CONVENTION APPLICATION FOR A PATENT

Hoechst Aktiengesellschaft
of 45 Bruningstrasse, D-6230 Frankfurt/Main 80,
Federal Republic of Germany

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

PROCESS FOR THE PRODUCTION OF GASES CONTAINING
METHYL CHLORIDE

which is described in the accompanying complete specification. This application is a
Convention application and is based on the application numbered

P31 07 105.8

for a patent or similar protection made in Federal Republic of Germany
on 26th February 1981

Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys,
50 Queen Street, Melbourne, Victoria, Australia.

DATED this 24th day of February 1982.

HOECHST AKTIENGESELLSCHAFT

by

Stephen K. Plymin
Registered Patent Attorney

To:

DECLAR
In support of the Convention application made under Part XVI. of the Patents Act 1952 by HOECHST AKTIENGESELLSCHAFT of 45, Brüningstrasse, D-6230 Frankfurt/Main 80, Federal Republic of Germany for a patent for an invention entitled:

PROCESS FOR THE PRODUCTION OF GASES CONTAINING METHYL CHLORIDE

We, Johann-Heinrich Reuter, 4 Bodenheimer Straße, D-6500 Mainz, Martin von Forster, 8 Wiesenstraße, D-6240 Königstein-Taunus; Federal Republic of Germany

do solemnly and sincerely declare as follows:

1. We are authorized by HOECHST AKTIENGESELLSCHAFT the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in the Federal Republic of Germany under No. P 31 07 105.8 on February 26, 1981 by HOECHST AKTIENGESELLSCHAFT

a) Wolfgang Grünbein, 35 Alt-Oberliederbach, D-6237 Liederbach

b) Wilhelm Lendle, 5 Hirschpfad, D-6232 Bad Soden am Taunus

c) Hendrik Willem Post, 4 Paulinenweg, D-6238 Hofheim am Taunus

d) Heinz Richter, 2 Wilhelm-Bonn-Straße, D-6242 Kronberg-Taunus

e) Manfred Rossberg, 8 Am Rotfeld, D-6273 Waldems

are the actual inventor(s) of the invention and the facts upon which HOECHST AKTIENGESELLSCHAFT is entitled to make the application are as follows:

The said HOECHST AKTIENGESELLSCHAFT is the assignee of the said Wolfgang Grünbein, Wilhelm Lendle, Hendrik Willem Post, Heinz Richter and Manfred Rossberg

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 Frankfurt/Main, Federal Republic of Germany this 7th day of January 1982.

To the Commissioner of Patents

Hoechst Aktiengesellschaft
Prokurist Authorized signatory

(ppa.Reuter) (i.V.von Forster)
DOCUMENTS LODGED WITH THIS APPLICATION ARE UNSUITABLE FOR REPRODUCTION AND MAY BE INSPECTED AT THE PATENT OFFICE A.C.T.
Claim 1. A process for the production of gases containing methyl chloride from methanol and gases containing hydrogen chloride, by reaction in a water-containing zinc chloride solution at an elevated temperature, which comprises using, as the gas containing hydrogen chloride, a mixture of the composition

\[
\begin{align*}
\text{CH}_3\text{Cl} & \quad 15 - 80 \% \text{ by volume} \\
\text{CH}_4 & \quad 3 - 50 \% \text{ by volume} \\
\text{N}_2 & \quad 10 - 25 \% \text{ by volume} \\
\text{HCl} & \quad 0.1 - 5 \% \text{ by volume} \\
\text{CCl}_3\text{H} + \text{CCl}_4 & \quad 0.1 - 5 \% \text{ by volume} \\
\text{CH}_2\text{Cl}_2 & \quad 5 - 20 \% \text{ by volume} \\
\text{Cl}_2 & \quad 0 - 0.1 \% \text{ by volume.}
\end{align*}
\]
Process for the Production of Gases Containing Methyl Chloride

The following statement is a full description of this invention, including the best method of performing it known to us.
The present invention relates to a process for the preparation of gases containing methyl chloride from methanol and gases containing hydrogen chloride, in the gas phase on a liquid catalyst.

In the industrial chlorination of methane, hydrogen chloride which must be reprocessed is also produced, in addition to the chlorination products, such as methyl chloride or methylene chloride. The same is true for the chlorination of methyl chloride, methylene chloride or chloroform. In addition to the electrolysis of aqueous hydrogen chloride with recovery of chlorine, the reaction of hydrogen chloride with methanol is of interest since, in this case, an industrial chlorination product of methane can be obtained without using chlorine and methane.

The reaction of hydrogen chloride and methanol, the so-called "methanol esterification", can inter alia be carried out in an approximately 70% strength aqueous zinc chloride solution. According to Ullmann, Enzyklopädie der technischen Chemie [Encyclopedia of Industrial Chemistry], 3rd Edition, 1954, Volume 5, page 401, almost equimolar quantities of methanol and hydrogen chloride are passed continuously through the zinc chloride melt at 130 – 150°C. The crude methyl chloride which is evolved entrains the water of reaction. In addition to unreacted starting products, the exit gas also contains dimethyl ether as an undesired impurity.
Disadvantageously, the hydrogen chloride obtained in the chlorination of methane is not pure, but contains at least equimolar quantities of chlorination products of methane. In some cases, the chlorination is carried out in the presence of an inert gas, such as, for example, nitrogen, which leads to a further decrease in the content of hydrogen chloride in the reaction gases.

In industry, the separation of hydrogen chloride from this mixture is in most cases carried out by washing with water and expelling the HCl from the aqueous absorption solution by heating. Hydrogen chloride can also be isolated from the reaction products of the chlorination of methane or methyl chloride by washing out with chloromethanes and subsequent liquefaction, or a relatively pure dry hydrogen chloride can be obtained by direct liquefaction and fractional distillation under pressure. This hydrogen chloride can be used for the methanol esterification. For example, according to German Offenlegungsschrift 1,806,988, a gas stream composed of 87 mole % of HCl and 13 mole % of methyl chloride can be mixed with methanol and fed into a methanol esterification apparatus.

It is a disadvantage of this process that separation operations must be carried out before the methanol esterification. This is even more true if the chlorination of methane (or methyl chloride) takes place in the presence of inert gases.

It was therefore the object to discover a process in which the hydrogen chloride from the chlorination of methane or methyl chloride in the presence of nitrogen can
obtained contains products carried, for example, the content of chloride washing absorption can also chlorination such chloro-actively pure liquefac-

This esterification fenlegungs-mole % of opposed with apparatus.

In the process of the state of the art, the melt of water-containing zinc chloride is present in an acid-resistant vessel (ceramics or a steel vessel with an acid-resistant brick lining). According to a special embodiment of the process according to the invention, however, the reaction takes place in a column with downward flow of the zinc chloride solution.

It is particularly advantageous to feed the gas containing hydrogen chloride and the methanol into the
lower part of the column and, at the top of the column, to charge the zinc chloride solution and to take off the resulting gas mixture. In addition to a little hydrogen chloride and dimethyl ether, this gas mixture contains all the methyl chloride and the water of reaction.

The zinc chloride solution flowing out at the bottom of the column will therefore preferably be recharged directly to the top of the column, that is to say it will be circulated. The column used can be e.g. a packed column or a bubble-cap tray column.

To suppress the formation of dimethyl ether, it is advantageous to select a methanol/HCl molar ratio of less than 1:1, preferably in the range from 0.3:1 to 0.95:1. For the same reason, it is advantageous to feed methanol to a column tray which is located below the tray where the gas mixture containing HCl is fed in.

It is surprising that, as a result of this procedure, a considerable proportion of the hydrogen chloride in the gas mixture used reacts with methanol to give methyl chloride, without it becoming necessary to separate off HCl, and that at the same time the dimethyl ether content of the resulting gas is several times lower than that obtained in the industrial methanol esterification.

Admittedly, it is known (Chemie-Ing.-Technik 42 (1970), page 1215) that the reaction equilibrium in the reaction of CH₃OH and HCl is on the side of the end products and that the reaction rate is not influenced by the end products. However, this literature reference
relates to the formation of methyl chloride over a solid Al₂O₃ catalyst.

The invention is explained in more detail by the examples which follow.

5 Examples

The experimental apparatus is shown in the figure. The reaction takes place in a glass column with bubble-cap trays (internal diameter 5 cm, one bubble-cap per tray, 20 trays). Hot aqueous zinc chloride solution (17) is taken from the bottom vessel (1) via line (12), in which the pump (5) is inserted, and is recharged to the column top. Liquid methanol is fed via line (13) to a vaporizer (6) and vaporized therein. The methanol vapor is fed via line (14) into the bubble-cap tray column (2) in the vicinity of the lowest tray (of course, the methanol vaporizer (6) can be omitted and methanol in the liquid form can be metered in). The gas which is to be reprocessed and contains hydrogen chloride is charged via line (7) to a column tray located higher up. It is preferred when there are at least 3 trays between the methanol feed and the hydrogen chloride feed.

The column (2) and bottom vessel (1) have an insulation layer (3 and 4 respectively) on the outside, but facilities for cooling or heating are not excluded. During the experiments, the column is kept at an internal temperature of 98°C by gentle heating of (3). The gas depleted of hydrogen chloride flows at the top of the column (2) via line (15) into a condenser (8) in which the water of reaction condenses. The
condensate (16) also contains a little dissolved hydrogen chloride and residual methanol. The condensate collects in the vessel (9) and can be taken off by means of the valve (11). The non-condensed fractions of the reaction gas leave the condenser (8) via line (10). The further processing can comprise a condensation of the chlorinated hydrocarbons and a subsequent (fractional) distillation.

Example 1:

Per hour, 330 l of a gas containing

19.1 % by volume of CH₃Cl
8.3 % of CH₂Cl₂
2.1 % of CHCl₃
0.2 % of CCl₄
14 % of HCl
30 % of N₂

were fed to the fourth tray (counted from the bottom) of the bubble-cap-tray column. An aqueous solution prepared from 30 parts by weight of water and 70 parts by weight of zinc chloride was taken from the bottom vessel by means of the pump, heated to 80 - 85°C in a heat exchanger (not shown) and charged to the top of the column (pump delivery: 6 - 8 l/hour). Liquid methanol was metered in to the second tray of the column at a rate of 56 ml/hour.

On cooling the resulting reaction gas to 16°C, 33 ml of a condensate containing 26.7% by weight of HCl and 0.9% of methanol were obtained. The remainder was water. The remaining gas phase had the following composition:
Example 2:

Per hour, 260 l of a gas mixture containing

28.9 % by volume of CH₃Cl
8.4 % of CH₂Cl₂
2.2 % of CHCl₃
0.2 % of CCl₄
15 ppm of dimethyl ether

Remainder of CH₄.

were passed into the gas space of the bottom vessel of the bubble-cap tray column. Methanol in the form of vapor was fed in at a rate of 30 g/hour. The remaining conditions corresponded to those of Example 1. 27.6 g of a condensate containing 29.6% by weight of HCl and 0.7% of methanol were obtained, as well as a residual gas having the following composition:

50.1 % by volume of CH₃Cl
13.5 % of CH₂Cl₂
2.7 % of CHCl₃
0.2 % of CCl₄
3.2 % of HCl
15 ppm of dimethyl ether.
Example 3:

Per hour, 280 l of a gas mixture containing

- 45.8% by volume of CH₃Cl
- 15.3% of CH₂Cl₂
- 2.9% of CHCl₃
- 0.2% of CCl₄
- 16.3% of HCl
- Remainder N₂

were fed to the 4th tray of the column. Methanol (30 g/hour) was fed in the form of vapor. 27.6 g of a condensate containing 30.6% by weight of HCl and 0.28% of CH₃OH (remainder: water) were obtained, as well as a residual gas of the following composition

- 55.8% by volume of CH₃Cl
- 15.7% of CH₂Cl₂
- 3.1% of CHCl₃
- 0.2% of CCl₄
- 4.3% of HCl
- 2 ppm of dimethyl ether
- Remainder N₂.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the production of gases containing methyl chloride from methanol and gases containing hydrogen chloride, by reaction in a water-containing zinc chloride solution at an elevated temperature, which comprises using, as the gas containing hydrogen chloride, a mixture of the composition

\[
\begin{align*}
\text{CH}_3\text{Cl} + \text{CH}_4 & \quad 15 - 80 \text{ \% by volume} \\
\text{N}_2 & \quad 3 - 50 \text{ \% by volume} \\
\text{HCl} & \quad 10 - 25 \text{ \% by volume} \\
\text{CCl}_3\text{H} + \text{CCl}_4 & \quad 0.1 - 5 \text{ \% by volume} \\
\text{CH}_2\text{Cl}_2 & \quad 5 - 20 \text{ \% by volume} \\
\text{Cl}_2 & \quad 0 - 0.1 \text{ \% by volume.}
\end{align*}
\]

2. The process as claimed in claim 1, wherein the reaction is carried out in a column with downward flow of a water-containing zinc chloride solution.

3. The process as claimed in claim 2, wherein the gas containing hydrogen chloride and the methanol are fed into the lower part of the column and, at the top of the column, the zinc chloride solution is charged and the resulting gas mixture is taken off.

4. The process as claimed in claim 2, wherein the zinc chloride solution is circulated.

5. The process as claimed in claim 1, wherein the methanol/hydrogen chloride molar ratio is less than 1:1.

DATED this 24th day of February 1982.

HOECHST AKTIENGESELLSCHAFT
DRAWINGS