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# METHOD FOR PRODUCING CHLORINE BY GAS PHASE OXIDATION

#### (57) Abstract:

-21 - Method for Producing Chlorine By Gas Phase Oxidation Abstract The present invention provides a process for producing chlorine by the catalytic gas phase oxidation of hydrogen chloride with oxygen, wherein the reaction is performed on at least two catalyst beds under adiabatic conditions, as well as a reactor system for performing the process. Figure 1

### Method for Producing Chlorine By Gas Phase Oxidation

#### Abstract

The present invention provides a process for producing chlorine by the catalytic gas phase oxidation of hydrogen chloride with oxygen, wherein the reaction is performed on at least two catalyst beds under adiabatic conditions, as well as a reactor system for performing the process.

Figure 1

#### Method for Producing Chlorine By Gas Phase Oxidation

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The present invention provides a process for producing chlorine by the catalytic gas phase oxidation of hydrogen chloride with oxygen, wherein the reaction is performed on at least two catalyst beds under adiabatic conditions, as well as a reactor system for performing the process.

The process for the catalytic oxidation of hydrogen chloride with oxygen in an exothermic equilibrium reaction, developed by Deacon in 1868, was devised at the very beginning of industrial chlorine chemistry:

$$4 \text{ HCl} + \text{O}_2 \Rightarrow 2 \text{ Cl}_2 + 2 \text{ H}_2\text{O}$$

However, chloralkali electrolysis pushed technical application of the Deacon process right into the background. Almost the entire production of chlorine was achieved using the electrolysis of aqueous common salt solutions. The attractiveness of the Deacon process has increased again in recent times, however, because the worldwide requirement for chlorine is growing more strongly than the demand for caustic soda solution, an associated product from the electrolysis of NaCl. A process for producing chlorine by the oxidation of hydrogen chloride that is independent of the production of caustic soda solution fits in with this development. In addition, the intermediate hydrogen chloride is readily available; it is produced in large amounts, for example during phosgenation reactions, as an associated product from the production of isocyanates.

The dissipation and use of the heat of reaction is an important point when performing the Deacon process. An uncontrolled rise in temperature, that can amount to 600 to 900°C from start to finish of the Deacon reaction, would lead on the one hand to permanent damage to the catalyst and, on the other hand, to an unfavourable shift of the reaction equilibrium in the direction of the feedstocks at

high temperatures, with a corresponding impairment in the yield. Therefore, it is advantageous to keep the temperature of the catalyst bed during the course of the reaction within the range 150 to 600°C.

In established processes, the catalyst is used in the form of a fluidised, thermally stabilised bed. According to EP 0 251 731 A2, the catalyst bed is held at constant temperature via the outer wall; in accordance with DE 10 2004 006 610 A1, the fluidised bed is held at constant temperature via a heat exchanger located within the bed. The effective removal of heat in this process is counterbalanced by problems due to non-uniform distribution of residence times and catalyst abrasion, both of which lead to losses in conversion.

A narrow distribution of residence times and low catalyst abrasion are possible in reactors with fixed catalyst beds. However, problems with maintaining a constant temperature in the catalyst beds arise in such reactors. Therefore thermostated multitube-flow reactors are generally used, these having a very costly cooling circuit, particularly in the case of large reactors (WO 2004/052776 A1).

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In order to improve the removal of heat from the catalyst bed, R&D Report "Sumitomo Kagaku", vol. 2004-1, suggests the use of a fixed-bed catalyst made of ruthenium oxide on titanium oxide as support. In addition to the high catalyst activity, the good thermal conductivity of the catalyst system is mentioned as an advantage. Since, however, even in the event of high thermal conductivity within the catalyst pellets, the thermal conductivity of the bed is still low, the removal of heat is not substantially improved by this measure.

EP 1 170 250 A1 suggests using catalyst packings in multitube-flow reactors, these having different activities in each of the different regions of the cooled contact tube. In this way, progress of the reaction is slowed down sufficiently for the heat of reaction being produced to be more easily removed via the wall of the contact tube. A similar result should be achieved by targeted dilution of the catalyst bed with an

inert material. The disadvantages of this solution are that two or more catalyst systems have to be developed and used in the contact tubes and that the capacity of the reactor is impaired by the use of an inert material.

The possibility of the adiabatic catalytic oxidation of hydrogen chloride is 5 mentioned, although in general terms, in WO 2004/037718 and WO 2004/014845, in addition to the preferred isothermal process. Concrete embodiments of an adiabatically managed hydrogen chloride oxidation, however, are not described. Thus it is still not at all clear how the heat of reaction is removed from the 10 exothermic reaction and how damage to the catalyst can be avoided in the event of a completely adiabatic procedure for the overall process. According to these documents, however, the oxidation of hydrogen chloride actually takes place isothermally, as a fixed-bed process in multitube-flow reactors that, as mentioned above, require a cooling system that is extremely costly to regulate. Basically, all the 15 multitube-flow reactors described are also very complex and demand high investment costs. Problems with regard to mechanical strength and uniform thermostating of the catalyst bed increase rapidly with the size of the structure and make large units of equipment of this type uneconomic.

It would therefore be advantageous to provide a simple process that can be performed in a simple reactor without a costly system for managing the heat in the reactor. Such reactors would be easy to transfer to an industrial scale and are inexpensive and robust, whatever the size. The enthalpy of reaction is reflected quantitatively, in this type of reactor, in the temperature difference between the feedstock gas stream and the product gas stream.

Hitherto, neither has the use of such reactors been described nor have suitable catalysts and suitable processes been demonstrated, for the exothermic gas phase oxidation of hydrogen chloride with an oxygen-containing gas stream.

The catalysts initially used for the Deacon process, for example supported catalysts containing the active substance CuCl<sub>2</sub>, have only low activities. Although the activity could be increased by raising the reaction temperature, the disadvantage was that the volatility of the active component led to rapid deactivation of the catalyst at elevated temperature. In addition, the oxidation of hydrogen chloride to give chlorine is an equilibrium reaction. The position of the equilibrium shifts with increasing temperature, to the disadvantage of the desired end product.

Therefore, catalysts with the highest possible activity are generally used, these allowing the reaction to proceed at a lower temperature. Known highly active catalysts are based on ruthenium. DE-A 197 48 299 describes supported catalysts containing the active substance ruthenium oxide or a ruthenium mixed oxide. In these, the concentration of ruthenium oxide is 0.1 wt.% to 20 wt.% and the average particle diameter of ruthenium oxide is 1.0 nm to 10.0 nm. The reaction is performed at a temperature between 90°C and 150°C. Other supported catalysts based on ruthenium are disclosed in DE-A 197 34 412: ruthenium chloride catalysts that contain at least one compound of titanium oxide or zirconium oxide, rutheniumcarbonyl complexes, ruthenium salts of inorganic acids, ruthenium-nitrosyl complexes, ruthenium-amine complexes, ruthenium complexes of organic amines or ruthenium-acetylacetonate complexes. The reaction is performed at a temperature between 100°C and 500°C, preferably between 200°C and 380°C. In both the applications DE-A 197 48 299 and DE-A 197 34 412, the catalyst is used in a fixedbed or a fluidised bed. Air or pure oxygen is used as the oxygen starting substance. However, the Deacon reaction is still an exothermic reaction and temperature control is required, even when using such highly active catalysts.

Thus, there is the task of providing a process for the catalytic oxidation of hydrogen chloride to give chlorine that can be performed in a simple reactor without a complex system for heat management in the reactor.

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Surprisingly, the inventor of the present invention found that it is possible to achieve the object described above by performing the reaction on at least two catalyst beds under adiabatic conditions.

The present invention therefore provides a process for producing chlorine by the catalytic gas phase oxidation of hydrogen chloride with oxygen, characterised in that the reaction is performed on at least two catalyst beds under adiabatic conditions. The reaction is preferably performed on at least two catalyst beds connected in series.

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The process gas may contain, in addition to oxygen and hydrogen chloride, other secondary constituents, e.g. nitrogen, carbon dioxide, carbon monoxide or water. The hydrogen chloride may arise from an upstream production process, e.g. for producing polyisocyanates, and may contain other impurities, e.g. phosgene.

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According to the invention, performing the process under adiabatic conditions on the catalyst beds means that substantially no external heat is supplied to and no heat is removed from the catalyst in the relevant catalyst beds (with the exception of the heat that is supplied or removed by the reaction gas entering and leaving). Technically, this is achieved by isolating the catalyst beds in a manner known per se. An essential feature of the invention is that the individual catalyst beds are operated adiabatically, so that in particular no means for removing heat is provided therein. If the process is considered as a whole, then, according to the invention, the case in which the heat of reaction is removed, for example using heat exchangers connected between the individual catalyst beds, is also included.

The advantage of the adiabatic procedure in the catalyst beds according to the invention, as compared to the conventional isothermal procedure, comprises in particular that agents for the removal of heat do not have to be provided in the catalyst beds and this is associated with considerable simplification of the design.

This produces in particular simplifications when manufacturing the reactor and also when changing the scale of the process.

Here, a catalyst bed is understood to be an arrangement of the catalyst in any manifestation known per se, e.g. fixed-bed, fluidised bed or moving bed. A fixed-bed arrangement is preferred. This includes a catalyst bed in the true sense, i.e. a loose, supported or unsupported catalyst in any form at all, as well as in the form of suitable packings.

The expression catalyst bed, as used here, also includes coherent regions of suitable packings on a support material or structured catalyst support. These would be, for example, ceramic honeycomb structures with comparatively large geometric surface areas that are coated, or corrugated layers of metal gauze, on which are immobilised, for example, granules of catalyst.

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In the new process, fixed-bed catalysts are preferably used.

Another preferred embodiment of the process is characterised in that the process gas mixture emerging from at least one catalyst bed is then passed over at least one heat-exchanger located downstream of the catalyst bed.

In another particularly preferred embodiment of the process, at least one, preferably one, heat-exchanger, over which the emerging process gas mixture is passed, is located downstream of each catalyst bed.

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In a preferred embodiment at least one heat-exchanger is located downstream of at least one catalyst bed. Particularly preferably at least one, more preferably only one, heat exchanger, over which the gas mixture emerging from the catalyst bed is passed, is located downstream of each of the catalyst beds.

Preferably more than two catalyst beds may also be connected in series for the process, in particular up to 12, preferably up to 8, catalyst beds. Processes with 3 to 8 catalyst beds connected in series with each other are particularly preferred.

The catalyst beds may be arranged in one reactor or divided between several reactors. Arranging the catalyst beds in one reactor leads to a reduction in the number of units of equipment used.

In addition, some of the catalyst beds connected in series may, independently, also be replaced or supplemented by one or more catalyst beds connected in parallel. The use of catalyst beds connected in parallel enables in particular the exchange or topping up of these while maintaining continuous overall operation of the process.

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However, the process according to the invention preferably has at least two catalyst beds connected in series. In particular, catalyst beds connected in parallel and in series may also be combined with each other. However, the process according to the invention particularly preferably has catalyst beds connected exclusively in series.

If catalyst beds connected in parallel are preferably used, then in particular at most 5, preferably 3, particularly preferably at most 2 process lines, optionally consisting of catalyst beds connected in series, are connected in parallel. Accordingly, the new process can be operated with for example up to 60 and with at least two catalyst beds.

The reactors preferably used according to the invention may consist of simple containers with one or more thermally isolated catalyst beds such as are described, for example, in Ullmanns Encyclopedia of Industrial Chemistry (Fifth, Completely Revised, Edition, vol. B4, pages 95-104, pages 210-216). That is, for example, simple or multistage fixed-bed reactors, radial-flow reactors or else shallow-bed reactors may be used. Multitube-flow reactors, however, are preferably not used, according to the invention, due to the disadvantages described above. Since,

according to the invention, removal of heat does not take place from the catalyst beds, these types of reactors are also unnecessary for holding the catalyst beds.

The catalysts or catalyst beds thereof are mounted, in a manner known per se, on or between gas-permeable partitions in the reactor. In particular in the case of thin catalyst beds, industrial devices for uniform distribution of gas are mounted above, below or above and below the catalyst beds. These may be perforated plates, bubble-cap trays, valve trays or other inserts that bring about uniform entrance of the gas into the catalyst bed by producing a small, but uniform, pressure loss.

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The guideline speed for the gas in the catalyst bed in the case of the embodiment using a fixed-bed is preferably 0.1 to 10 m/s.

In a particular embodiment of the process according to the invention, a molar ratio between 0.25 and 10 equivalents of oxygen to one equivalent of hydrogen chloride prior to introduction into the catalyst bed is preferably used. By increasing the ratio of equivalents of oxygen to one equivalent of hydrogen chloride, on the one hand the reaction can be accelerated and thus the space-time yield (amount of chlorine produced per reactor volume) can be increased and, on the other hand, the equilibrium of the reaction can be shifted positively in the direction of the products.

In another particularly preferred embodiment of the process, the inlet temperature of the gas mixture entering the first catalyst bed is 150 to 400°C, preferably 200 to

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370°C.

The feedstock stream containing hydrogen chloride and oxygen may also preferably be introduced only upstream of the first catalyst bed. This has the advantage that the entire feedstock gas stream can be used for taking up and removing the heat of reaction in all the catalyst beds. However, it is also possible to add hydrogen chloride and/or oxygen to the gas stream as required upstream of one or several of

the catalyst beds that follow after the first catalyst bed. The temperature of reaction can also be controlled by supplying gas between the catalyst beds that are used.

In a particularly preferred embodiment of the process according to the invention, the reaction gas is cooled after at least one of the catalyst beds used, particularly preferably after each of the catalyst beds used. For this purpose, the reaction gas is passed through one or more heat exchangers that are located downstream of the relevant catalyst beds. These may be heat exchangers familiar to a person skilled in the art such as e.g. shell-and-tube, parallel plate, annular groove, spiral, fin-tube or micro heat exchangers. In a particular embodiment of the process, steam is produced when cooling the product gas in the heat exchangers.

In a preferred embodiment of the process, the catalyst beds connected in series are operated with mean temperatures that increase or decrease from catalyst bed to catalyst bed. This means that the temperature may be allowed to either rise or sink from catalyst bed to catalyst bed within a sequence of catalyst beds. Thus, it may be particularly advantageous initially to allow the mean temperature to rise from catalyst bed to catalyst bed in order to increase the catalyst activity and then to allow the mean temperature to drop again in the subsequent final beds, in order to shift the equilibrium. This can be adjusted, for example, via the control system for the heat exchangers located between the catalyst beds. Further possibilities for adjusting the mean temperature are described below.

In a preferred secondary step in the new process, the chlorine formed is separated.

The separation step generally includes several stages, that is the separation and optionally the recycling of unreacted hydrogen chloride from the product gas stream for catalytic oxidation of hydrogen chloride, drying of the stream containing substantially chlorine and oxygen and the separation of chlorine from the dried stream.

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The separation of unreacted hydrogen chloride and of water vapour that is formed can be achieved by condensing out aqueous hydrogen chloride from the product gas stream for the oxidation of hydrogen chloride by cooling. Hydrogen chloride may also be absorbed in dilute hydrochloric acid or water.

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In a preferred embodiment of the process, unreacted hydrogen chloride and/or oxygen are recycled to the reaction, after separating chlorine and water from the product stream and after diverting a small amount of the gas in order to keep constant the gaseous components that may be entrained with the feedstocks. The recycled hydrogen chloride and/or oxygen are reintroduced upstream of one or more catalyst beds and are first returned to the inlet temperature, optionally using a heat exchanger. Cooling of the product gas and heating of the recycled hydrogen chloride and/or oxygen is advantageously achieved by running the gas streams past each other in counterstream through heat exchangers.

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The new process is preferably operated at a pressure of 1 to 30 bar, more preferably 1 to 20 bar, particularly preferably 1 to 15 bar.

The temperature of the feedstock gas mixture upstream of each of the catalyst beds is preferably 150 to 400°C, more preferably 200 to 370°C, particularly preferably 250 to 350°C. The gas mixture is preferably homogenized before introduction to the individual catalyst bed.

The thicknesses of the catalyst beds being traversed are chosen to be identical or different and are expediently 1 cm to 8 m, preferably 5 cm to 5 m, particularly preferably 30 cm to 2.5 m.

The catalyst is preferably used immobilised on a support. The catalyst preferably contains at least one of the following elements: copper, potassium, sodium, chromium, cerium, gold, bismuth, ruthenium, rhodium, platinum, as well as the elements from subgroup VIII in the Periodic Table of Elements. These are preferably

used as oxides or halides or mixed oxides/halides, in particular chlorides or oxides/chlorides. These elements or compounds thereof may be used individually or in any combination with each other.

5 Preferred compounds of these elements include: copper chloride, copper oxide, potassium chloride, sodium chloride, chromium oxide, bismuth oxide, ruthenium oxide, ruthenium oxychloride, rhodium oxide.

The catalyst component particularly preferably consists entirely or partly of ruthenium or compounds thereof; the catalyst particularly preferably comprises a halide and/or oxygen-containing compounds of ruthenium.

The support component may consist entirely or partly of: titanium oxide, tin oxide, aluminium oxide, zirconium oxide, vanadium oxide, chromium oxide, silicon oxide, silica, carbon nanotubes or a mixture or compound of the substances mentioned, such as in particular mixed oxides such as silicon-aluminium oxides. Particularly preferred support materials are tin oxide and carbon nanotubes.

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Ruthenium supported catalysts may be obtained, for example, by soaking the support material with aqueous solutions of RuCl<sub>3</sub> and optionally a promoter for doping purposes. The catalyst can be moulded into shape after or, preferably, before soaking the support material.

Promoters that are suitable for doping the catalyst are alkali metals such as lithium, sodium, potassium, rubidium and caesium, preferably lithium, sodium and potassium, particularly preferably potassium, alkaline earth metals such as magnesium, calcium, strontium and barium, preferably magnesium and calcium, particularly preferably magnesium, rare earth metals such as scandium, yttrium, lanthanum, cerium, praseodymium and neodymium, preferably scandium, yttrium, lanthanum and cerium particularly preferably lanthanum and cerium, or mixtures of these.

The moulded items may then be dried and optionally calcined at a temperature of 100 to 400°C, preferably 100 to 300°C, under an atmosphere of for example nitrogen, argon or air. The moulded items are preferably first dried at 100 to 150°C and then calcined at 200 to 400°C.

The temperature of the catalyst in the catalyst beds is expediently within a range of 150°C to 800°C, preferably 200°C to 450°C, particularly preferably 250°C to 400°C. The temperature in the catalyst beds is preferably regulated by at least one of the following measures:

- appropriate sizing of the catalyst beds,
- regulating the removal of heat between the catalyst beds,
- supplying feedstock gases between the catalyst beds,
- molar ratio of the feedstocks,
- concentrations of the feedstocks,
  - adding inert gases, in particular nitrogen, carbon dioxide, upstream of and/or between the catalyst beds.

In principle, the catalysts and supported catalysts may have any shape at all, e.g. beads, rods, Raschig rings or granules or tablets.

The composition of the catalysts in the catalyst beds used according to the invention may be identical or different. In a preferred embodiment identical catalysts are used in each bed. However, different catalysts may also advantageously be used in the individual beds. Thus, a less active catalyst may be used in particular in the first bed when the concentration of the reaction products is rather high, and the activity of the catalyst may then be increased from catalyst bed to catalyst bed in the subsequent beds. The catalyst activity may also be controlled by diluting with inert materials or support material.

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Using the process according to the invention, 0.1 g/h to 10 g/h of chlorine, preferably 0.5 g/h to 5 g/h of chlorine, can be produced per 1 g of catalyst. The process according to the invention is thus characterised by high space-time yields, associated with a reduction in the size of the equipment used and also simplification of the equipment and the reactors.

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The feedstock for the process according to the invention is hydrogen chloride that has been produced and transferred e.g. as an associated product during the phosgenation of organic amines, in particular diamines, to give isocyanates, in particular diisocyanates, or during the gas phase phosgenation of phenyl to give diphenyl carbonate.

Oxygen may be supplied as pure oxygen or, preferably, in the form of an oxygencontaining gas, in particular air.

The chlorine produced may be used e.g. to produce phosgene, and optionally recycled to linked production processes.

The invention also provides a reactor system for reacting a gas that contains hydrogen chloride and oxygen, containing at least pipework for hydrogen chloride and oxygen or for a mixture of hydrogen chloride and oxygen and at least two thermally isolated catalyst beds connected in series.

Preferred specific examples of the process according to the invention are shown in figures 1 to 4, without thereby restricting the invention thereto.

#### **Examples**

#### Example 1

Fig. 1 shows the process according to the invention with three catalyst beds in series divided between three separate reactors. The feedstock gases are mixed upstream of the first reactor and supplied to the reactor. After each of the reactors, the emerging product gas is cooled using a shell-and-tube heat exchanger of the conventional type. After emerging from the third heat exchanger, chlorine and water are separated from the product gas.

#### Example 2

Fig. 2 shows the process according to the invention with three catalyst beds in series in an integrated reactor. The feedstock gases are mixed upstream of the reactor and fed to this. Following each of the catalyst beds, the emerging product gas is cooled using a heat exchanger also integrated in the pressurised container for the reactor. After emerging from the reactor, chlorine and water are separated from the product gas.

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#### Example 3

Fig. 3 shows the process according to the invention with a layout that corresponds by and large to the one shown in Fig. 1. The difference is that, upstream of the second and third reactors in series, fresh feedstock gas is introduced into the cooled product gas from the preceding reactor.

#### Example 4

Fig. 4 shows the process according to the invention with a layout that corresponds by and large to the one shown in Fig. 3. The difference is that the hydrogen chloride and

oxygen separated from the product gas stream are recycled and admixed with the feedstock gas stream upstream of the first reactor.

#### Example 5

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#### Working example

Chlorine was produced by the catalytic gas phase oxidation of hydrogen chloride with oxygen in an experimental plant. Calcined ruthenium chloride on tin dioxide as support material was used as the catalyst. The experimental plant consisted of six reactors connected in series, each with a thermally isolated catalyst bed. A heatexchanger was located between each of the reactors, that is a total of five, that cooled the gas stream emerging from each of the relevant upstream reactors to the inlet temperature required for each of the relevant downstream reactors. Oxygen (29 kg/h), together with nitrogen (25 kg/h) and carbon dioxide (13.5 kg/h), was heated to about 305°C using an electrical preheater and then introduced to the first reactor. The hydrogen chloride (47.1 kg/h) was heated to about 150°C and then divided into a total of 6 substreams. One of each of these substreams of hydrogen chloride was supplied to each reactor, wherein, in the first reactor, the hydrogen chloride substream was added to the gas stream consisting of oxygen, nitrogen and carbon dioxide, in between the electrical preheater and the reactor inlet. Each of the other hydrogen chloride substreams was added to the gas stream upstream of one of the five heat-exchangers. Table 1 shows the temperature of the gas mixture introduced to and emerging from all six reactors as well as the amount of hydrogen chloride supplied to each reactor. The total conversion of hydrogen chloride was 82.4 %.

Table 1:

Reactor number	Hydrogen chloride substream [kg/h]	Inlet temperature [°C]	Outlet temperature [°C]
1	10.5	290.4	381.0
2	7.3	321.5	377.0
3	6.7	332.8	379.3
4	7.0	332.2	376.7
5	8.2	332.0	373.1
6	7.4	332.9	367.5

## Key to the numbering on the figures:

	1	Hydrogen chloride (feedstock)
	2	Oxygen (feedstock)
5	3	Mixed feedstock gas stream
	4, 5, 6	Product gases from the reactors
	7, 8, 9	Product gases cooled by heat exchangers
	10	Hydrogen chloride (from product gas)
	11	Oxygen (from product gas)
10	12	Chlorine
	13	Water
	14, 16, 18	Cooling medium supply
	15, 17, 19	Cooling medium discharge
	20, 21	Supply of fresh feedstock gas (hydrogen chloride and/or oxygen)
15	22	Recycled hydrogen chloride and/or oxygen separated from the product gas
	I, II, III	Reactor beds
	IV, V, VI	Heat exchangers
20	VII	Material separation for product stream in accordance with the prior art

#### **Claims**

- 1. Process for producing chlorine by catalytic gas phase oxidation of hydrogen chloride with oxygen, that comprises at least: reacting hydrogen chloride with oxygen on at least two catalyst beds under adiabatic conditions.
  - Process according to Claim 1 characterised in that the reaction takes place on at least two catalyst beds connected in series.
- 10 3. Process according to Claim 1 or 2, characterised in that the temperature of the catalyst in the catalyst beds particularly during reaction is 150°C to 800°C, preferably 200 to 450°C.
- Process according to at least one of Claims 1 to 3, characterised in that the
   process gas mixture emerging from at least one catalyst bed is then passed over at least one heat-exchanger downstream of the catalyst bed.
- Process according to Claim 4, characterised in that at least one heat-exchanger, preferably a single heat-exchanger, over which the emerging
   process gas mixture is passed, is located downstream of each catalyst bed.
  - 6. Process according to at least one of Claims 1 to 5, characterised in that the reaction is performed at a pressure of 1 to 30 bar.
- 25 7. Process according to at least one of Claims 1 to 6, characterised in that the inlet temperature of the gas mixture entering a first catalyst bed is 150 to 400°C, preferably 200 to 370°C.
- 8. Process according to Claim 7, wherein the inlet temperature of the gas mixture entering each of the catalyst beds is 150 to 400°C, preferably 200 to 370°C, particularly preferably 250 to 350°C.

9. Process according to one of Claims 1 to 8, characterised in that the catalyst beds connected in series are operated at a mean temperature that increases or decreases from catalyst bed to catalyst bed.

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10. Process according to one of Claims 1 to 9, characterised in that the molar ratio of oxygen to hydrogen chloride upstream of the inlet to each catalyst bed is 0.25 to 10 equivalents of oxygen, preferably 0.5 to 5 equivalents of oxygen, to one equivalent of hydrogen chloride.

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- 11. Process according to at least one of Claims 1 to 10, characterised in that the reaction is performed on 2 to 12, preferably 2 to 8, particularly preferably 3 to 8 catalyst beds connected in series.
- 15 12. Process according to one of Claims 1 to 11, characterised in that one or more individual catalyst beds may each be replaced, independently, by two or more catalyst beds connected in parallel.
- Process according to one of Claims 1 to 12, characterised in that the inlet gas
   stream containing hydrogen chloride and oxygen is supplied only to the first catalyst bed.
  - 14. Process according to one of Claims 1 to 13, characterised in that fresh hydrogen chloride and/or oxygen is metered into the process gas stream upstream of one or more catalyst beds located downstream of the first catalyst bed.
- 15. Process according to one of Claims 1 to 14, characterised in that the catalyst contains at least one element that is chosen from the group comprising: copper, potassium, sodium, chromium, cerium, gold, bismuth, ruthenium,

rhodium, platinum and elements from subgroup VIII in the Periodic Table of Elements.

- 16. Process according to one of Claims 1 to 15, characterised in that the catalyst 5 is based on ruthenium or a ruthenium compound.
  - 17. Process according to one of Claims 1 to 16, characterised in that the activities of the catalysts in the individual catalyst beds differ and in particular increase from catalyst bed to catalyst bed.
  - 18. Process according to one of Claims 1 to 17, characterised in that the catalyst in the catalyst beds is applied to an inert support.
- 19. Process according to Claim 18, characterised in that the catalyst support 15 consists entirely or partly of titanium oxide, tin oxide, aluminium oxide, zirconium oxide, vanadium oxide, chromium oxide, silicon oxide, silica, carbon nanotubes or a mixture or compound of the substances mentioned.
- 20. Reactor system for reacting a gas containing hydrogen chloride and oxygen, 20 containing at least pipework for hydrogen chloride and oxygen or for a mixture of hydrogen chloride and oxygen and at least two thermally isolated catalyst beds connected in series.









