials, polyurea-based materials and polyisocyanurate-based materials in chemical, resin and paint industries.

2. Description of the Prior Art

Various methods have already been proposed for the preparation of xylylene diisocyanate.

Processes to prepare isocyanates by reacting organic amines with phosgene, that is, so-called phosgenation processes, have been proposed. Processes which have also been proposed other than phosgenation processes are, for example, a process for reacting aromatic compounds containing chloromethyl groups with an alkali cyanate in the presence of a copper catalyst (Japanese Patent Laid-Open Publication SHO 52-46042(1977)), and a process for the vapor phase oxidation of N-substituted formamides by an oxygen containing...
gas in the presence of a catalytic amount of metal [Japanese Patent Laid-Open Publication SHO 54-39018(1979), which corresponds to USP 4207251 and EP 602].

Additionally, phosgenation processes which prepare isocyanates by conducting the reaction of organic primary amines with phosgene in an inert solvent have been known.

In these processes, aromatic primary amines can be converted with comparative ease to high-purity aromatic isocyanates by passing phosgene gas through a suspension of the free aromatic amines, their carbonates or hydrochlorides in the solvent.

On the other hand, aliphatic primary amines generally require lengthy times in the reaction with phosgene as compared to aromatic primary amines, and also generate, as well known in the art, chloroderivatives as by-products due to a deamination reaction.

Xylylene diamine is classified in the aliphatic diamine compound. In the preparation of xylylene diisocyanate by reacting xylylene diamine with phosgene according to a conventional process, a monoisocyanate is formed as a by-product as in the preparation of ordinary aliphatic isocyanates. The monoisocyanate is a chloroderivative (hereinafter referred to as chlorinated impurity) having the formula (I):

\[ \text{CH}_2\text{NCO} \]

\[ \begin{array}{c}
\text{Q} \\
\text{CH}_2\text{Cl}
\end{array} \]

(I)

The chlorinated impurity is usually formed in an amount of 3 to 10 % by weight and sometimes goes up to 20 % by weight. Hence the yield of the desired product undergoes a corresponding decrease.
When xylylene diisocyanate contains the chlorinated impurity, the chlorinated impurity affects the reaction of isocyanate groups with active hydrogen containing compounds in the preparation of polyurethane resins from xylylene diisocyanate. The chlorinated impurity inhibits the reaction, accelerates gelation of the prepolymer and further exerts an adverse effect upon the properties of the resulting polyurethane resin.

No difference is generally observed between the properties of the chlorinated impurity and corresponding isocyanate except that the chlorinated impurity has a boiling point from 5 to 20°C lower than that of the isocyanate. Specific procedures are hence required for the separation and purification of xylylene diisocianate as proposed in Japanese Patent Publication SHO 49-13786(1974).

The formation of the above chlorinated derivative is mostly not found in the preparation of aromatic isocyanates, and is observed in the preparation of aliphatic isocyanates.

Consequently, processes have been proposed in order to inhibit the formation of the impurity as much as possible and to enhance the efficiency of separation and purification steps. These processes include, for example, (1) a process for preparing isocyanates by reacting xylylene diamine with phosgene at 120 to 160 °C under pressure of 0.5 to 10 kg/cm²G [Japanese Patent Publication SHO 42-179797(1967), which corresponds to USP 340227 and GB 1162155 ], and (2) a process for converting xylylene diamine or its hydrochloride to xylylene diisocyanate at a reaction temperature of 120 to 160°C in a range of from 18/1 to 30/1 by weight ratio of solvent/amine raw material [GB 1086782].
These processes, however, have been disadvantageous in that extensive equipment is required for the preparation because the reaction is conducted under pressure, and uses a large amount of solvent which leads to low volume efficiency and very poor economy. As a result, conventional processes have been unsatisfactory in view of industrial production.

Summary of the Invention

The object of this invention is to inhibit the formation of the by-product, that is, the chlorinated impurity having the above formula (I) and to provide a process for preparing xylylene diisocyanate that yields good efficiency in industry.

The present inventors have carried out an intensive investigation on the preparation of xylylene diisocyanate by phosgenation of xylylene diamine or its hydrochloride. As a result, it has been surprisingly found that xylylene diisocyanate having a very small content of the chlorinated impurity can be prepared by using an ester as a reaction solvent.

According to the present invention there is provided a process for the preparation of xylylene diisocyanate in the presence of an ester as a reaction solvent as to inhibit the formation of chloromethylbenzyl isocyanate which comprises reacting xylylene diamine with hydrogen chloride gas in a first step at a temperature of 30°C or less, and in a second step reacting the resultant xylylene diamine hydrochloride with phosgene at a temperature of from 120 to 170°C.
Detailed Description of the Invention

Xylylene diamine used in the process of this invention is m-xylylene diamine, p-xylylene diamine, o-xylylene diamine or a mixture containing various proportions of these isomers. Accordingly, unless otherwise noted hereinafter, the term "xylylene diamine" includes any of these amines and the isocyanates prepared from these amines are referred to as xylylene diisocyanate.

The process of this invention has a remarkable characteristic of reacting xylylene diamine or its hydrochloride with phosgene in the presence an ester as a reaction solvent.

Free xylylene diamine is used as the raw material, converted to hydrochloride in the reaction system and then can be subjected to reaction with phosgene.

The reaction solvent used in the process of this invention is esters. Various kinds of esters can be used, and fatty acid esters and aromatic carboxylic acid esters are preferred in particular. Exemplary fatty esters include amyl formate, n-butyl acetate, isobutyl acetate, n-amyl acetate, isoamyl acetate, methylisoamyl acetate, methoxybutyl acetate, sec-hexyl acetate, 2-ethylbutyl acetate, 2-ethylhexyl acetate, cyclohexyl acetate, methylcyclohexyl acetate, benxyl acetate, ethyl propionate, n-butyl propionate, isoamyl propionate, ethyl acetate, butyl stearate, butyl lactate and amyl lactate. Aromatic carboxylic acid esters include, for example, methyl salicylate, dimethyl phthalate and methyl...
benzoate. More preferred esters are aliphatic esters having a boiling point of 120 to 170°C under atmospheric pressure. The use of these esters is preferred in view of preventing the decomposition of isocyanates due to overheating. These solvents can be used singly or in combination.

The amount of the solvent used in the process of this invention is preferably in a weight ratio of solvent/raw material amine in the range of 8/1 to 16/1.

When the weight ratio is less than 8/1, a large amount of amine hydrochloride is deposited and the reaction mixture becomes difficult to stir. On the other hand, a weight ratio exceeding 16/1 has little effect on the acceleration of the reaction rate and requires larger amounts of the solvent. Hence thermal efficiency in the concentration step is reduced and volume efficiency becomes industrially unfavorable.

The reaction is carried out by using free xylylene diamine as a raw material, reacting it with hydrogen chloride gas in an ester type solvent to form hydrochloride and then reacting the hydrochloride with phosgene.

In the above reaction, xylylene diamine is first reacted with hydrogen chloride gas in an ester type solvent to form xylylene diamine hydrochloride. The temperature during the formation of xylylene diamine hydrochloride is 30°C or less. When the temperature exceeds 30°C, the chlorinated impurity is liable to increase. When the temperature is 30°C or less, good
results can be obtained even in the vicinity of 0°C. Although hydrochloride formation can also be conducted at lower temperatures than this range, it is unfavorable because extensive refrigeration is required. The reason for the good results obtained by conducting hydrochloride formation at 30°C or less is not clear, but is thought that the results depend upon the solubility and particle size of xylylene diamine hydrochloride.

The temperature for reacting the resultant xylylene diamine hydrochloride with phosgene is from 120 to 170°C, more preferably from 130 to 150°C.

When phosgenation is conducted for a long time at a temperature exceeding 170°C in any of the above methods, decomposition of the resultant xylylene diisocyanate results from poor thermal stability and leads to an increase in tar content and a decrease in yield. When the reaction temperature rises, formation of the chlorinated impurity, that is, chloromethylbenzyl isocyanate (hereinafter abbreviated as CBi), tends to increase. A reaction temperature lower than 120°C is unfavorable because the reaction rate becomes too slow.

In the process of this invention, the reaction is usually carried out under atmospheric pressure. In order to increase the reaction rate and to inhibit the formation of CBi, the isocyanate can also be prepared under increased pressure.

Typical preferred embodiments of the process of this invention will be illustrated hereinafter.
In the practical procedures corresponding to the above reaction method xylylene diamine is used as a raw material, its hydrochloride is formed and then the hydrochloride is reacted with phosgene. For example, xylylene diamine as the raw material and an ester as a reaction solvent are charged to a reaction vessel, and a prescribed amount of hydrogen chloride gas is blown into the suspension of xylylene diamine while controlling the internal temperature 30°C or less to form xylylene diamine hydrochloride. Thereafter the reaction mixtures is heated to a prescribed temperature and phosgene is introduced to complete the conversion to isocyante.

After completing the reaction in the above method, unreacted phosgene and hydrogen chloride are purged with nitrogen and the solvent is removed. The residue is distilled to obtain pure xylylene diisocyanate.

According to the process of this invention, xylylene diisocyanate having an extremely low content of CB1 can be obtained. Accordingly, post treatment steps such as distillation purification can be simplified and the loss of product due to thermal deterioration in the post treatment step can be reduced. Consequently, the process of the present invention is industrially very valuable.

The present invention will hereinafter be illustrated in detail by way of examples and comparative examples.

Example 1

To a 2ℓ reaction flask equipped with a reflux
condenser, thermometer, phosgene or hydrogen chloride inlet tube, and a stirrer, 136.2 g (1.0 mole) of m-
5 xyylene diamine raw material (hereinafter abbreviated and m-XDA) and 1200 g of amyl acetate as a solvent were charged.

Then 80 g of hydrogen chloride gas was blown into
10 the flask
over 2 hours with stirring and cooling. The internal temperature rose to 60 °C. The resulting mixture was successively heated to 135 °C and phosgene was introduced at a rate of 25 g/hr. The reaction was continued for 15 hours while maintaining the temperature from 135 to 140 °C.

After completing the reaction, unreacted phosgene and hydrogen chloride were purged with nitrogen. After removing the solvent, the residue was vacuum distilled at 1 to 2 mm Hg.

m-Xylylene diisocyanate (hereinafter abbreviated as m-XDi) containing 0.8 % by weight of m-chloromethylbenzyl isocyanate (hereinafter abbreviated as m-CBi) was obtained at a yield of 172.7 g. The yield converted to a purity basis was 91.0 %. The amount of CBi formed was 0.76 mol % per mole of m-XDA.

Example 2

To the same reaction flask as used in Example 1, m-XDA and amyl acetate were charged by the same procedures as Example 1 and cooled to 5 °C.

Phosgene was introduced at a rate of 200 g/hr for 3 hours while maintaining the internal temperature from 0 to 5 °C. Phosgene was further introduced at a rate of 20 g/hr and the reaction mixture was heated to 135 °C. Thereafter the reaction was conducted for 12 hours while maintaining the internal temperature from 135 to 140 °C.

After completing the reaction, the post-treatment was carried out by the same procedures as conducted in Example 1. m-XDi obtained was 170.7 g. The yield converted to a purity basis was 89.6 %. The m-XDi contained 1.2 % m-CBi by weight. The amount of CBi formed was
1.13 mol % per mole of m-XDA.

Example 3 and Comparative Examples 1-3

The reaction and post-treatment were carried out by the same procedures as conducted in Example 1 except that the solvents illustrated in Table 1 were used. The effect of the solvents on the amount of m-CBi formed was investigated. Results are illustrated in Table 1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>m-XDi yield (mol %/m-XDA)</th>
<th>m-CBi amount (mol %/m-XDA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 3</td>
<td>Hexyl acetate</td>
<td>90.8</td>
</tr>
<tr>
<td>Comparative</td>
<td>o-Dichlorobenzene</td>
<td>87.7</td>
</tr>
<tr>
<td>Example 1</td>
<td>Mesitylene</td>
<td>86.2</td>
</tr>
<tr>
<td>Comparative</td>
<td>DMi</td>
<td>50.8</td>
</tr>
<tr>
<td>Example 3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: DMi is 1,3-dimethyl-2-imidazolidinone

Example 4

To a 2 ℓ reaction flask equipped with a reflux condenser, thermometer, phosgene or hydrogen chloride inlet tube and a stirrer, 136.2 g (1.0 mole) of m-XDA raw material and 1200 g of amyl acetate as a solvent were charged.

Then 80 g of hydrogen chloride gas was blown into the flask over 2 hours with stirring and cooling while maintaining the internal temperature from 25 to 30 °C to form hydrochloride of m-XDA. Then
the reaction mixture was heated to 135 °C.

After raising the temperature, phosgene was introduced to the reaction mixture at a rate of 25 g/hr and the reaction was continued for 15 hours while maintaining the temperature from 135 to 140 °C.

After completing the reaction, unreacted phosgene and hydrogen chloride were purged with nitrogen, and the solvent was removed. The residue was vacuum distillated at 1 to 2 mm Hg. m-XDi containing 0.4 % m-CBi by weight was obtained in a yield of 173.3 g. The yield converted to a purity basis was 91.7 %. The amount of m-CBi formed was 0.38 mol % per mole of m-XDA.

Example 5-7 and Comparative Examples 4-5

The reaction and post-treatment were carried out by the same procedures as conducted in Example 1 except that the solvents and hydrochloride forming temperatures were used as illustrated in Table 2.

Results are illustrated in Table 2

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Hydrochloride forming temperature (°C)</th>
<th>m-XDi yield (mol % /m-XDA)</th>
<th>m-CBi amount (mol % /m-XDA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 5</td>
<td>Amyl acetate</td>
<td>0 - 5</td>
<td>91.2</td>
</tr>
<tr>
<td>Example 6</td>
<td>Hexyl acetate</td>
<td>25 - 30</td>
<td>90.8</td>
</tr>
<tr>
<td>Example 7</td>
<td>Butyl propionate</td>
<td>25 - 30</td>
<td>91.0</td>
</tr>
<tr>
<td>Comparative</td>
<td>o-Dichloro-</td>
<td>50 - 55</td>
<td>87.9</td>
</tr>
<tr>
<td>Example 4</td>
<td>benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative</td>
<td>o-Dichloro-</td>
<td>25 - 30</td>
<td>88.1</td>
</tr>
<tr>
<td>Example 5</td>
<td>benzene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the preparation of xylylene diisocyanate in the presence of an ester as a reaction solvent as to inhibit the formation of chloromethylbenzyl isocyanate which comprises reacting xylylene diamine with hydrogen chloride gas in a first step at a temperature of 30°C or less, and in a second step reacting the resultant xylylene diamine hydrochloride with phosgene at a temperature of from 120 to 170°C.

2. A process according to claim 1 wherein the ester reaction solvent is an aliphatic ester.

3. A process according to claim 1 or 2 wherein the ester reaction solvent is used in an 8/1 to 16/1 weight ratio of solvent to xylylene diamine or its hydrochloride.

4. A process for the preparation of xylylene diisocyanate according to any one of claims 1 to 3, substantially as hereinbefore described with reference to the Examples.

DATED this 9th day of September, 1991
Mitsui Toatsu Chemicals, Inc.
By Its Patent Attorneys
DAVIES & COLLISON