610384

COMMONWEALTH of AUSTRALIA
Patents Act 1952

APPLICATION FOR A STANDARD PATENT

I/We

Atochem

of

La Defense 10, 4 & 8 Cours Michelet, Puteaux, 92800, France

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

Process for the preparation of ferric chloride from ferrous chloride

which is described in the accompanying complete specification.

Details of basic application(s):-

Number	Convention Country	Date
88 05800	France	29 April 1988

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 SEVENTH day of APRIL 1989

To: THE COMMISSIONER OF PATENTS

Keith Davies

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

Davies & Collison, Melbourne

008530 27/04/89

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 4.3.91

AM 0288

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952–1973

DECLARATION IN SUPPORT OF CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the Application made for a patent ~~patent of addition~~ for an invention entitled : "PROCESS FOR THE PREPARATION OF FERRIC CHLORIDE FROM FERROUS CHLORIDE"

Insert title of invention

I ~~We~~ Michel ROCHET,

Insert full name(s) and address(es) of declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

of: ATOCHEM, a French Body Corporate of:
La Defense 10, 4 & 8 Cours Michelet, 92800 PUTEAUX, France.

do solemnly and sincerely declare as follows :–

Cross out whichever of paragraphs 1(a) or 1(b) does not apply

1(a) relates to application made by individual(s)
1(b) relates to application made by company; insert name of applicant company.

1. (a) ~~I am We are the applicant for the patent patent of addition~~

or (b) I am authorized by

ATOCHEM,

the applicant ~~s~~ for the patent ~~patent of addition~~ to make this declaration on its ~~their~~ behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply

2(a) relates to application made by inventor(s)
2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

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

or (b) RENE CLAIR and ALAIN GALLET

of: La Vrignoise, Saint-Julien, 13500 MARTIGUES, France
and 11 Avenue de la Durance, 13117 LAVERA, France.

~~is are~~ the actual inventor S of the invention and the facts upon which the applicant ~~is~~ entitled to make the application are as follows :–

State manner in which applicant(s) derive title from inventor(s)

"The applicant would, if a patent were granted upon an application made by the inventors, be entitled to have the patent assigned to it".

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application ~~was~~ as defined by Section 141 of the Act made

in FRANCE:NO. 88 05800 on the 29th April, 1988
by ATOCHEM
in ..... on the .....
by .....
in ..... on the .....
by .....

4. The basic application referred to in paragraph 3 of this Declaration ~~was~~ the first application made in a Convention country in respect of the invention the subject of the application.

Insert place and date of signature.

Declared at ATOCHEM La Défense 10 4 et 8, Cours Michelet 92800 PUTEAUX France RCS Nanterre B 319 632 790 Tel (1) 49 00 80 80 - Telex ATO 611 92 F this 19th day of April 1989

Signature of declarant(s) (no attestation required)

Michel ROCHET

Note: Initial all alterations.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-33722/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 610384

(54) Title
PROCESS FOR THE PREPARATION OF FERRIC CHLORIDE FROM FERROUS CHLORIDE

International Patent Classification(s)
(51)[4] **C01G 049/10**

(21) Application No. : **33722/89** (22) Application Date : **27.04.89**

(30) Priority Data

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88 05800	29.04.88	FR FRANCE

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(71) Applicant(s)
ATOCHEM

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(56) Prior Art Documents
AU 33721/89 C01G 49/10
AU 33723/89 C01G 49/10

(57) Claim

1. Process for the preparation of ferric chloride from ferrous chloride, which comprises the following steps:

a) bringing chlorine and a solution containing ferrous chloride into contact in the presence of ferric chloride,

b) decompressing the product obtained in a)

c) partially recycling the liquid phase obtained in b) to step a); and recovering ferric chloride from the remaining part.

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COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

NAME & ADDRESS
OF APPLICANT:

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NAME(S) OF INVENTOR(S):

Rene CLAIR
Alain GALLET

ADDRESS FOR SERVICE:

DAVIES & COLLISON
Patent Attorneys
1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

Process for the preparation of ferric chloride from ferrous chloride

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

The present invention relates to a process for the preparation of ferric chloride from ferrous chloride. It relates more particularly to the preparation of ferric chloride in aqueous solution with analyses by titration at, say, 35 to 45% by weight. This ferric chloride formulation can be employed as a flocculating agent in water treatment. Reference may be made to Kirk-Othmer, 3rd edition, volume 24, pages 394-396 (1984) and to volume 10, page 498 (1980), where this application is mentioned. The simplest process consists in digesting iron with concentrated hydrochloric acid; a solution containing approximately 36% by weight of ferrous chloride ($FeCl_2$) is thus obtained and this is chlorinated to obtain a solution of ferric chloride ($FeCl_3$) analysing by titration at about 41% by weight and capable of being employed directly as a flocculating agent. This 41% solution is the usual commercial form. A concentrated solution of $FeCl_2$ must be obtained because $FeCl_2$ and $FeCl_3$ can undergo partial hydrolysis in the course of concentration by evaporation, giving HCl. The presence of HCl in $FeCl_3$ is a hindrance in water treatment. This process requires the use of concentrated hydrochloric acid.

US Patent 4,066,748 describes a process starting with a solution of $FeCl_2$ originating from a descaling bath. This process makes it necessary to concentrate the ferrous chloride and requires a two-step chlorination.

US Patent 3,682,592 describes a process similar to the preceding one but the ferrous chloride solution is brought into contact with oxygen.

A very simple process has now been found, according to the present invention, which makes it possible to prepare a concentrated solution of ferric chloride by chlorination of a dilute solution of ferrous chloride.

The process of the invention consists in preparing ferric chloride from ferrous chloride and comprises the following steps:

a) chlorine and a solution containing ferrous chloride are brought into contact in the presence of a solution containing ferric chloride,

b) the product obtained in a) is decompressed,

c) the liquid phase obtained in b) is partially recycled to step a); the remaining part forms the ferric chloride output.

The ferrous chloride is used in the form of an aqueous solution, as is the ferric chloride. "In the presence of ferric chloride" means that ferric chloride is added, eg. injected, into step a) in addition to ferrous chloride, this ferrous chloride being then chlorinated to ferric chloride. Liquid or gaseous chlorine, or a gas or liquid containing chlorine may be employed. The contact may be effected in any manner; it suffices to ensure contact between the chlorine and the ferrous chloride. For example,

a stirred reactor or a column of the distillation column or absorption column type may be employed. A column equipped with contact devices such as plates or packing rings or with a number of these devices may be advantageously employed. Typically ferrous chloride solution and ferric chloride solution feed the column at the top and the chlorine is introduced at the bottom of this column. A little chlorine is collected at the top of this column if an excess thereof (relative to the quantity of ferrous chloride) has been employed, together with the gases which may have accompanied the chlorine, and a little water vapour entrained by its vapour pressure. A ferric chloride solution is obtained at the bottom of the column. It is possible to introduce the ferric chloride and ferrous chloride solutions at a number of points in the column; the same applies in the case of the chlorine, which may be introduced at a number of points.

Step b) consists in decompressing the solution collected in step a). This decompression causes a partial vaporization of the water present in the ferric chloride solution; a concentration of the ferric chloride solution thus results. This decompression can be carried out in any storage vessel; it suffices that its geometry should permit the separation of the vapour phase and the liquid phase.

Step c) of the process of the invention consists in recycling a part of the above liquid phase to step a) and the remaining part which is recovered forms the output of ferric

chloride; this quantity corresponds, in the number of moles, to the quantity of ferrous chloride introduced into step a).

This solution is advantageously returned to ambient temperature.

The ferrous chloride solution which feeds step a) may be of any concentration; it may also contain hydrochloric acid. A ferrous chloride solution not containing hydrochloric acid is advantageously employed, and this makes it possible to employ the resulting ferric chloride directly as a flocculating agent for water treatment.

Step a) takes places advantageously at a moderate temperature, that is to say that this temperature, together with the residence time in step a) does not result in hydrolysis of $FeCl_2$.

The reaction between the ferrous chloride and chlorine is generally complete. A ferrous chloride residence time of at least 10 seconds and preferably shorter than 4 hours is advantageously observed.

It is not necessary to chlorinate all the $FeCl_2$; ferric chloride specifications can sometimes permit from 0.1 to 1% by weight of $FeCl_2$ in the ferric chloride solution. However it is possible to employ an excess of chlorine relative to the stoichiometry.

The temperature of the reaction medium in this step a) is advantageously fom 50 to 100°C. Any pressure may be

used in step a); for convenience, the operation is carried out from atmospheric pressure and up to 6 bars, and preferably from atmospheric pressure to 1 bar gauge.

The pressure to which the product obtained in a) is decompressed is related to the quantity of water which it is intended to evaporate. The greater the decompression, the more water is evaporated off. The quantity of water evaporated off also depends on the flow rate of the solution which is decompressed; the larger this quantity, the more is evaporated off. The quantity of ferric chloride which is recycled is advantageously from 1 to 10 times the output.

The quantity of water to be evaporated off depends on the concentration of the $FeCl_2$ solution and on the desired concentration for the $FeCl_3$ produced. The quantity of $FeCl_3$ which is recycled also makes it possible to control the temperature; the higher the recycle flow rate, for the same quantity of $FeCl_2$, the lower the temperature at the outlet of a). The heat energy supplied by the $FeCl_2$ chlorination reaction is essentially consumed by the decompression, which is reflected in a lowering of temperature. If it is desired to evaporate off more water, energy must be supplied; the product obtained in a) is advantageously heated before the decompression. The heating advantageously does not exceed 110°C, so as not to decompose the $FeCl_3$. The heating-decompression cycle can also be repeated a number of times; it is obviously sufficient to recompress the liquid phase after the decompression, for

example with the aid of a pump. Advantageously, the decompression is taken to an absolute pressure of between 0.05 and 0.3 bars. The vacuum is provided, for example, by a pump or a steam ejector.

According to another aspect of the invention, the ferric chloride solution may also be heated after the decompression and before it is recycled into step a), but quite obviously after the withdrawal of the output; this makes it possible to provide heat energy at a low level and hence to make full use of the heat energy and also not to raise the temperature of $FeCl_3$ too much.

According to another preferred form of the invention, and provided that the temperature levels are compatible, the heat energy may be transferred from the output of ferric chloride to the ferrous chloride solution feeding step a), and this makes it possible to preheat it. This recovery enables some heat energy to be gained and hence more water to be evaporated off during the decompression and less additional heat energy to be supplied before this decompression.

The advantage of the present invention is that it makes it possible to employ a dilute solution of ferrous chloride to produce a concentrated solution of ferric chloride, while avoiding the use of evaporators.

The accompanying Figure shows, diagrammatically, an example of an embodiment of the present invention. (1) represents a column in which step a) is carried out, (3) is

a decompression pot, and (2) and (4) are pumps. The ferrous chloride solution is introduced at (5), the recycled ferric chloride at (6) and the chlorine at (7). The product is led by means of pipe (8) via exchanger (11) towards the decompression pot (3). The pot (3) is connected to the vacuum system by the pipe (9). The liquid phase is removed from the decompression pot by pump (4). The output is recovered at pipe (10). The inerts introduced with the chlorine are collected at (12).

The following Examples further illustrate the present invention.

EXAMPLE 1

A device as shown in the Figure is employed, in which the column (1) is made of glass, with an inner diameter of 0.35 m and has a packing height of 10 m.

A solution of 296 kg/h of $FeCl_2$ and 705 kg/h of water at 80_oC is introduced at (5) and a flow of 82.7 kg/h of chlorine and 5 kg/h of inerts at (7). The 5 kg/h of inerts are collected at (12) and a ferric chloride solution at 85°C at (8). The column (1) operates at a pressure of 1.1 bars absolute. The ferric chloride is reheated from 85 to 94°C by the exchanger (11) and it is then decompressed to a pressure of 0.25 bars absoute. A solution containing 2272 kg/h of $FeCl_3$ and 3269 kg/h of water is recycled at (6) and 379 kg/h of $FeCl_3$ diluted in 545 kg/h of water are withdrawn at (10).

EXAMPLE 2

The procedure is as in Example 1, but a more dilute solution of $FeCl_2$ is introduced at (5), that is to say 296 kg/h $FeCl_2$ in 963 kg/h of water. The $FeCl_3$ solution at (8) is at 76°C; it is reheated to 106°C and is then decompressed to 0.15 bars absolute; the temperature of the liquid phase drops to 62°C. The same concentrated solution of $FeCl_3$ is obtained at (10)

EXAMPLE 3

The procedure is as in Example 1, but in a column 0.4 m in diameter and with a more dilute solution of $FeCl_2$ being introduced at (5), that is to say 296 kg/h of $FeCl_2$ in 963 kg/h of water. The $FeCl_3$ solution at (8) is at 69°C; it is reheated to 92°C and is then decompressed to 0.15 bars absolute. The same concentrated solution of $FeCl_3$ is obtained at (10); on the other hand, the recycle flow rate at (6) is 3790 kg/h of $FeCl_3$ diluted in 5450 kg/h of water.

The claims defining the invention are as follows:

1. Process for the preparation of ferric chloride from ferrous chloride, which comprises the following steps:

a) bringing chlorine and a solution containing ferrous chloride into contact in the presence of ferric chloride,

b) decompressing the product obtained in a)

c) partially recycling the liquid phase obtained in b) to step a); and recovering ferric chloride from the remaining part.

2. Process according to claim 1 in which step b) is preceded by heating.

3. Process according to claim 1 or 2, in which the quantity of ferric chloride which is recycled is from 1 to 10 times the amount recovered.

4. Process according to any one of claims 1 to 3, in which the ferric chloride recovered is employed to heat the ferrous chloride solution upstream of step a).

5. Process according to claim 1 substantially as described in any one of the Examples.

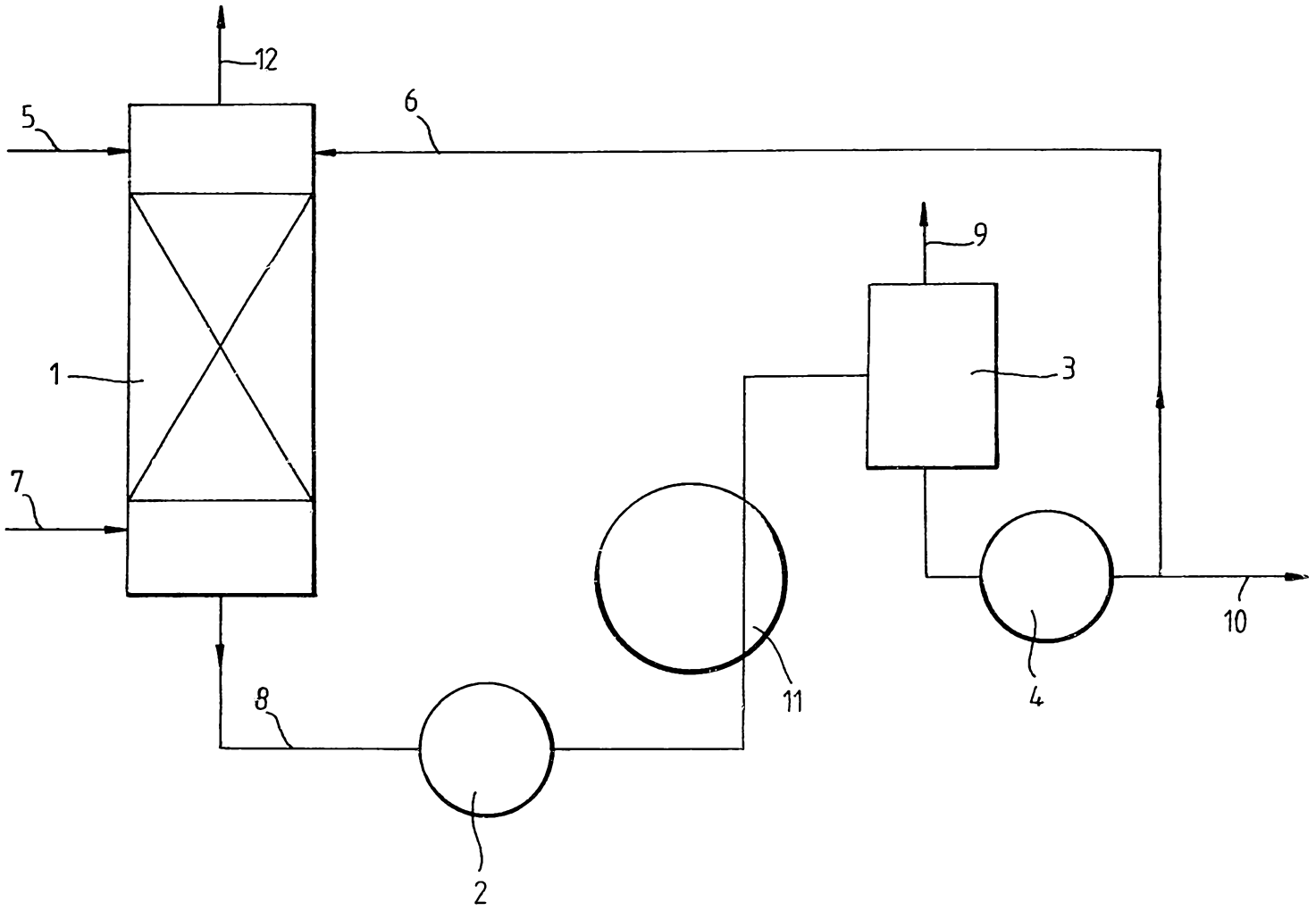
6. Ferric chloride whenever prepared by a process as claimed in any one of the preceding claims.

7. The steps, features, compositions and compounds disclosed herein or referred to or indicated in the specification and/or claims of this application, individually or collectively, and any and all combinations of any two or more of said steps or features.

DATED this TWENTY SEVENTH day of APRIL 1989

Atochem

by DAVIES & COLLISON
Patent Attorneys for the applicant(s)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