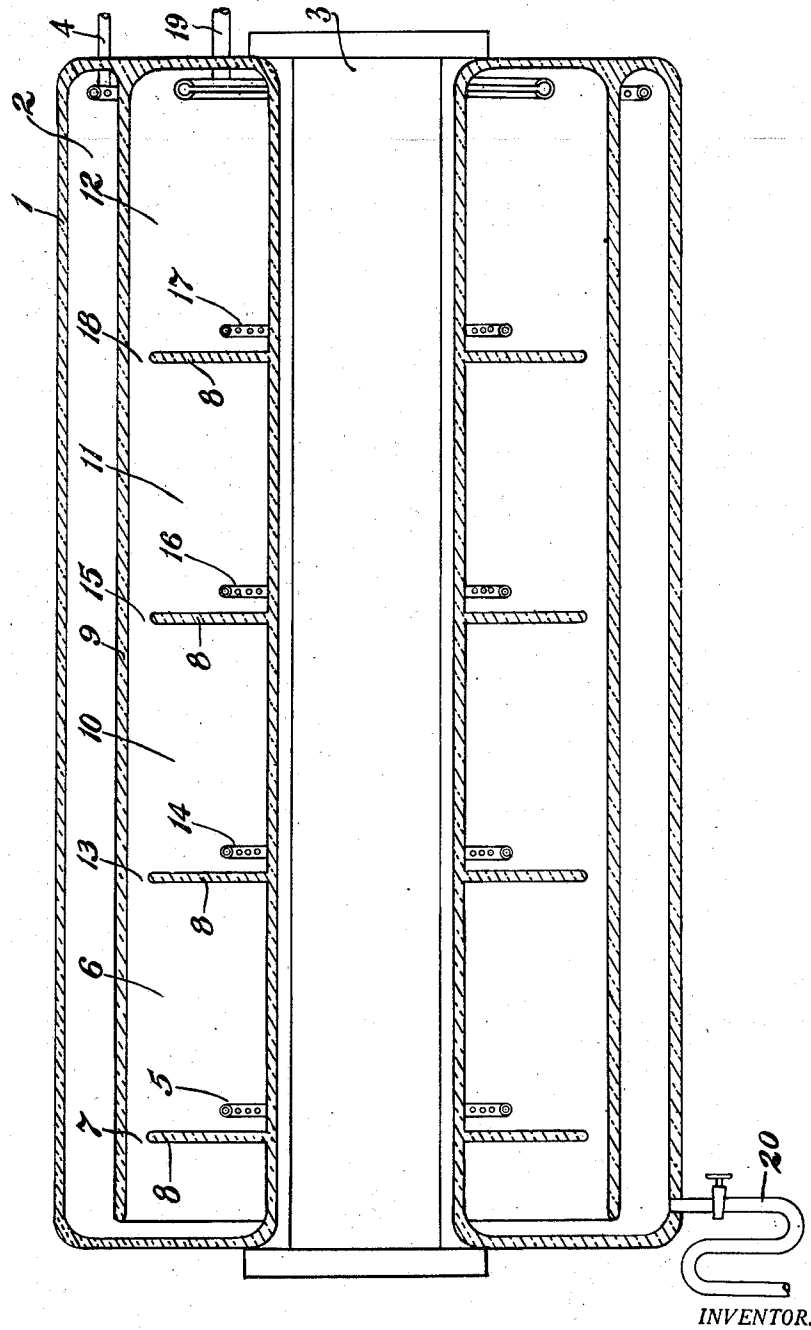
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PREPARATION OF POLYCHLORINATED SATURATED ALIPHATIC HYDROCARBONS

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PREPARATION OF POLYCHLORINATED SATURATED ALIPHATIC HYDROCARBONS

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My invention relates to a process for the preparation of polychlorinated saturated aliphatic hydrocarbons and, more specifically, for the preparation of polychlorination products of methane.

Whereas the preparation of the monohalogen compounds of saturated aliphatic hydrocarbons may be easily brought about, it has been difficult to prepare the higher chlorination products directly from the hydrocarbon and chlorine on account of the highly explosive properties of mixtures containing more than one part of chlorine to one part of hydrocarbon. If, for instance, a mixture of methane and chlorine in the right proportions to yield carbon tetrachloride is caused to react, an instantaneous explosion occurs.

In order to overcome this difficulty it has been suggested to add gaseous diluents to the chlorination mixture, or to mix only small amounts of chlorine with the hydrocarbon, to separate out the obtained lower chlorination products and to subject them afterwards separately to further chlorination, or to carry out the chlorination at gas velocities in excess of the speed of flame propagation. All these methods require rather complicated and spacious installations.

The principal object of this invention is to provide a simple method of obtaining highly chlorinated products of saturated aliphatic compounds at the normal gas velocities and reaction temperatures.

Other objects and advantages will be apparent from a consideration of the specification and the claims.

According to this invention, a safe preparation of the poly chloro substitution products of saturated aliphatic hydrocarbons is obtained in a single operation, without intermediate cooling or separating manipulations, by using the reaction products themselves, i. e., hydrogen chloride and the lower chlorosubstitutionproducts, as diluents and to adjust the proportions of the hydrocarbon and the chlorine over the whole reaction zone in such a way that at no point an explosive mixture is produced and that no excessive heat is generated by the reaction.

The chlorine is added in several steps, and the formation of explosive mixtures while adding chlorine to the heated gases coming from a precedent chlorination step is avoided, without the use of diluents and without cooling the gases below the reaction temperature, by maintaining at all points of chlorine admixture a dilution rate of the reacting hydrocarbon of at least 1:1, i. e., the amount of the reaction products at these points must be equal to, or in excess of, the amount of hydrocarbon.

In order to bring about this condition I mix chlorine and hydrocarbon below reaction temperature, preferably in the dark at a temperature of less than 60° C., in such proportions that

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the mol ratio between the hydrocarbon and the chlorine is higher than 1:1 and not higher than 3:1. The gases are then allowed to react. After consumption of the chlorine a mixture is obtained which contains still a large part of the unreacted hydrocarbon but at the same time a larger amount of chlorination products consisting of hydrogen chloride and lower chlorides of the hydrocarbon.

Additional chlorine is now added stepwise in such amounts that the mol ratio between chlorine and the other components of the mixture does not substantially exceed the ratio 1:1 in order to avoid a dangerous heat generation by the chlorination reaction. The addition of chlorine is repeated and the chlorination continued until the desired degree of chlorination of the hydrocarbon is obtained. The chlorinating temperature is maintained throughout the passage of the gases through the reactor, and no reaction products are removed or separated out during this passage.

My new process eliminates any risk of ignition since the starting mixture is not explosive when heated to the reaction temperature and since the admixture of the additional chlorine is carried out under equally safe conditions. Any apparatus may be used which permits the admixture of the additional chlorine to the gases in such a way that the chlorine is substantially prevented from entering the preceding sections of the apparatus against the direction of the gas flow. A diagrammatic sectional view of one suitable form of apparatus is shown in the accompanying drawing.

1 is a double-walled cylindrical tube enclosing a heater 3. The annular space between the two walls of the tube 1 forms the reaction chamber. A third wall 9 extends axially through almost the whole length of the chamber leaving only a small passage for the gases at the end opposite to the gas inlet; the wall 9 divides the reaction chamber into an outer section 2 and an inner section which is subdivided by annualr rings or partition walls 8 into the sections 6, 10, 11, and 12. Between the rings 8 and the wall 9 narrow passages 7, 13, 15, 18 are provided, which impart to the gases passing from one section to the next section of the reaction chamber an increased velocity prior to the addition of chlorine through the inlet pipes 5, 14, 16. The inlet pipe 17 may be used to introduce hydrocarbon at the end of the chlorination process.

The gases enter the reactor through the inlet pipe 4, pass through the sections 2, 6, 10, 11, and 12, and leave the reactor through the exit pipe 19. An outlet pipe 20 for removing condensed reaction products is provided for the use of the reactor for photo-chlorination at low temperatures, in which case the heater 3 is replaced by a light source.

The invention may be better understood by the following example which is illustrative of the new

process. All parts given for the composition of the gaseous mixtures are by volume.

A reaction chamber as shown in the drawing is heated to, and maintained at, a temperature of about 360° C. 2 parts of methane and 1 part of chlorine are mixed in a mixing chamber (not shown) at a temperature not exceeding 60° C. in the absence of light. 90 liters per hour of this mixture are introduced through inlet tube 4 into the first section 2 of the reaction chamber, the composition of the partly chlorinated mixture passing through the annular passage 7 is the following: methane, 1.25 parts; hydrogen chloride, .95 part, methyl chloride, .6 part; methylene chloride and chloroform, .15 part; and unreacted chlorine, .05 part. These figures show that 1.25 parts of unreacted methane are diluted with .95 part of hydrogen chloride and .75 part of partially chlorinated compounds, which amounts to a rate of dilution of

$$\frac{HCl+CH_{4-x}Cl_x}{CH_4}=\frac{1.70}{1.25}=1.36$$

The lower safety limit of the rate of dilution for methane is about 1. It is, therefore, safe to add to the gas mixture at the reaction temperature, i. e., at about 360° C., chlorine in an amount of 3 parts—corresponding to 90 liters per hour; the addition is effected through inlet pipe 5 without any danger of ignition or explosion. After these additionally introduced three parts of chlorine have reacted in the second section 6 of the reactor and at the moment when the reaction mixture passes through the annular passage 13 into the third section 10, the chlorine has entered into the following compounds, calculated on the total chlorine input: hydrogen chloride 45.5%, methyl chloride 1%, methylene chloride 14%, chloroform 24%, carbon tetrachloride 6.5%; 9% of the chlorine have not reacted.

When it is desired to chlorinate further in order to obtain mainly carbon tetrachloride, about 120 liters per hour—corresponding to 4 more parts of chlorine—may be admixed by means of inlet pipe 14 to the gases passing through the passage 13 into the third section 10 of the reaction chamber 1. After reaction in this third section the gases will contain a very high percentage of carbon tetrachloride and hardly any methyl chloride.

The sections 2, 6, 10, 11, and 12 of the reaction chamber have, in this particular example, each a volume of about 375 ccm. The velocity of the gas flow in the passages 7, 13, 15, and 18, immediately prior to the admixture of the chlorine, is maintained about ten times higher than the average velocity of the gas flow through the reaction chamber by narrowing the passages to about one twentieth of the height of the partitions 8. The best location of the inlet pipes 5, 14, and 16 may be determined by tests, i. e., by ascertaining where the previously added chlorine is substantially used up by the chlorination reaction. In a given apparatus, the various factors controlling the reaction, e. g., the speed of the gases, the amounts of chlorine added, the reaction temperature, may be adjusted in such a manner that the gases are substantially free of chlorine at the fixed locations of the inlet pipes.

Within the limits set forth hereinbefore, the amounts of chlorine added through the consecutive inlet pipes may be varied. It is possible to introduce through one or the other of the inlet pipes less chlorine than described in the example or even to keep one or the other inlet pipe entirely closed. Any desired composition of the polychlorinated end products may be obtained by regulating the admixture of chlorine through the various inlet pipes and by providing a suitable length of the reaction zone.

If it is desired to prepare the polychlorinated end products completely free from unreacted chlorine, a small amount of the hydrocarbon may be admixed to the gases near the end of the reaction zone, e. g., through inlet pipe 17. This hydrocarbon must be added in excess over the chlorine content of the gases in order to secure the complete removal of the chlorine in form of chlorination products.

The gaseous end products leave the reaction chamber through the exit pipe 19 and pass through a scrubber, which removes the hydrogen chloride. The polychlorination products are then condensed and, if desired, separated from each other.

The process and apparatus may also be used for the polychlorination of other saturated aliphatic hydrocarbons such as ethane, propane, butane, or pentane, at suitable temperatures. In the case of ethane, for instance, the best temperature range is from 230° to 270° C.

While I have illustrated and described a specific example of my new process, I do not intend to be limited to the details shown since various modifications and changes may be made without departing in any way from the spirit of my invention.

I claim:

1. A process for preparing polychlorinated saturated aliphatic hydrocarbons from gaseous saturated aliphatic hydrocarbons and chlorine in a single operation comprising the steps of mixing said hydrocarbons with part of the chlorine below reaction temperature in such proportions that the mol ratio between the hydrocarbon and chlorine in said mixture is higher than 1:1 and not higher than 3:1, heating said mixture to reaction temperature, causing the chlorine to react with said hydrocarbon, and admixing to said heated chlorinated gas mixture the rest of the chlorine stepwise at a speed below that of the flow of said mixture and in such amounts that the mol ratio between chlorine and the other components of the mixture does not substantially exceed the ratio 1:1.

2. A process as claimed in claim 1 in which the saturated aliphatic hydrocarbon is methane.

3. The process of claim 1 wherein the mixing of the saturated aliphatic hydrocarbon with chlorine is effected at a temperature of less than 60° C. in the absence of light.

4. In the process as claimed in claim 1 the step of removing unreacted chlorine at the end of the reaction zone by causing said chlorine to react with newly admixed hydrocarbon.

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