

## UNITED STATES PATENT OFFICE

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## PROCESS FOR PHOTOCHEMICAL CHLORINATION OF HYDROCARBONS

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This invention relates to a process for the photochemical chlorination of hydrocarbons. More particularly it relates to the production of chlorinated paraffinic hydrocarbons of five or more carbon atoms in which a major portion, e. g. fifty to approximately ninety per cent, of the hydrogen atoms have been, replaced by chlorine.

An object of the present invention is a process for chlorinating paraffinic hydrocarbons of five or more carbon atoms to a chlorinated product in which a major portion of the hydrogen atoms, e. g. fifty to approximately ninety per cent, have been replaced by chlorine atoms, while substantially eliminating difficulties usually encountered in controlling the course of the highly exothermic reaction. Another object is a process for obtaining a chlorinated product of the aforementioned kind in which the starting material comprises an initially partially chlorinated paraffinic hydrocarbon of five or more carbon atoms per molecule and a chlorine content insufficient in amount to prevent violent reaction upon further chlorination. A further object is a process of the foregoing nature wherein the reaction is conducted under liquid phase conditions.

In the photochemical chlorination of hydrocarbons the reaction is frequently so vigorous that, even with cooling to relatively low temperatures, e. g. 25° C. to 30° C., miniature explosions are liable to occur. The reaction may become so violent as the result in destruction of the hydrocarbon molecule, setting carbon free. When the operation is conducted in liquid phase, the free carbon darkens the liquid and this obstructs penetration of the actinic light. The further progress of the reaction is thus rendered difficult and in some cases a point may be reached at which further chlorination becomes virtually impossible. This is the chief reason for the well known difficulty of carrying photochemical chlorination of paraffinic hydrocarbons to the higher ranges of chlorine content, particularly in liquid phase.

The problem of controlling the violence of the reaction has been recognized in several early patents, and a variety of proposals to overcome this difficulty have ensued. Probably the most satisfactory of these proposals is the use of a diluent for the chlorine such as an inert gas. Such use of a diluent facilitated to some degree the control of the reaction since it prevented or decreased excessive decomposition and carbon formation by absorbing a large part of the heat of reaction, thus preventing occurrence of ignition and explosions. Among the diluents most commonly

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proposed are nitrogen and carbon dioxide. Another investigator proposed the use of hydrogen chloride as an inexpensive diluent and pointed out the advantage of its use as it is present as a by-product of the reaction and can be recycled.

While an inert gas, such as nitrogen, carbon dioxide or hydrogen chloride, is very effective for the purpose of preventing explosions, as the reaction proceeds it becomes less and less vigorous, even when there is no obscuring of the liquid by carbon or dark colored products from side reactions. It has therefore not been possible with the use of diluted chlorine to replace a major portion, e. g. fifty to approximately ninety per cent, of the hydrogen by chlorine. This is particularly true when paraffinic hydrocarbons having five or more carbon atoms are chlorinated in liquid phase. In co-pending application Serial No. 596,217, filed May 28, 1945, there is disclosed a process for carrying the chlorination to the desired point, by making use of chlorine mixed with an inert diluent, such as nitrogen or carbon dioxide, during the initial stage of the reaction, or until the danger of explosive reaction is passed, and then finishing with undiluted chlorine.

According to the present invention, there is provided an improved process for the production of chlorinated paraffinic hydrocarbons of five or more carbon atoms in which a major portion of the hydrogen atoms have been replaced by chlorine atoms, which comprises subjecting the material, under actinic light, to the action of chlorine diluted with hydrogen chloride during the initial stage of the reaction and to the action of undiluted chlorine during the remainder of the reaction. As an additional feature of the invention, the hydrogen chloride employed as the diluent gas may be that obtained during the latter stage of the reaction.

Now having indicated in a general way the nature and purpose of my invention, the following example is given, not by way of limitation, but rather in illustration of a preferred method of carrying out my invention. In the example the parts are given by weight unless otherwise indicated.

*Example*

Two hundred and sixty-five pounds of liquid heptane were charged into a 150 gallon jacketed and enamelled reactor, equipped with light and thermometer wells and a reflux condenser. The heptane was initially at 27° C. A mixture of chlorine and hydrogen chloride in about equal proportions was passed into the heptane with



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cooling. The temperature was allowed to rise slowly. After 24 hours, when the temperature had reached 32° C. and sufficient hydrogen atoms had been replaced by chlorine so that no danger of explosion existed, the dilution with hydrogen chloride was discontinued. After 72 hours, with the temperature at 90° C., chlorine began to be found in the exit gas. After 156 hours the temperature was 117° C. and the exit gas contained substantially fifty per cent chlorine. After 204 hours the temperature was 129° C., the chlorine content of the product had reached 80.5 per cent by weight, corresponding approximately to  $C_7H_5Cl_{11}$ , and the exit gas contained more than fifty per cent chlorine. This exit gas mixture containing chlorine and hydrogen chloride was therefore available for use during the first 24 hours of the next cycle of the reaction. Liquid phase conditions were maintained throughout the entire chlorination reaction.

While heptane has been used in the example in illustration of a normally liquid paraffinic hydrocarbon having five or more carbon atoms, other hydrocarbons which are equally operable are pentane, hexane, octane, nonane, decane and higher hydrocarbons.

While my invention has been described in detail in connection with the chlorination of paraffinic hydrocarbons as starting materials, it is within the scope of the invention to employ as starting material an initially partially chlorinated paraffinic hydrocarbon having five or more carbon atoms per molecule and having a chlorine content insufficient in amount to prevent violent reaction upon further chlorination. Examples of such starting materials are partially chlorinated paraffinic hydrocarbons having five or more carbon atoms and preferably not over two chlorine atoms per molecule.

While I prefer to carry out my invention with the aid of cooling, I do not wish to be limited thereto, as with sufficient dilution of the chlorine and a reactor of relatively large radiation surface per unit of volume the temperature may be made self-regulating.

Furthermore, if cooling is used, although I prefer to maintain the temperature during the initial stage of the reaction between about 25° C. and about 30° C., this temperature may be varied over a considerable range, as may the later temperatures as the reaction progresses.

In the carrying out of this process the chlorine is preferably initially diluted with an equal volume of the hydrogen chloride. However, the ratio of the diluent to the chlorine may be varied over a wide range depending upon the violence of the reaction, etc.

It will be understood that the time of the reaction shown in the example is illustrative only and with a change in the conditions of the reaction, reactants, etc. a similar change may be made in the time of the reaction.

By the term "initial stage of the reaction" within the intention of the specification and claims is meant that period in which sufficient chlorine atoms are substituted so that when undiluted chlorine is then introduced the reaction rate has been sufficiently retarded that danger of explosions has been eliminated. This point is generally reached, for example in the chlorination of heptane, when about twenty per cent of the hydrogen atoms have been replaced by chlorine.

To produce the actinic light necessary in the carrying out of this process, as illustrated in the

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example, any of the well-known types of commercial lights may be used which will induce or speed the reaction in the chlorination of a paraffinic hydrocarbon, such as tungsten filament lamp, mercury vapor arc lamp, and the like.

As indicated above, during the second stage of the reaction there is obtained an exit gas comprising hydrogen chloride and unreacted chlorine. It is not difficult to separate hydrogen chloride from chlorine contained in this exit gas by a method such as absorption of the hydrogen chloride in water, but the chlorine is thereby left in a wet condition, in which it is unsuitable for use as such in the next batch. I therefore have found it advantageous either to store this exit gas and use it at the start of the next batch, or to arrange two or more batches in series and use the exit gas from the second stage of one to start the chlorination of the next. In this way the separation of the chlorine from the hydrogen chloride and drying of the chlorine are avoided. The hydrogen chloride of the mixture which is thus recycled to the start of another chlorination, augmented if desired or necessary by make-up hydrogen chloride, issues from the initial stage of the second reactor substantially free from chlorine, and may therefore be withdrawn as by-product from the system, during the early part of the reaction in the second reactor. After a few repetitions of the cycle a natural balance is reached at which the hydrogen chloride discharged and withdrawn in this way just equals that formed during the complete cycle.

By my process I accomplish the following objectives: namely, moderation and avoidance of decomposition during the early stage of the reaction without the necessity for providing any extraneous inert diluent gas; chlorination to a higher chlorine content than heretofore possible; and utilization of any unreacted chlorine contained in the exit gas during the latter part of the reaction, without the necessity of separating it from the hydrogen chloride and drying it.

Other advantages will be apparent from the foregoing disclosure to those skilled in the art, and while a specific example has been used to illustrate my invention, it is to be understood that the scope of this invention is not limited to this embodiment, but is defined by the appended claims.

What I claim is:

1. A process for the chlorination of heptane in liquid phase which comprises reacting the heptane with elemental chlorine diluted with approximately an equal volume of hydrogen chloride under actinic light while maintaining a temperature between about 25° and about 30° C. for approximately 24 hours and reacting the resultant partially chlorinated heptane with undiluted elemental chlorine under actinic light for a further period of about 180 hours at a temperature gradually increasing to about 129° C.

2. A process for the chlorination of heptane in liquid phase which comprises reacting the heptane with elemental chlorine diluted with approximately an equal volume of hydrogen chloride under actinic light while maintaining a temperature between about 25° and about 30° C. for approximately 24 hours, reacting the resultant partially chlorinated heptane with undiluted elemental chlorine under actinic light for a further period of about 180 hours at a temperature gradually increasing to about 129° C. and utilizing the exit elemental chlorine in the second stage of the chlorination, diluted with hydrogen chloride, in



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the initial stage of a heptane chlorination process under actinic light.

3. A process conducted entirely in the liquid phase for the production of a chlorinated paraffinic hydrocarbon containing from five to ten carbon atoms per molecule in which from about fifty to about ninety percent of the hydrogen atoms have been replaced by chlorine which comprises reacting in the liquid phase a paraffinic hydrocarbon having the same number of carbon atoms per molecule as the chlorinated hydrocarbon to be produced with elemental chlorine diluted with a substantial amount of hydrogen chloride under actinic light as an initial stage of the reaction, reacting the resultant partially chlorinated mixture in the liquid phase with undiluted elemental chlorine under actinic light, continuing the reaction until the exit gas contains a substantial amount of elemental chlorine and utilizing the exit elemental chlorine diluted with hydrogen chloride during the initial stage of the above hydrocarbon chlorination process carried out under actinic light.

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