Aug. 11, 1959 D. S. ROSENBERG 2,899,370

PHOTOCHEMICAL CHLORINATION PROCESS

Filed April 16, 1956 2 Sheets-Sheet 1

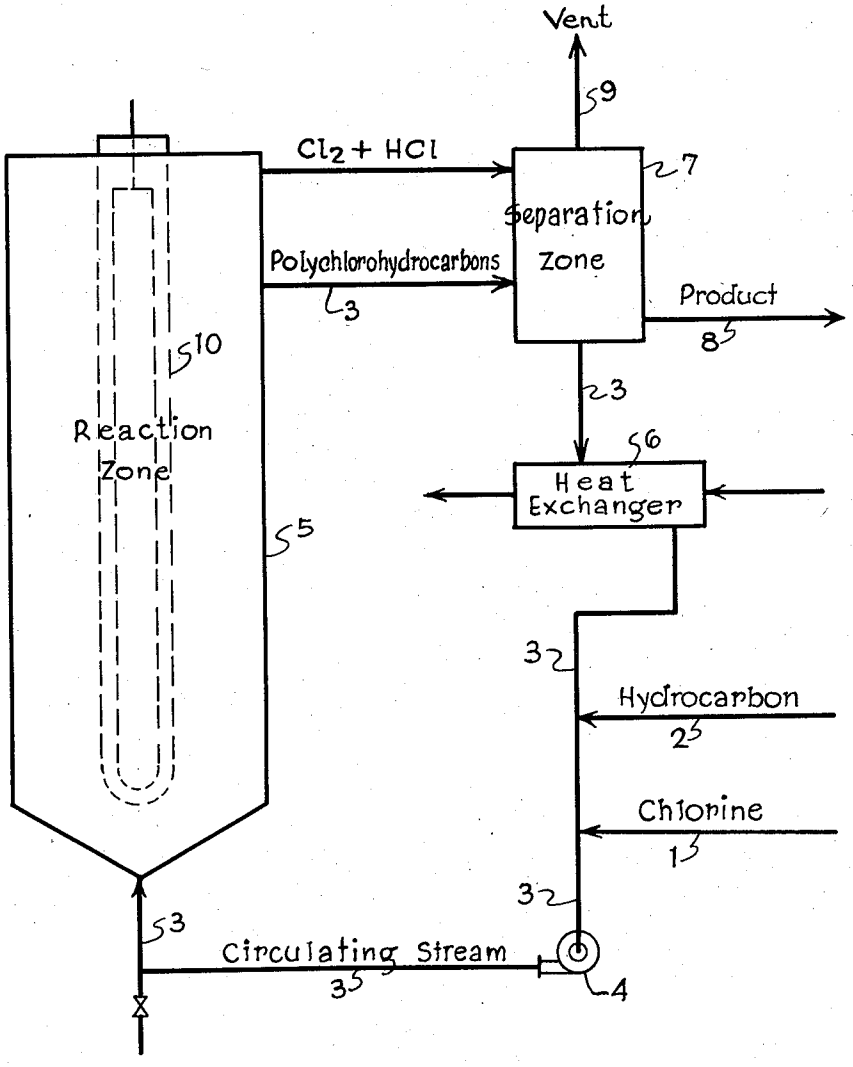


Fig. 1

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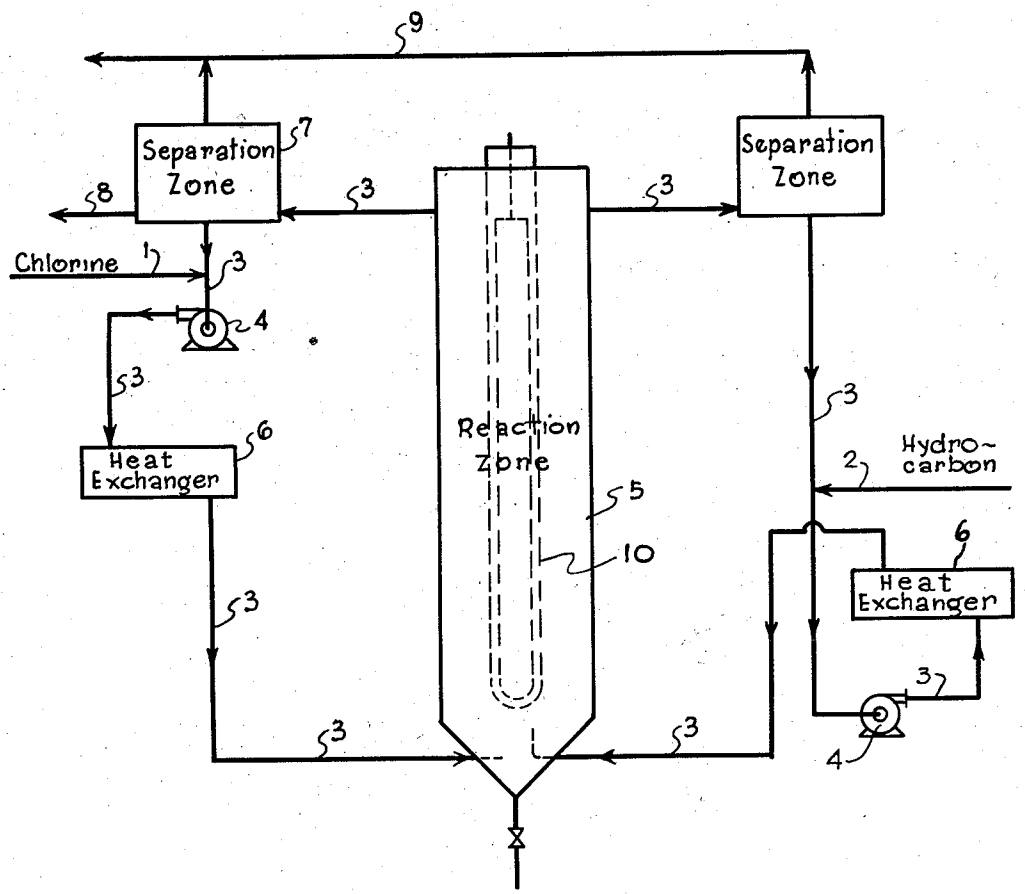


Fig 2

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PHOTOCHEMICAL CHLORINATION PROCESS

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10 Claims. (Cl. 204—163)

This invention relates to a process for the chlorination of aliphatic and alicyclic hydrocarbons. More particularly, this invention relates to a continuous process for the photochemical chlorination of aliphatic and alicyclic hydrocarbons and partially chlorinated hydrocarbon derivatives thereof, containing three to eight carbon atoms in the molecule.

It is known in the art that the photochemical chlorination of aliphatic and alicyclic hydrocarbons containing three to eight carbon atoms in the molecule may be effected in chlorinators wherein gaseous hydrocarbon and gaseous chlorine are introduced continuously into a liquid mixture of the product in a reaction zone by diffusion means at points substantially removed from one another so as to minimize the possibility of an explosion. The usual method of diffusion provided is the dispersion of the gaseous feed by use of a porous thimble or a fritted glass plate. Mechanical dispersion with a turbo-mixer can also be employed. The disadvantages inherent in the use of diffusers are numerous. For example, the pore-size of the diffusers normally used is about 15–20 microns, and pores of this size are readily plugged by trace contaminants entrained in the gases. Further, gaseous feeds require the use of an elaborate vaporization system operating under pressure to force the starting material through the small pores of the diffuser. When gaseous reactants are introduced into the photochemical chlorinator, bubbles of gaseous reactants may coalesce and form explosive mixtures. These conditions have imposed severe restrictions on operation of chlorinators using a feed system based on diffusion of gaseous reactants. Because the risk of explosions in using such reactants is so great exceptional precautions must be taken in order to avoid explosions.

It has long been known in the art that the chlorination of hydrocarbons may be effected by using liquid reactants. One such process involves introducing liquid chlorine directly into a body of liquid hydrocarbon or partially chlorinated hydrocarbon under conditions of extremely low temperature in order to avoid the risk of explosions which is even greater when using liquid reactants in this manner than when using gaseous reactants. To my knowledge, the risk and danger in these processes has been so great that none have been put to use on a large commercial scale.

The principal object of this invention is to provide a new continuous process for the photochemical chlorination of aliphatic and alicyclic hydrocarbons and partially chlorinated hydrocarbon derivatives thereof, wherein increased overall efficiency and economy are realized from improved operating conditions.

Another object of this invention is to provide a safe and economical process which employs liquid chlorine and liquid hydrocarbon or partially chlorinated hydrocarbons as reactants which avoids the wasteful procedure of first vaporizing the reactions external to the reactor and in effect recondensing them in the chlorinator.

Another object of this invention is to provide a continuous process for photochemical chlorination wherein the mechanical difficulties of the prior art are substantially reduced.

Still another object of this invention is to provide a process wherein the danger of explosion in using liquid reactants is even less than the danger involved in using gaseous reactants wherein the gaseous reactants may coalesce to form explosive mixtures.

I have now found that these and related objects may be accomplished in a continuous process for the photochemical chlorination of aliphatic and alicyclic hydrocarbons, and partially chlorinated hydrocarbon derivatives thereof, containing three to eight carbon atoms in the molecule inclusive, by the application of new process techniques wherein the risk of explosion is minimized which comprises maintaining an external circulating stream of liquid polychlorohydrocarbon in communication with a reaction zone containing the main body of the liquid polychlorohydrocarbon. The reactants consisting of liquid chlorine and liquid hydrocarbon are separately injected into said circulating stream of liquid polychlorohydrocarbon, while maintaining the chlorine feed rates and the chlorinator temperature such that 90 percent of the reactants entering the said reaction zone are in the liquid phase. The mixture so produced is passed through an illuminated zone to effect chlorination of the organic feed. A portion of the circulating stream leaving the reaction zone is withdrawn as product of the reaction zone.

The manner in which the process of the present invention is carried out will be more clearly understood from the following description of the accompanying drawings in which Figure 1 is a diagrammatic flow sheet showing the separate injection of the reactants into a circulating stream and is one method which may be employed in the performance of this process. Figure 2 is a diagrammatic flow sheet showing a modification of the process of this invention wherein the reactants are injected into separate circulating streams.

Referring to Figure 1: Liquid chlorine **1** and liquid hydrocarbon starting material **2** are separately injected through nozzles into a circulating stream **3** of liquid polychlorohydrocarbon having a specific gravity between about 1.3 and about 1.8. The external stream is circulated through the system by means of pumps **4**. The temperature of the reaction medium in the photochemical clorinator **5** is maintained between about 25 degrees and about 150 degrees centigrade by means of an external heat exchanger **6**. A portion of the polychlorohydrocarbon is withdrawn in the product withdrawal zone **7** to a product recovery zone **8** wherein the desired product is obtained. Effluent gases, such as chlorine and hydrogen chloride, are removed from the chlorinator and vented **9** to a recovery system. The photochemical energy is supplied from a mercury vapor lamp suspended in a light well **10**.

Referring to Figure 2: Liquid chlorine **1** and liquid hydrocarbon starting material **2** are injected through nozzles into separate circulating streams **3** of liquid polychlorohydrocarbon having a specific gravity between about 1.3 and about 1.8. The streams are circulated through the system by means of pumps **4**. The temperature of the reaction medium in the photochemical chlorinator **5** is maintained between about 25 degrees and 150 degrees centigrade by means of external heat exchangers **6**. A portion of the polychlorohydrocarbon is withdrawn in a product withdrawal zone **7**, to a product recovery zone **8** wherein the desired product is obtained. Effluent gases, such as chlorine and hydrogen chloride, are removed from the chlorinator and vented **9** to a recovery system. The photochemical energy is supplied from a mercury-vapor lamp suspended in a light-well **10**.

The above description of the drawings and the following examples further illustrate our invention but it is to be understood that the specific details given in the drawings and examples have been chosen for the purpose of illustration and are not intended to limit our invention except as defined in the appended claims.

Example 1

The chlorination apparatus employed to obtain the data of the following example consisted of an eight-inch diameter nickel pipe, seventy inches long, fitted with a jacketed light well assembly which consisted of a two inch diameter Pyrex pipe mounted inside a four-inch diameter Pyrex pipe and supported on the vertical axis of the chlorinator. A 3,000 watt Westinghouse BH–9 mercury vapor lamp suspended in the light well was used to furnish the photochemical energy for this experiment. The chlorinator had a conical bottom section, six and one half inches long, wherein the circulating liquid streams entered the chlorinator through a one-inch nickel pipe. A drain valve was provided at the bottom. A two-inch diameter liquid overflow at the top of the chlorinator provided a liquid depth of fifty-six and one-half inches in the straight section giving a net liquid volume of eight and eight-tenths gallons. Exit gases were withdrawn through a one-inch diameter nickel pipe mounted nine inches above the liquid overflow. A thermometer well extended into the body of the chlorinator for measuring the liquid temperature.

After the light source had been turned on and had reached normal operating intensity the circulating stream of polychloropentanes of specific gravity 1.670 was started at a maximum flow rate of 22,500 pounds per hour. During the usual induction period, the flow rates were adjusted so that at least 50 percent of the chlorine feed was reacted. In a manner after the foregoing description of the process 110.0 pounds per hour of chlorine and 12.1 pounds per hour of pentane were injected through 0.0625 inch and 0.040 inch diameter orifices, respectively, into the circulating stream of liquid polychlorohydrocarbon. The ratio of polychloropentane circulating rate to the chlorine feed rate was 204. During the reaction period of 9.5 hours, the chlorine to pentane mole ratio was kept between 9.0 and 9.5 to 1. The temperature of the reaction medium was maintained between about 83 degrees and about 88 degrees centigrade. The average temperature drop through the heat exchanger was 5 degrees centigrade. Under these conditions 95 percent of the chlorine feed was in solution in the stream entering the reactor. The hydrogen chloride/chlorine gas stream leaving the reactor contained about 27 percent chlorine. Approximately 80.5 pounds per hour of chlorine was reacted. A product having a specific gravity of 1.621 at 20 degrees centigrade corresponding to an average composition of $C_5Cl_{6.6}H_{5.5}$ was recovered.

Example 2

The chlorination apparatus employed to obtain the data of the following example consisted of a thirty-eight inch length of two-inch diameter Pyrex pipe which was illuminated externally by 6–100 watt AH–4 lamps distributed spirally at uniform intervals (6 inches) along the reaction zone to furnish photochemical energy for the experiments. A drain valve was provided at the bottom of the chlorinator. A one-inch diameter liquid overflow was provided at the top of the chlorinator and gave a net liquid volume of 0.37 gallon. Exit gases were withdrawn through a one-inch diameter Pyrex pipe mounted above the liquid overflow. A thermometer well extended into the body of the chlorinator for measuring the liquid temperature.

After the light source had been turned on and had reached normal operating intensity the circulating stream of polychloropropanes of specific gravity 1.633 was started at a maximum flow rate of 1 gallon per minute. During the usual induction period the flow rates were adjusted so that at least 50 percent of the chlorine feed was reacted.

In a manner after the foregoing description of the process 1050 grams per hour of chlorine and 141 grams per hour of propane were injected through one millimeter and 0.5 millimeter diameter orifices, respectively, into the circulating stream of liquid polychlorohydrocarbon. The ratio of the polychloropropane circulating rate to the chlorine feed rate was 340. During the reaction period of 12.3 hours, the chlorine to propane mole ratio was kept between 4.43 and 4.76 to 1. The temperature of the reaction medium was maintained between about 60 degrees and about 65 degrees centigrade. The average temperature drop through the heat exchanger was 5 degrees centigrade. Under these conditions 98 percent of the chlorine feed was in solution in the stream entering the reactor. The hydrogen chloride/chlorine gas stream leaving the reactor contained about 6 percent chlorine. A product having a specific gravity of 1.614 at 20 degrees centigrade corresponding to an average composition of $C_3H_{3.5}Cl_{4.4}$ was recovered.

The mole ratio of chlorine to hydrocarbon starting material is maintained between about 3 to 1 and about 12 to 1. The circulating stream is passed through an irradiated reaction zone to effect the chlorination of the hydrocarbon in a reaction medium of liquid polychlorohydrocarbon. The reaction is catalyzed by exposing the main liquid body of polychlorohydrocarbons to the action of actinic light having a wave length from about 3,000 to about 5,000 A. The temperature of the liquid body of polychlorohydrocarbon employed as a reaction medium for the chlorination is maintained between about 25 degrees and about 150 degrees centigrade and preferably between about 50 degrees and about 125 degrees centigrade by means of external heat exchangers located in the circulating stream. A portion of the liquid polychlorohydrocarbon stream leaving the reaction zone is withdrawn continuously to maintain a constant liquid volume in the reaction system.

The liquid reactants are separately injected through nozzles into the circulating stream of liquid polychlorohydrocarbon at any point that would permit dissolving the reactants externally so that reactants enter the chlorination zone as a homogeneous solution. Addition of the reactants precedent to the product withdrawal zone would provide a product recovery problem. As the reactants are liquid, any method for adding liquid material is satisfactory. A preferred embodiment is that shown in the drawings wherein the liquid chlorine and liquid hydrocarbon starting materials are injected into separate circulating streams of liquid polychlorohydrocarbons at a flow point precedent to the pumps to reduce the possibility of forming explosive mixtures should any part of the system fail to operate properly. As stated, this procedure is particularly applicable to hydrocarbons containing three to eight carbon atoms in the molecule. Since the C–3 hydrocarbons have the lowest boiling points, any procedure applicable to these compounds can be used for the higher-boiling members of the series.

The photochemical chlorinator contains liquid polychlorohydrocarbons having a specific gravity between about 1.3 and about 1.8 as the coolant and diluent for the chlorination of hydrocarbons. The reaction is catalyzed by exposing the liquid body of polychlorohydrocarbons containing the dissolved reactants to the action of actinic light having a wavelength from about 3,000 to about 5,000 A. The temperature of the reaction medium is maintained between about 25 degrees and about 150 degrees centigrade and preferably between about 50 degrees and about 125 degrees centigrade by removing the heat of reaction and the heat of the mercury arc lamps by circulating the polychlorohydrocarbons through external heat exchangers. The heat load is reduced by about 25 percent by using liquid feed instead of gaseous

feed. Since undesired chlorinalysis of the polychlorohydrocarbons is initiated at temperatures about 150 degrees centigrade, it is preferred to maintain the reaction medium temperature below about 125 degrees centigrade. The volume of mixed polychlorohydrocarbons in the chlorinator is kept substantially constant by continuous withdrawal of liquid polychlorohydrocarbon from the external circulating stream as the reaction proceeds.

The flow rate of the circulating stream of liquid polychlorohydrocarbons having a specific gravity between about 1.3 and about 1.8 is maintained by pumping means, such as a centrifugal pump, and is dependent upon the available heat exchanger capacity and the chlorine feed rate required for the desired production. It is assumed that all heat of reaction is removed in the heat exchanger, as is consistent with sound design principles. The economics of heat exchanger capacity dictate the maximum flow rate while the minimum flow rate is dictated by the chlorine feed rate required. In the process of this invention at least 90 percent and preferably substantially all of the chlorine should be in solution on entrance to the chlorinator. Therefore, a minimum ratio must be maintained between the rate of circulation of the polychlorohydrocarbon and the chlorine feed flow rate to maintain the desired solubility. This minimum ratio is dependent upon the chlorination temperature.

In the following table, the minimum allowable ratio of polychlorohydrocarbon circulation rate to chlorine feed rate at various chlorination temperatures is given for chlorination of n-pentane.

Chlorination temperature, ° C.	Minimum allowable ratio of polychlorohydrocarbon circulation rate to chlorine feed rate, lb. PCP/lb. Cl_2	
	90% Cl_2 in solution [1]	100% Cl_2 in solution [1]
50	5	150
75	80	274
95	160	400
120	285	630

[1] Percent Cl_2 in solution at inlet to chlorinator.

The table illustrates that at a circulating rate of 22,500 pounds per hour of polychloropentane, in order to keep 90% of the chlorine in solution, the minimum chlorine feed rates are 281 and 141 pounds per hours at 75 degrees and 95 degrees centigrade, respectively. For hydrocarbons below pentane in the series somewhat higher circulation rates are needed because of lower hydrocarbon solubility in the polychlorinated product, and for hydrocarbons above pentane, somewhat lower circulation rates are needed. For example, in Example 2 the preferred ratio of the polychloropropane circulating rate to the chlorine feed rate is 340, which is somewhat higher than the 210 ratio which is the minimum ratio for polychloropentane under substantially the same reaction conditions.

The reaction between chlorine and a hydrocarbon is especially sensitive to certain impurities. Therefore, the starting materials should be free from harmful inhibitors or materials which may delay or slow down the reaction between the hydrocarbon and the chlorine. Presence of reaction inhibitors such as free oxygen or oxygenated organic compounds in the system will inhibit chlorination and they should be eliminated before starting chlorination.

An operational hazard arises from the possibility of accumulating an explosive mixture of chlorine and the hydrocarbon vapor. When the hydrocarbon feed rate exceeds the limit at which all the hydrocarbon is reacted, explosive mixtures of gaseous chlorine and hydrocarbon may be present. An excellent control procedure is provided in a circulating system by measurement of the concentration of chlorine in the streams entering and leaving the chlorinator, since chlorine consumption is also a measure of the amount of hydrocarbon which is reacted.

From the foregoing specification it is apparent that various modifications are possible within the scope of this invention and it is therefore not to be construed as limiting except as defined by the appended claims.

I claim:

1. A continuous process for the photochemical chlorination of aliphatic and alicyclic hydrocarbons and partially chlorinated hydrocarbon derivatives thereof, containing three to eight carbon atoms in the molecule inclusive, which comprises: maintaining a circulating stream of liquid polychlorohydrocarbon in communication with a reaction zone containing the main body of liquid polychlorohydrocarbon said stream being external to said reaction zone; separately injecting the reactants consisting of liquid chlorine and liquid hydrocarbon into said externally circulating stream of liquid polychlorohydrocarbon, maintaining the chlorine feed rate and the chlorinator temperature such that 90 percent of the reactants entering said reaction zone are in the liquid phase; passing the mixture so produced through an irradiated reaction zone to effect chlorination of the organic feed; withdrawing a portion of said externally circulating stream leaving the reaction zone and recovering said portion as a product.

2. A process according to claim 1 wherein the body of liquid polychlorohydrocarbon maintained as a reaction medium has a specific gravity between about 1.3 and 1.8.

3. A process according to claim 2 wherein the liquid hydrocarbon starting material is liquid propane and partially chlorinated hydrocarbon derivatives thereof.

4. A process according to claim 3 wherein the mole ratio of liquid chlorine to liquid propane is maintained between 3 to 1 and about 8 to 1.

5. A process according to claim 4 wherein the temperature of the body of liquid polychlorohydrocarbon maintained as a reaction medium is maintained between about 50 degrees and about 100 degrees centigrade.

6. A process according to claim 2 wherein the liquid hydrocarbon starting material is liquid pentane and partially chlorinated hydrocarbon derivatives thereof.

7. A process according to claim 6 wherein the mole ratio of liquid chlorine to liquid pentane is maintained between about 3 to 1 and about 12 to 1.

8. A process according to claim 6 wherein the temperature of the body of liquid polychlorohydrocarbon maintained as a reaction medium is maintained between about 50 degrees and about 125 degrees centigrade.

9. A continuous process for the photochemical chlorination of aliphatic and alicyclic hydrocarbons, and partially chlorinated hydrocarbon derivatives thereof, containing three to eight carbon atoms in the molecule inclusive, which comprises: maintaining separate circulating streams of liquid polychlorohydrocarbon in communication with a reaction zone containing the main body of liquid polychlorohydrocarbon said stream being external to said reaction zone; separately injecting the reactants consisting of liquid chlorine and liquid hydrocarbons into said separate externally circulating streams of liquid polychlorohydrocarbons; maintaining the chlorine feed rates and the chlorinator temperature such that 90 percent of the reactants entering said reaction zone are in the liquid phase; passing the mixture so produced through an irradiated reaction zone to effect chlorination of the organic feed; withdrawing a portion from said externally circulating streams leaving the reaction zone to a product recovery zone, passing the remaining portions of the circulating streams through heat exchangers to maintain the temperature of said liquid polychlorohydrocarbon in said irradiated reaction zone between about 25 degrees and about 150 degrees centigrade.

10. A continuous process for the photochemical chlorination of aliphatic and alicyclic hydrocarbons, and partially chlorinated hydrocarbon derivatives thereof, contain-

ing three to eight carbon atoms in the molecule inclusive, which comprises: maintaining separate circulating streams of liquid polychlorohydrocarbon in communication with a reaction zone containing the main body of liquid polychlorohydrocarbon said streams being external to said reaction zone; separately injecting the reactants consisting of liquid chlorine and liquid hydrocarbons into said separate externally circulating streams of liquid polychlorohydrocarbon so that the reactants entering said reaction zone are substantially in solution; passing the mixture so produced through an irradiated reaction zone to effect chlorination of the organic feed; withdrawing a portion from a circulating stream leaving the reaction zone to a

product recovery zone; passing the remaining portions of the circulating streams through heat exchangers to maintain the temperature of said liquid polychlorohydrocarbon in said irradiated reaction zone between about 25 degrees and about 150 degrees centigrade.

References Cited in the file of this patent

UNITED STATES PATENTS

2,473,161	McBee et al.	June 14, 1949
2,473,162	MeBee et al.	June 14, 1949
2,571,901	Lawlor	Oct. 16, 1951
2,744,862	Nicolaisen	May 8, 1956