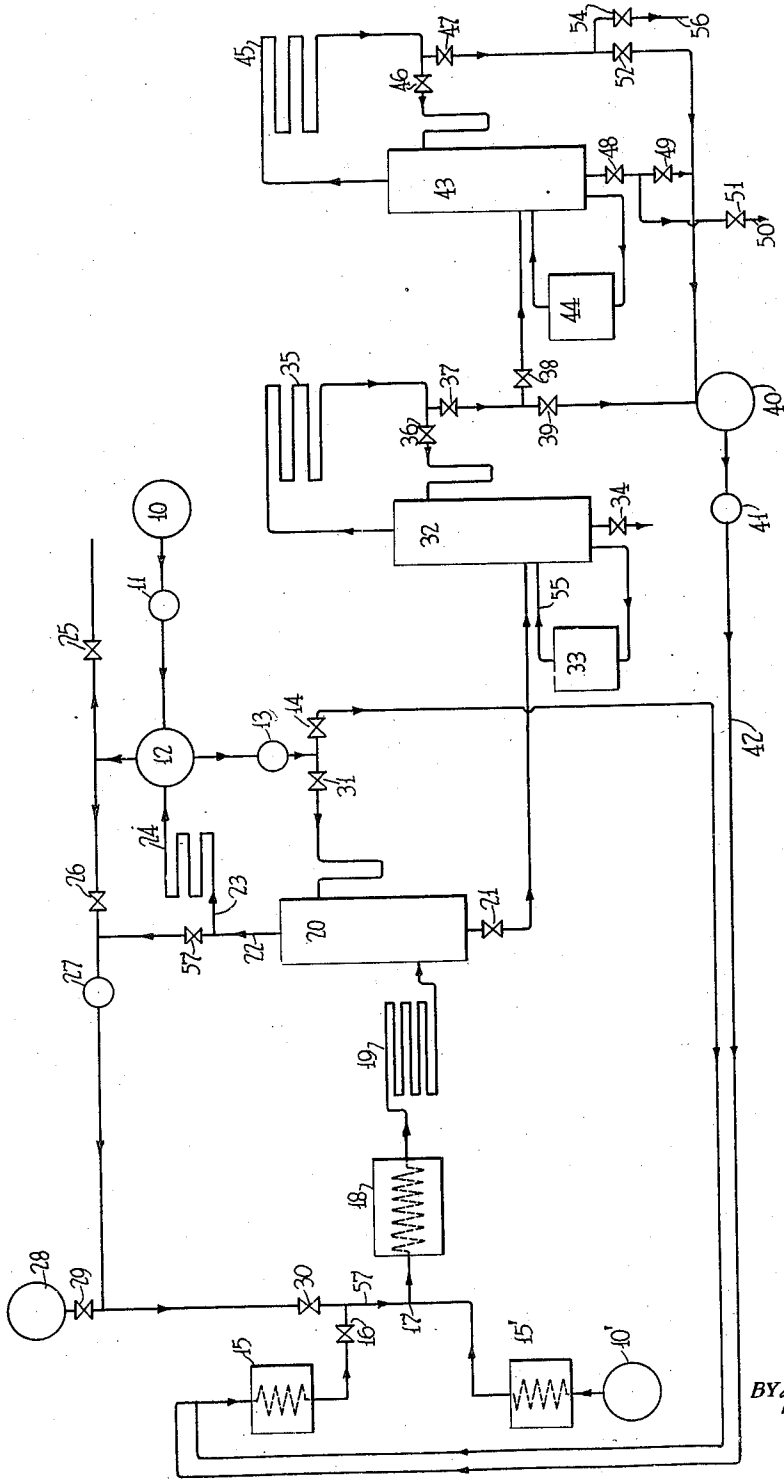
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METHOD OF CHLORINATING HYDROCARBONS

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METHOD OF CHLORINATING HYDROCARBONS

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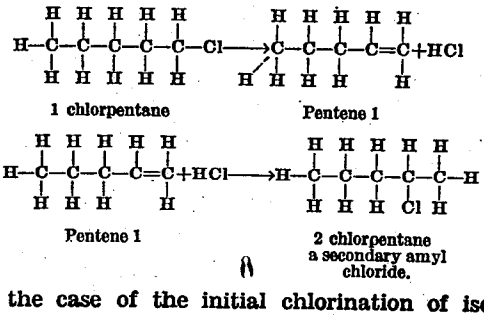
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2 Claims. (Cl. 260—166)

The present invention relates to the vapor phase chlorination of hydrocarbons and hydrocarbon substitution products and it has had as its principal object the development of a method of chlorinating these compounds in such a manner as to effect an adequate control of the end products to selectively produce desired mono- or poly-chlorination products.

Further objects of the invention pertain to the avoidance of the formation of undesired products such as unsaturated hydrocarbons, carbon, gummy residues and undesired polychlorides in the performance of chlorination reactions and to the development of a process of chlorination which effectively affords novel and adequate provision for the avoidance of the danger of explosion and facilitates the economical large scale separation of the reactants from the resultants of the reaction.

The problems of explosion and degradation of the end products resulting in the production of undesired products have been among the principal difficulties heretofore encountered in the practice of chlorination of hydrocarbons. Where ignition is allowed to persist, decomposition of the chlorinated hydrocarbon into unsaturated compounds and/or carbon and hydrogen chloride frequently occurs and explosions are sometimes caused by the heat generated in the decomposition reactions. In the case of hydrocarbons having more than two carbon atoms, decomposition is additionally objectionable because of the nature of the products obtained when the unsaturated hydrocarbons formed by such decomposition recombine with hydrogen chloride which is present. Thus where primary amyl chloride is decomposed into pentene 1, this pentene 1 tends to recombine with the hydrogen chloride split off from the amyl chloride molecule. Such recombination almost invariably results in the formation of a secondary amyl chloride, as indicated by the following equations:



In the case of the initial chlorination of isopentanes to form iso-amyl chlorides, the corresponding decomposition and addition reactions result in the formation of tertiary amyl chloride. As these secondary and tertiary chlorides are less desired than the primary chlorides, it is evident that it is usually desirable to avoid reactions such as those indicated above, and it has been a purpose of the present invention to minimize them.

The problems discussed above are particularly acute in connection with attempts to re-chlorinate chlorinated hydrocarbons to produce polychlorinated derivatives of the hydrocarbons. The present invention, therefore, has as an additional object the vapor phase production of polychlorhydrocarbon derivatives in such a manner as to carefully control the nature of the chlorinated derivatives produced and avoid excessive decomposition resulting in the production of unsaturated compounds and other undesired products.

In the practice of the invention, the chlorine and the hydrocarbon are fed to the zone of reaction in the presence of an inert gas which serves as a diluent for the reacting constituents and thus absorbs a large part of the heat of reaction and prevents occurrence of ignition and explosions. In the preferred embodiment, the gas which serves as a diluent is the hydrogen chloride formed as a byproduct in the practice of the invention. By making use of the hydrogen chloride formed, it is possible to effect the desired dilution without entailing the expense incident to the purchase of a special gas for use in this connection. The use of this gas also precludes the necessity of a special step in the process or special apparatus for separating the diluent from other constituents of the mixture after the completion of the chlorination reaction. As hydrogen chloride formed in the reaction must be separated from the remaining constituents in any case, the portion of the hydrogen chloride which is to be separated may be separated without adding serious complications to the method or apparatus.

The use of hydrogen chloride as a diluent has important advantages from a chemical standpoint in addition to these advantages from the standpoint of plant operation. Thus, the chemical effect of the presence of a large quantity of hydrogen chloride in the mixture tends to minimize the decomposition of the hydrocarbon chlorides. As the hydrogen chloride is a resultant of such decomposition reaction as indicated by Equation 1, above, its presence in excess operates

in accordance with the laws of mass action to preclude the decomposition of the chlorinated hydrocarbons into unsaturated compounds and the incidental subsequent combination of these unsaturated hydrocarbons with hydrogen chloride to form undesired secondary and tertiary chlorides.

The details of procedure involved in the practice of the present invention will be better understood by reference to the attached flow sheet. In the practice of the process as illustrated, hydrocarbon which is to be chlorinated is drawn from a storage tank 10 to a pump 11 and fed by this pump to a tank 12. From the tank 12 it is fed by a pump 13 through valve 14 to a vaporizer 15. The hydrocarbon vapor is then passed through a valve 16 to a mixing zone 17 where it is mixed with chlorine from tank 10', the chlorine being vaporized at 15' during its flow from the storage tank 10' to the mixing zone 17.

The mixed gases may be passed from the zone 17 through a reactor 18 in which the chlorination reaction takes place. While the reactor 18 may be of any known type and may depend upon the effect of light, heat or catalyst to effect the chlorination of the hydrocarbon without departing from the spirit of the invention, the preferred embodiment of the invention involves the chlorination of the hydrocarbon under the influence of heat, as taught in the patent to Ayres No. 1,717,136 of June 11, 1929. The rate of flow at the zone of confluence between the hydrocarbon and chlorine vapors should also be rapid, as taught in that patent, in order that explosions and persistence of ignition may be avoided. During the initial stages of the chlorination procedure, the quantity of hydrocarbon fed to the reaction zone should be in large excess of the molecular ratio involved in the reaction. By the observance of these precautions, it is possible to minimize the formation of poly-chlorides by the same expedients by which explosions and ignition are avoided.

As an alternative to the operation discussed in the preceding paragraph, the hydrocarbon and chlorine may be heated in the vaporizers 15 and 15' to temperatures sufficiently high to cause prompt reaction between them when they are passed into confluence with each other, as indicated at 17. In case such high temperatures are attained in connection with the heating operations, it will be unnecessary to provide a reactor 18 as a separate element from the mixing zone 17 and this mixing zone will, therefore, become in effect the reactor.

By the above-described chlorination reaction, a mixture of chlorinated hydrocarbon, unconverted hydrocarbon and hydrogen chloride is formed. This mixture is passed through a cooler 19 to a fractionating column 20, where the chlorinated hydrocarbon is condensed and separated from the hydrogen chloride and unchlorinated hydrocarbon passing from the reaction zone. A reflux of hydrocarbon is established into the top of column 20 in order to effect the desired fractionation, the valve 31 being opened to admit hydrocarbon from the tank 12 for this purpose. The mixed vapors of hydrogen chloride and hydrocarbon pass from the top of column 20 through lines 22 and 23 into a condenser 24. In this condenser, the hydrocarbon condenses from a non-condensing mixture of hydrogen chloride and hydrocarbon vapors. Separation of the liquid from the gas occurs in the tank 12 after the mixture has passed from the condenser 24 into that tank.

After operation has been conducted for some time in the manner described above, a pressure due to the presence of the non-condensed hydrogen chloride and hydrocarbon vapors will be developed in the system. The valve 25 is then opened and a mixture of air, which originally filled the system, hydrogen chloride and hydrocarbon vapor is allowed to pass through the valve 25. The rate of emission of gas through this valve is carefully controlled to maintain a steady desired pressure within the system. The mixed gases withdrawn through the valve 25 may be passed through any conventional equipment for the absorption of hydrogen chloride in water to form hydrochloric acid of commercial strength. The tail gas from this operation is compressed and cooled to recover hydrocarbon, which may then be returned to the storage tank for re-introduction into the system, as required. The absorption, compression, condensing and collection equipment are not shown. The valve 57 may be wholly or partially opened during the chlorinating operation if desired, thus enabling the operator to recycle material passing through this valve without passing such material through the condenser 24.

When the system has been purged of air by the emission of gases through the valve 25, valve 26 is opened so that the mixed vapors of hydrogen chloride and hydrocarbon from the tank 12 will pass through valve 26 and compressor 27 and valve 30 to the mixing zone 17, whence they are recycled through the reactor and fractionation apparatus. In this connection, it is important to note that recycled gases are mixed with fresh hydrocarbon in the zone 57 before this hydrocarbon is contacted with chlorine at 17. The possibility of ignition is thus minimized by the preliminary dilution of the hydrocarbon.

The valve 29 may be opened during a part of the chlorinating operation if desired, thus allowing a part of the mixture of hydrocarbon and hydrogen chloride to be passed to the storage tank 28. The mixture of gases stored in this tank may be fed to the chlorinating apparatus during the preliminary stages of subsequent chlorination operations prior to the formation of these gases in the operation of the system in sufficient quantity to develop the necessary pressure for continuous recycling in sufficient quantities to effect the desired dilution.

When the lower boiling hydrocarbons are being chlorinated, it will be possible to vaporize so much hydrocarbon in the vapor from the tank 12 that the introduction of hydrocarbon through the pump 13 to the vaporizer 15 may be discontinued. In this case, valves 14 and 16 will be closed and valves 25 and 30 manipulated to maintain a sufficient volume of returned vapors to effect the desired mixture with the chlorine fed to the zone of confluence.

When higher boiling hydrocarbons are introduced, it will be undesirable to maintain temperatures in the tank 12 sufficient to vaporize hydrocarbon freely into the hydrogen chloride gas. The entire supply of hydrocarbon must then be fed to the zone 17 through the vaporizer 15. In this connection it should be noted that the temperature attained in the vaporizer must be sufficient to overcome the cooling effect of gases meeting at the zone of confluence 57 of the fresh hydrocarbon and other gases.

From the above discussion, it will be seen that

the relative amounts of hydrocarbon introduced into the system through the vaporizer 15 and through vaporization into the vapor stream passing upwardly through the tank 12, depends upon the hydrocarbon under treatment. Careful precautions, however, must be taken in connection with either method of introduction to insure a sufficient dilution of the reactants by the hydrogen chloride and/or excess hydrocarbon present to avoid ignition or explosion.

When it is desired to produce poly-chlor derivatives of the hydrocarbon material under treatment, the chlorinated products condensed in the fractionating column 20 may be continuously passed through the valve 21 to a column 32. Heat is applied to material entering this column by means of a heater 33, which may be heated by steam or direct fire and indirectly heats the material in the column 32 by continuous passage of heated liquid between the heater and the column through conduit 55. Conditions in the column 32 may be maintained at a temperature and pressure adapted to condense the poly-chlorides to the exclusion of the mono-chlorides passing through the column. Mono-chloride material passing from the column 32 is condensed at 35 and refluxed to the column through the valve 36. When the proper conditions of reflux have been established, a certain proportion of the chlorinated material may be withdrawn to container 40 at the desired rate by opening the valves 37 and 39 and restricting the rate of flow through the valve 36, if necessary.

Any desired portion of the chlorinated hydrocarbon passing to the tank 40 may be passed through the line 42 by the pump 41 to vaporizer 15 and recycled through the system in contact with fresh chlorine to effect the rechlorination of such chlorinated hydrocarbon to form poly-chlorides, and other chlorinated hydrocarbon material reaching the tank 40 may be withdrawn for use without being subjected to rechlorination.

It may be desired, in some cases, to effect the rechlorination of only a particular mono-chloride isomer or group of isomers. In such case, the mono-chlorinated material may be fractionated by closing the valve 39 and opening the valve 38 to allow passage of the chlorinated hydrocarbon into column 43 where it is heated by means of a heater 44 which is analogous to the heater 33 which causes vaporization of the mono-chlorides in the column 32. The overhead fraction from the column 43 is condensed at 45 and refluxed through valve 46 to the top of the column until proper reflux conditions are established. The valve 47 is then opened to allow a certain proportion of the overhead product to be passed to the tank 40 or separately collected, as may be desired. Liquid material collecting at the bottom of column 43 is withdrawn through valve 48 and returned to the tank 40 or withdrawn from the system as may be desired.

In the operation of this portion of the system, when a portion of the overhead fraction of the column 43 is to be rechlorinated, the valves 54 and 49 will be closed and valves 52 and 51 opened in order that the overhead product may be passed to the tank 40 from which it may be recycled after its separation from the liquid derivative in the column 43. In this case, the higher boiling material is separately collected by passage through the valves 48 and 51 and line 50 to a suitable receptacle. If, on the other hand, it is desired to re-chlorinate a portion of the higher boiling material passing through the column 43, valves 51 and 52 are closed and valves 49 and 54 are opened to allow the higher boiling liquid passing from the column 43 to be passed to the tank 40 and the overhead product to be separately collected by passage through the valve 54 to a suitable receptacle connected with the line 56. It will thus be seen that by the application of the process described, desired chlorinated derivatives may be simultaneously formed and separately collected. By the passage of chlorinated derivatives from the tank 40 to the reaction zone, these chlorinated derivatives may be rechlorinated simultaneously with the chlorination of fresh hydrocarbon material.

The process described is adapted to the separate collection of a desired chlorinated fraction or to the collection of a portion of any desired chlorinated fraction and the rechlorination of another portion of that same fraction. Thus, the final product from the process may be di-chloride alone, poly-chlorides of a higher order than di-chlorides, poly-chlorides mixed with other poly-chlorides or mono-chlorides, or separate isomers of any of these compounds.

From the above description, it will be seen that the objects of the invention have been amply attained. By the simple feature of recycling hydrogen chloride formed in the reaction, a dilution of the hydrocarbon passing to the reaction is obtained, and the mixture so formed may be further diluted by the use of excess hydrocarbon as desired. By proper fractionation and recycling desired fractions of varying composition may be produced.

It will be evident from the above description that, by the practice of the above invention, a dilution of the materials passing to the reactor is attained in a highly effective and inexpensive manner. In view of the fact that the diluent employed is the hydrogen chloride formed in the reaction, important advantages are attained in the avoidance of decomposition of the chlorinated product and in the avoidance of expensive separating operations which would be necessary if an inert diluent requiring separation from the products of reaction were added to the system. It will also be obvious that the practice of the invention involves an effective and inexpensive method of separately obtaining desired mono-chlor and poly-chlor derivatives or desired mixtures of mono- and poly-chlor derivatives.

Modifications will be obvious to those skilled in the art. It may, for example, be found desirable in certain instances to collect chlorinated hydrocarbon formed in the practice of the process and to chlorinate this material separately from unchlorinated hydrocarbon by using this chlorinated hydrocarbon as a source of supply in the same manner as the original hydrocarbon material from the supply tank 10. In view of the feasibility of adopting this and other alternatives, I do not wish to be limited except by the scope of the subjoined claims.

What I claim is:

1. The process of chlorinating saturated aliphatic hydrocarbons containing three or more carbon atoms in vapor phase which comprises passing such hydrocarbons through a reactor in the presence of chlorine, separating chlorinated derivatives formed in the reactor from undesired material by passing material from the reactor through a fractionating column while maintaining a reflux of hydrocarbons to be chlorinated in said fractionating column and thereby absorbing a portion of the reflux hydrocarbons in the

hydrogen chloride and finally recycling said hydrogen chloride in which a portion of the reflux hydrocarbons has been absorbed through the reactor and thereby chlorinating additional hydrocarbons.

2. The process of chlorinating saturated aliphatic hydrocarbons in vapor phase which comprises passing such hydrocarbons through a reactor in the presence of chlorine, separating chlorinated derivatives formed in the reactor from undesired material, passing hydrogen chloride formed in the reaction into contact with a body of liquid hydrocarbons which it is desired to chlorinate and thereby saturating said hydrogen chloride with said hydrocarbons, passing said saturated hydrogen chloride to the reactor and concurrently passing liquid hydrocarbons from said body of liquid hydrocarbons through a vaporizing chamber into contact with said recycled saturated hydrogen chloride and through said reactor to thereby effect chlorination of additional hydrocarbons.

LEE H. CLARK.