PROCESS FOR CONDENSING HYDROGENOUS CHLORINE GAS

Heinz Schmidt, Paul Reinschagen, Waldemar Ziessner, and Franz Holzinger, all of Frankfurt am Main, Germany, assignors to Farbwerke Hoechst Aktiengesellschaft, Frankfurt am Main, Germany, a corporation of Germany.

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The present invention relates to a process for the condensation of hydrogenous chlorine gas.

The high requirements today demanded of chlorine in further processing call for a development of processes which enable chlorine gas to be condensed practically quantitatively and the maximum yield to be obtained in liquid form.

The same holds true for the case where only part of the chlorine undergoes condensation but where there is no use for the inferior quality chlorine residue of the condensation.

Chlorine from plants which decompose aqueous solutions of alkali metal chlorides contains always certain amounts of CO₂, H₂O and N₂.

The gases, which are uncondensable under the pressure and temperature conditions of the chlorine condensation, appear in cell chlorine in a proportion of 1—2% dependent on the process applied and the operating conditions in modern plants, but the proportion of these gases in cell chlorine may be considerably greater when the process used is disturbed or when the plants are in poor condition. When, for example, the gas used as starting material has been produced electrolytically by the mercury process, it is found in a 90% condensation that the residual gas normally contains already about 4% of H₂O, which is said to be the tolerable upper limit for a non-explosive character of the escaping gas mixture.

A process has already been described in the pertinent literature (Ind. & Eng. Chem., September 1953, page 1832) wherein a 98.5% condensation is reached in that the compression is carried out in two stages and liquefaction is brought about by cooling; in this process the escaping gases are diluted with air following each stage to be below the explosion limit.

This known process involves, however, the disadvantage that stronger load variations imply a constant control of the amount of air introduced in order to prevent too strong or too low an air dilution and accordingly a deterioration of the condensation degree in the second stage, or the evolution of explosive gas mixtures.

A further disadvantage of the known process resides in the fact that it is carried out under a relatively high pressure, for example under a pressure of 1.26 atmospheres gauge in the first stage and under a pressure of 3.85 atmospheres gauge in the second stage of the process, and an error in dosing the air gives rise easily to an ignition of the gas mixture in the second stage.

The known process is further complicated in that the air must be carefully dried prior to being used for dilution.

Processes are also known which are carried out in the absence of preventive measures whatsoever against the evolution of highly explosive residual gases. The risks involved in these processes, i.e., that walls of iron contain, conduits or fittings may burn off in the chlorine current, following the ignition at a temperature slightly above 100° C. are well known in the art.

We have found that the aforesaid disadvantages can be avoided and that hydrogenous chlorine gas can be liquefied almost quantitatively without the danger of explosion by liquefying more than 99.5% of the chlorine gas, that is 1% more than in the known process referred to above.

In carrying out the process of this invention chlorine gas is forced into a cooling device by means of a con
eveyor, wherein the condensation is carried out in various stages, preferably in two stages, provided the chlorine gas is condensed in the first stage or first stages by means of a cooler of known design so that the evolution of explosive residual gas is avoided and provided that the chlorine is condensed in the second or following cooling stages, for example to an extent of more than 99.5%, to evolve explosive residual gas, the latter stages being so designed that the gas is distributed into smallest spaces for condensation.

The following statements are made to illustrate the invention.

Chlorine is compressed in one stage and cooled in at least two stages, the pressure and temperature applied being so selected that the chlorine is condensed in the first cooling stage or cooling stages to evolve a residual gas the hydrogen content of which is below the explosion limit, that is below 4%. In the second stage or the following stages, the chlorine is cooled to so low a temperature that more than 99.5% of the chlorine used is liquefied. The residual gas evolved has an explosive character. In order to prevent the expansion of an explosion wave in the case of an ignition, if any, the gas chambers are so narrowly designed that at a local ignition the dissipation of the heat evolved takes place so rapidly that the explosion wave cannot expand. In order to prevent explosive gas mixture from diffusing into the larger spaces of the first cooling stage in the event the production is interrupted, nonreturn valves of suitable design are inserted between the first and second stages or the following stages which contain nonexplosive chlorine and explosive residual gas.

The coolers used in the second stage or the stages with explosive residual gas may be of various types. There may be employed, for example, a bundle of very narrow tubes or narrow annular spaces may be formed in more spacious tubes by means of replacement bodies. The cooling spaces may be filled with bodies which are in a good heat-conducting contact with the cooled walls and distribute the gas to be condensed into small units of volume.

In order to prevent that the heat transmission is handicapped, it is advantageous to very carefully purify the chlorine to be treated. In accordance with today's drying technique with sulfuric acid, the purifying apparatus is shifted towards the side of dry chlorine. In this case, purification may be brought about by means of a mechanical or electrostatic filter. When the chlorine is dried in known manner by cooling the moist chlorine gas to a temperature which, advantageously, is lower than 0° C. in the presence of hydrogen chloride, then it is suitable to purify the chlorine electrostatically.

In order to avoid the ignition, all apparatus parts are grounded so that differences in potential, for example owing to static electricity, which may involve spark formation cannot occur.

The following example serves to illustrate the invention, but it is not intended to limit it thereto:

Example

Chlorine from a mercury cell plant of the following composition

98.8 percent by volume of chlorine
0.6 percent by volume of CO₂
0.4 percent by volume of H₂
0.2 percent by volume of N₂ + O₂
was compressed to a total pressure of 2.5 atmospheres absolute. The first stage was cooled to a temperature of
-20° C.; about 90% of the chlorine was liquefied. The residual gas had the following composition:

89.35 percent of chlorine
3.55 percent H₂
5.33 percent CO₂
1.78 percent N₂+O₂

Between the first and second stages a nonreturn security means was inserted in the form of a check valve through which the residual gas of the first stage entered into the second stage. The chlorine in the second stage was cooled to -60° C. by means of boiling difluoromono-chloromethane (CHF₂Cl). The cooler consisted of a bundle of tubes (internal diameter: 5 mm.) which were charged with displacement rods provided with spacer nodes so that annular spaces were formed (diameter: 1.5 mm.).

99.8% of the chlorine was liquefied; the residual gas had the following composition:

7.69 percent of chlorine
30.77 percent H₂
46.16 percent CO₂
15.39 percent N₂+O₂

We claim:

1. A process for condensing hydrogen-containing chlorine gas which comprises cooling said gas in a first stage, while under superatmospheric pressure, to a temperature sufficient to condense a proportion of the chlorine therein that is insufficient to leave an uncondensed residual gas containing an explosive proportion of hydrogen, and further cooling said residual gas in a second stage for condensing additional chlorine and thereby forming a second stage residual gas containing an explosive proportion of hydrogen, said second stage comprising a plurality of small cooling zones capable of confining and rapidly dissipating the heat of any small local explosions of said second stage residual gas.

2. A process as defined in claim 1 wherein the first and second stage cooling steps are carried out at a pressure of approximately 2.5 atmospheres.

3. A process as defined in claim 1 wherein the proportion of chlorine condensed in the first stage is approximately 90% of the chlorine contained in the initial hydrogen-containing gas.

4. A process as defined in claim 1 wherein the proportion of chlorine condensed in the first stage is approximately 90% of the chlorine contained in the initial hydrogen-containing gas and the proportion of total chlorine condensed in the first and second stages is in excess of 99.5% of the chlorine contained in the initial hydrogen-containing gas.

5. A process as defined in claim 1 wherein the first and second stage cooling steps are carried out at a pressure of approximately 2 atmospheres, the initial gas is cooled to a temperature of about -20° C. in the first stage and to a temperature of about -60° C. in the second stage.

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