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PROCESS OF MANUFACTURING TETRACHLOROETHYLENE

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My invention relates to improvements in the process of manufacturing tetrachloroethylene C_2Cl_4 from ethane tetrachloride. Processes in which ethane tetrachloride or ethylene trichloride in mixture with the corresponding amount of chlorine at elevated temperature are passed in contact with the catalysts, such as active carbon, are known. In these processes tetrachloroethylene is produced while hydrogen chloride is split off. The reaction follows the following equation

$$C_2H_2+3Cl_2=C_2Cl_4+2HCl.$$

Accordingly in the known processes for 1 mol of acetylene 3 mols of chlorine are needed, 2 mols of chlorine being consumed for producing the tetrachloroethylene, while 1 mol is transformed, in one of the said known processes, into chloride of an alkaline earth or an alkali metal, or, in a more recent catalytical process, into hydrogen chloride.

One of the objects of the invention is to provide a process by means of which tetrachloroethylene can be obtained in a more simple and less expensive way. Another object of the invention is to provide a process which is more economical with reference to the consumption of chlorine and in which more particularly the amount of chlorine needed for transforming ethane tetrachloride into tetrachloroethylene is materially reduced. Another object of the invention is to provide a process in which the total amount of chlorine entered into the process is made use of for forming tetrachloroethylene. Other objects of the invention will appear from the following description describing an embodiment of the invention in detail.

I have discovered that tetrachloroethylene C_2Cl_4 can be manufactured with only 2 mols of chlorine per mol of acetylene if the ethane tetrachloride in the form of vapor and in the presence of oxygen or gaseous mixtures containing oxygen is passed at elevated temperature over catalysts causing the oxidation of hydrogen chloride to chlorine. The hydrogen chloride which is at first produced by the thermic reaction is oxidized by the oxygen into elementary chlorine, and the said chlorine is immediately consumed for forming tetrachloroethylene. The process may be represented in a general way by the following equations:

(1) $2C_2H_2Cl_4 \rightarrow 2C_2HCl_3+2HCl$
(2) $2HCl+\frac{1}{2}O_2=Cl_2+H_2O$
(3) $C_2HCl_3+Cl_2=C_2HCl_5$
(4) $C_2HCl_5 \rightarrow C_2Cl_4+HCl$
(5) same as 2, etc.

As catalysts any substances or mixtures of substances may be used which are suitable for oxidizing hydrogen chloride, for example copper compounds such as copper oxide, copper chloride (preferably cuprichloride) or copper sulphate, further, the corresponding compounds of iron, chromium, manganese, and cerium, which compounds may be used either separately or in mixture, further, all the aforesaid substances, either separately or in mixture, together with aluminum oxide, magnesium oxide, bismuth oxide etc. Preferably the said substances are applied to suitable carrier substances, such as clay, pumice, gypsum, silicic acid gel, alumina gel, and the like.

As in any other case, the velocity of the flow of the gases depends on the volume of the catalyst.

The longer the path of the gases through a catalyst, the higher may be the velocity of the flow thereof. The flow velocities and the temperatures are not at a definite ratio directly depending from one another, the formation of tetrachloroethylene being bound to definite temperature limits, as in any other catalytical process.

The process may be carried out at temperatures of from 300 to 500° C. and preferably at temperatures of from 370 to 450° C.

The amount of the ethane tetrachloride exposed to the action of the catalyst may be as high as from 100 to 150 grams ethane tetrachloride per hour and per liter of the catalyst, the filling consisting of clay in pieces of from 2 to 4 millimeters in diameter coated with from 5 to 10% copper chloride. In each case the said amount depends on the amount and the character of the catalyst per unity of volume.

A suitable material from which the reaction pipe may be made, is for example, ceramic material or other material resistant to hydrogen chloride and chlorine.

The formation of tetrachloroethylene begins also if the amount of oxygen is stoichiometrically insufficient. But it rises as the amount of oxygen is increased. Preferably the reaction is carried out with an excess of oxygen exceeding the stoichiometric ratio, for example, with an excess of from 20 to 80%, because in this case the product of the reaction contains much tetrachloroethylene. At a temperature of from about 400 to 430° and an excess of oxygen of more than 20% with a copper chloride-clay catalyst a reaction product was obtained which contained 90% and more of tetrachloroethylene.

The oxygen may be used in concentrated form or diluted with insert gases, for example, air.

The reaction products are collected while cooling in water, the hydrochloric acid which is present in comparatively small amounts being dissolved. The chlorinated products are precipitated, and after separation from the watery phase, they are separated from one another by fractionated distillation. This is the most simple method of separating the components though other separating methods may be used which are known in the art.

As compared to known processes my improved process is preferable because practically the whole amount of the chlorine entered into the process is made use of for producing tetrachloroethylene, while in known processes one third of the chlorine is transformed into chlorides of alkali or alkaline earth metals, which have no value whatever or into hydrogen chloride, the value of which is less than that of the tetrachloroethylene.

Example

Ethane tetrachloride vapor and a corresponding amount of air ascertained by calculation were passed at a temperature of from 430 to 450° C through a pipe containing pieces of pumice impregnated with cupri-chloride. The flow velocity of the gaseous mixture was about 120 grams of ethane tetrachloride per hour and per 800 cubic-centimeters of catalyst volume. In addition to some ethylene trichloride, ethane pentachloride and watery hydrochloric acid the product of the reaction substantially consisted of tetrachloroethylene.

While in describing the invention reference has been made to a particular example embodying the same I wish it to be understood that my invention is not limited to the specific process described herein, and that various changes may be made such as will readily suggest themselves to those skilled in the art.

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