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METHOD OF PRODUCING UNSATURATED
HYDROCARBONS

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5 The present invention relates to the produc-
tion of unsaturated hydrocarbons and is par-
ticularly concerned with the production of hy-
drocarbon material containing a relatively high
proportion of olefins having from 12 to 30 car-
bon atoms. The principal object of the inven-
tion has been to produce a mixture of this type
which is substantially free of diolefins and other
compounds of a higher degree of unsaturation
10 than the olefin material desired. A further ob-
ject has been to produce a mixture of this type
which contains only a relatively small propor-
tion of saturated hydrocarbons or impurities.

15 In the preferred practice of the invention, a
petroleum hydrocarbon fraction of desired boil-
ing range containing a large proportion of sat-
urated hydrocarbon of the paraffin series is
first chlorinated and the chlorinated hydrocar-
bon is thereafter subjected to a splitting opera-
20 tion to decompose the chloride molecules by the
splitting of hydrogen chloride from these mole-
cules to produce the desired olefin.

25 A feature of the invention consists in the utili-
zation of proportions of reactants adapted to
eliminate difficulties of fractionation which
might otherwise arise in attempts to obtain a
mixture of olefin material containing but a
small proportion of saturated hydrocarbons.

30 A second feature of the invention consists in
the practice of a method of splitting the chlori-
nated hydrocarbon which largely avoids the for-
mation of diolefins and likewise avoids the ex-
cessive re-combination of the hydrogen chloride
split from the chlorinated material with olefin to
35 re-form the alkyl chloride molecules. Further
features relating to the economical performance
of the process to obtain a high yield of the
desired product will be obvious from a reading of
the following description of the process.

40 In the practice of the invention, a hydrocar-
bon mixture consisting principally of saturated
hydrocarbon material is first obtained by care-
ful distillation of hydrocarbon material ob-
tained from petroleum. This hydrocarbon ma-
terial is subjected to a chlorinating operation by
45 passing chlorine in vapor phase into the mix-
ture while maintaining the temperature of the
mixture substantially low, preferably below 100°
C. The passage of chlorine into the hydrocar-
bon mixture is continued until the gain in
50 weight of the hydrocarbon material indicates
that the chlorination reaction has proceeded to
the substantial completion of the chlorination of
the entire hydrocarbon mixture. To this end, it
55 is preferred to continue the chlorination until

a quantity of chlorine which is in substantial
molecular excess of the quantity of hydrocarbon
under treatment has reacted therewith. A ratio
of 1.5 moles of chlorine per mole of hydrocarbon
has been found to effect a satisfactory chlorina-
5 tion of the hydrocarbon.

When the increase in the weight of the hydro-
carbon material indicates that the chlorination
reaction has been substantially completed, the
entire body of chlorinated hydrocarbon is sub-
10 jected to a catalytic splitting reaction to cause
the separation of hydrogen chloride from the
alkyl chloride molecules.

15 An important feature of the invention con-
sists in the performance of this reaction upon
the entire body of chlorinated material in the
liquid phase without the performance of any
fractionation of the chlorinated material prior
to the splitting reaction. The chlorinated hy-
drocarbon is refluxed in contact with a suitable
catalyst chosen from the classes of metallic
chlorides and oxides, this splitting operation be-
20 ing performed in such a manner as to avoid any
passage of hydrocarbon material overhead dur-
ing this stage of the operation. The hydrogen
chloride split from the alkyl chloride molecules
is passed overhead during the refluxing of the
25 mixture of hydrocarbon and alkyl chloride, thus
removing the hydrogen chloride evolved as the
result of the splitting operation from the zone
of reaction. The refluxing operation is prefer-
ably continued for several hours and yields a
material containing a very high proportion of
unsaturated hydrocarbon.

30 The residue is next distilled and the overhead
material collected. It yields a fraction of ap-
proximately the same boiling range as the hy-
drocarbon originally chlorinated, this fraction
containing a large proportion of the desired
olefin. The residue of this distillation includes
40 alkyl chlorides, chlorolefins, unchanged hydro-
carbon and catalyst.

45 The advantages of the practice of the inven-
tion should be obvious from the above descrip-
tion. By the utilization of a quantity of chlorine
in substantial molecular excess of the amount
of hydrocarbon material treated, the chlorina-
tion of this material proceeds to substantial
completion. This fact has a very important
50 bearing on the efficient practice of the process,
for olefin material of the range desired is very
difficult to separate from corresponding paraffin
hydrocarbon, these compounds of similar carbon
content having approximately the same boiling
55 range. It is, therefore, highly important that

the olefin material of the mixture be contaminated with as little paraffin as possible, in order that a mixture containing a large preponderance of olefin may be obtained without recourse to elaborate fractionation of the ultimate material produced by the process.

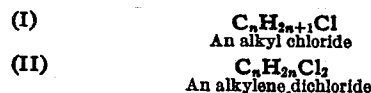
Further important advantages are obtained by the liquid phase splitting of the chlorinated molecules in the manner described above. The performance of the splitting operation in the liquid phase renders possible an operation in which the material under treatment is gradually refluxed and hydrogen chloride separated by the splitting operation is removed as it is formed. This fact has an important bearing upon the efficient performance of the process, as it not only avoids contamination with hydrogen chloride of the mixture ultimately obtained, but it avoids re-combination of this hydrogen chloride with the unsaturated hydrocarbon to re-form the alkyl chloride molecules. It will be appreciated that re-formation of these alkyl chloride molecules out of contact with the splitting catalyst would defeat the very purpose of the splitting operation. In the practice of the process as described, any re-combination which may occur takes place in the presence of the splitting catalyst and the re-chlorinated product is thus subjected to the same splitting action which causes the original splitting of the molecule.

Performance of the splitting operation in the liquid phase and the refluxing of the hydrocarbon material also avoid the accidental passage of hydrocarbon chloride from the zone of reaction and enable us to gradually complete the splitting operation to the desired degree without the necessity of recycling any of this material.

The importance of the particular nature of the splitting operation will also be apparent from the following theoretical considerations. When a saturated hydrocarbon is chlorinated, a mixture of chlorides and polychlorides is formed. These polychlorides are formed in part by reason of the attack of chlorine upon more than one of the hydrogen atoms of the hydrocarbon molecules under treatment and in part by the splitting of hydrocarbon chlorides formed and the attack of chlorine molecules upon the double bonds of olefins formed by the splitting reaction. When a dichloride is split to remove both of its chlorine molecules, a diolefin is produced. Since these diolefins and olefins of higher degrees of unsaturation constitute undesired constituents of the mixture, their avoidance constitutes an important advantage of the procedure adopted. When a dichloride is subjected to a splitting reaction, it is first decomposed to form the corresponding chlor-olefin. When the chlor-olefin is subjected to more intense splitting conditions, it may be split to form the corresponding diolefin. The splitting of chlor-olefins of a given carbon content to form diolefins requires much more intense reaction conditions from the standpoint of heat and catalysts, however, than does the splitting of corresponding alkyl chlorides. By the performance of the splitting reaction in the liquid phase under reflux conditions and in the presence of suitable catalysts, in the practice of the present invention, we have succeeded in selectively splitting the alkyl chloride molecules to the substantial exclusion of the chlor-olefin of the mixture.

Thus, where a paraffin of the formula C_nH_{2n+2} is chlorinated, we get a mixture including alkyl

monochlorides and alkylene dichlorides of the following type formulae:



When a mixture including compounds of the types indicated at I and II is subjected to splitting conditions, compound I decomposes to form an olefin of the type formula C_nH_{2n} . Under these conditions, compounds of the type indicated at II are first decomposed to split off a molecule of hydrogen chloride and form chlor-olefins of the type formula $C_nH_{2n-1}Cl$. If these chlor-olefins are subjected to intense splitting conditions, they may lose an additional molecule of hydrogen chloride to form diolefins of the type formula C_nH_{2n-2} .

It is the object of the invention to produce a mixture containing a large preponderance of olefins to the substantial exclusion of chlor-olefins, diolefins, and more highly unsaturated hydrocarbons or their chlor-derivatives. If a splitting operation of such intensity is adopted as to cause the production of a substantial quantity of diolefin material, a difficult problem of fractionation is presented in connection with any attempt to separate this diolefin material from the desired olefin. By the careful practice of liquid phase splitting in the presence of a suitable catalyst and under reflux conditions, the splitting of the chlor-olefin material to form the undesired diolefin is substantially eliminated. Since the alkyl chlorides can be more readily split than the corresponding chlor-olefins, it is possible to choose reaction conditions in the splitting operation adapted to effect the selective splitting of the alkyl chlorides to the substantial exclusion of the chlor-olefins and more highly unsaturated chlor-compounds. At the conclusion of the reaction, it is possible to separate the olefins formed, together with the other unchlorinated hydrocarbon material of the mixture and retain the chlorinated material including alkyl chlorides, alkylene dichlorides, higher chlorides and unsaturated chlor-compounds in the residue.

A number of catalysts chosen from the classes of metal salts have been found to be satisfactory in the performance of the splitting reaction in the practice of the invention. Thus, the metal chlorides such as ferric chloride, ferrous chloride, cuprous chloride, cupric chloride, cobalt chloride, cadmium chloride, antimony chloride, zinc chloride, barium chloride and manganese chloride have been found satisfactory in this connection. Iron oxide and mixtures thereof with one of the chlorides referred to above have also been found to have the desired catalytic effect. It is necessary to use only a very small amount of catalyst, one-half of one per cent of ferric chloride having been found to be satisfactory in the splitting of tetra-decyl chloride.

As an illustrative example of the practice of the invention, the following procedure was adopted. 200 pounds of hydrocarbon material obtained by the careful fractionation of Cabin Creek kerosene, and having an Engler distillation range from 243 to 258 degrees C. and having a specific gravity of 0.795 was chlorinated by the passage of chlorine through the hydrocarbon material until the chlorinated material had a weight of 252.5 pounds. This increase in weight represents a molecular ratio of chlorine to hydrocarbon of 1.5:1. By continuing the chlorination

reaction until the weight of the material under treatment indicates the presence of a substantial molecular excess of chlorine, the operator can assure himself that the major proportion of the hydrocarbon material has been chlorinated. The specific gravity of the chlorinated material at 20 degrees C. was approximately 0.954. At the completion of the chlorination reaction, 1.2 pounds of ferric chloride were dissolved in the hydrocarbon material and the entire body of chlorinated hydrocarbon was refluxed for three and one-half hours, hydrogen chloride being passed overhead and the entire body of hydrocarbon material being retained in the still. Hydrogen chloride was rapidly evolved during the early stages of the operation, but its rate of evolution became gradually less during the subsequent stages of the operation. After the evolution of hydrogen chloride had entirely ceased, the hydrocarbon material remaining in the still was distilled under reduced pressure to obtain a mixture containing a preponderance of olefin. The fraction having a boiling range from 155° to 175° C. at 100 mm. pressure was collected and contained from 80 to 85 percent of olefin having a specific gravity of 0.810. 110 pounds of olefin containing material were obtained. The olefin material contained a small amount of hydrogen chloride which was neutralized by washing with a one percent sodium hydroxide solution and decanting the mixture so obtained to effect the removal of brine.

When the term "a narrow boiling hydrocarbon fraction" is used in the subjoined claims, this term is used to designate a hydrocarbon fraction of such narrow boiling range that the chlorides and chlor-olefins corresponding in carbon content to the lowest boiling hydrocarbon constituents of the fraction have higher boiling points than the highest boiling olefins corresponding in carbon content to the highest boiling hydrocarbon constituents of said fraction.

Modifications will be obvious to those skilled in the art. The practice of chlorinating a hydrocarbon mixture of the type under treatment with an excess of chlorine to insure the formation of a mixture of mono- and poly-chlorides with a minimum of hydrocarbon may, for example, be practiced in connection with other subsequent steps of splitting of the chlorides than those discussed above. Similarly, the particular method of liquid phase splitting adopted may be

used in connection with other methods of halogenation than that described. Still other modifications may be adopted and we do not, therefore, wish to be limited except by the broad scope of the subjoined claims.

We claim:

1. The method of producing unsaturated aliphatic hydrocarbon material containing twelve or more carbon atoms and separating said unsaturated aliphatic hydrocarbon material from by-products produced in the manufacture thereof which comprises chlorinating to substantial molecular excess paraffine hydrocarbon material of a carbon content corresponding to the desired unsaturated hydrocarbon and consisting of a narrow boiling hydrocarbon fraction, splitting hydrogen chloride from the chlorinated material in the liquid phase to produce the desired unsaturated hydrocarbon, and thereafter separating the desired unsaturated hydrocarbon from the mixture resulting from the splitting operation by distilling said unsaturated hydrocarbon overhead from undesired chlorine derivatives obtained as by-products.

2. The method of producing unsaturated aliphatic hydrocarbon material containing twelve or more carbon atoms and separating said unsaturated aliphatic hydrocarbon material from by-products produced in the manufacture thereof which comprises chlorinating by substitution paraffine hydrocarbon material of a carbon content corresponding to the desired unsaturated hydrocarbon and consisting of a narrow boiling hydrocarbon fraction, the chlorination of the hydrocarbon being continued until the reaction of a substantial molecular excess of chlorine with the hydrocarbon to produce a mixture of mono-chlorinated and poly-chlorinated derivatives of said paraffine hydrocarbon containing not more than a relatively small proportion of unchlorinated hydrocarbon is completed, subjecting said mixture to a liquid phase splitting reaction of controlled degree adapted to effect the splitting of hydrogen chloride from the mono-chlor derivatives of saturated hydrocarbons and thereafter separating the desired unsaturated hydrocarbon material so formed from the undesired chlorine derivatives obtained as by-products by distilling said unsaturated hydrocarbon material overhead from undesired material.

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