Nov. 20, 1945. D. R. BLUMER 2,389,230

PROCESS FOR TREATING HYDROCARBONS

Filed Nov. 25, 1941 2 Sheets-Sheet 1

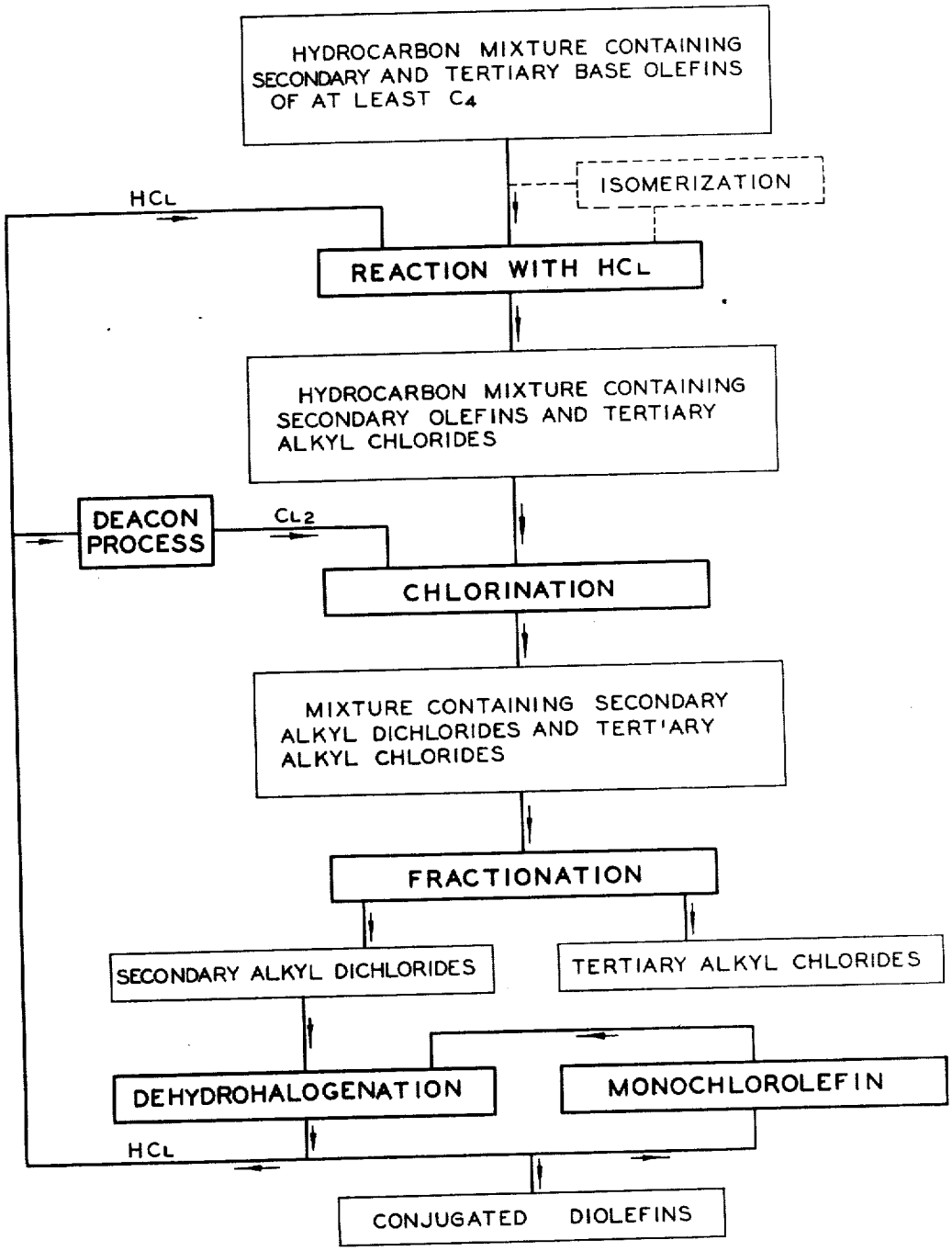


FIG. 1

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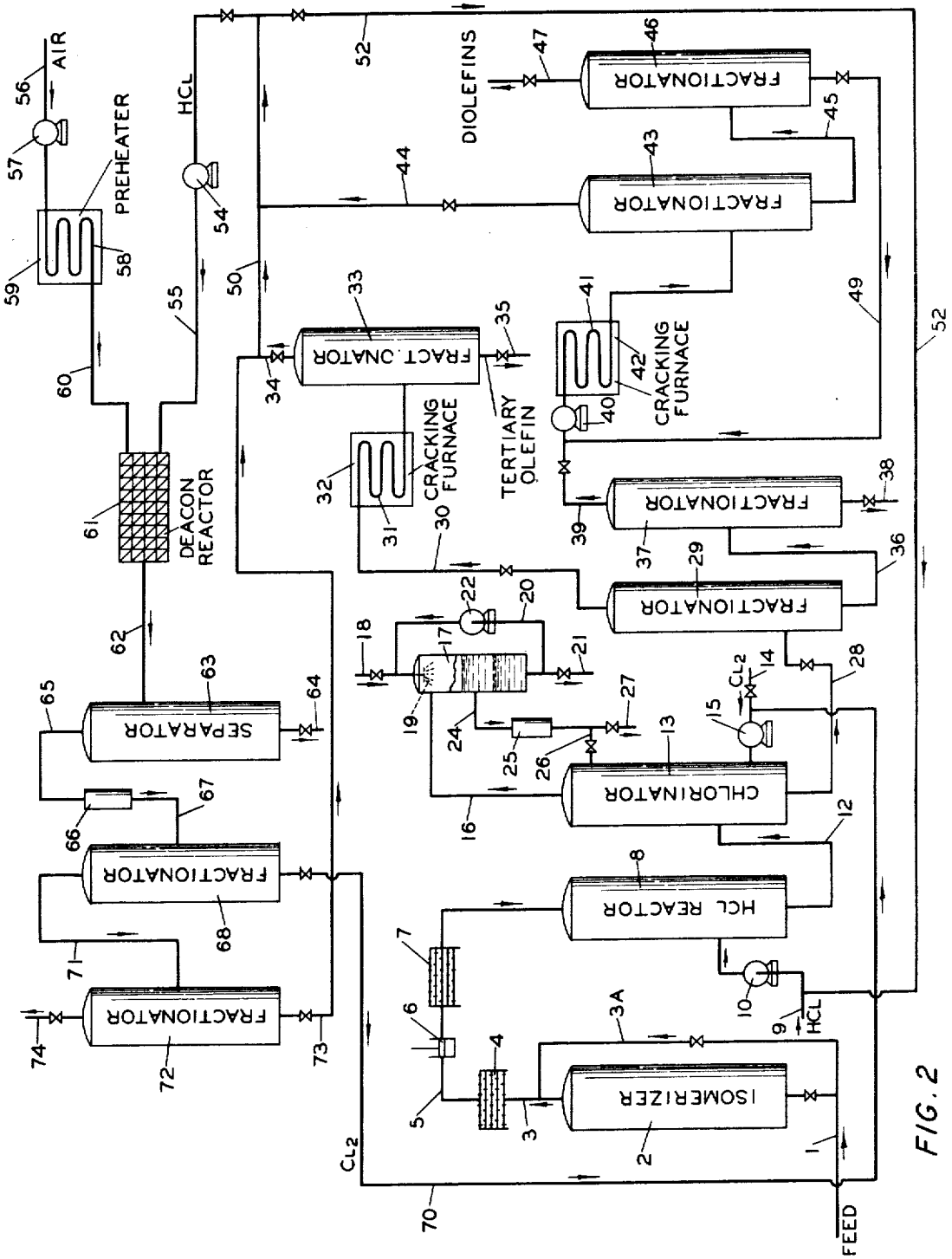


FIG. 2

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UNITED STATES PATENT OFFICE

2,389,230

PROCESS FOR TREATING HYDROCARBONS

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Application November 25, 1941, Serial No. 420,431

6 Claims. (Cl. 260—660)

This invention relates to the treatment of a hydrocarbon mixture containing C_4 or higher secondary and tertiary base olefins to convert the olefin content thereof into compounds which are readily separated in fairly pure form from the resulting conversion mixture and to recover therefrom conjugated diolefins which are useful as a starting material for the preparation of synthetic rubber, and other chemicals which are useful as raw materials for organic synthesis. More particularly it relates to a process of recovering conjugated diolefins such as butadiene, piperylene, etc. from the normal olefins of C_4 and higher and recovering tertiary alkyl chlorides from the tertiary base olefins of C_4 and higher.

The principal object of the present invention is to provide an improved process of recovering useful compounds from the C_4 and higher olefin content of hydrocarbon mixtures.

Another object is to separately recover aliphatic conjugated diolefin from the secondary olefin content of a hydrocarbon mixture containing both secondary and tertiary olefins of C_4 and higher.

Another object is to separately recover aliphatic conjugated diolefin products from the secondary and the tertiary olefin content of a hydrocarbon mixture containing both secondary olefins of C_4 and higher and tertiary olefins of C_5 and higher.

Another object is to recover pure butadiene from the normal butene content of a mixture containing both normal butenes and tertiary butene (isobutene).

Another object is to so treat a hydrocarbon mixture containing C_5 or higher normal and tertiary olefins as to convert the normal olefin content to straight chain aliphatic conjugated diolefins and the tertiary olefin content to branched chain aliphatic conjugated diolefins, the straight chain and the branched chain diolefins being separately recovered in such manner as to avoid the necessity for separating the same from one another.

Another object is to eliminate the necessity of fractionating or otherwise resolving at great expense a hydrocarbon stream containing olefins in limited amount and having boiling points close to one another and/or close to paraffins present, to recover separate olefin fractions therefrom for conversion to diolefins.

Another object is to make possible more effective utilization of halogen in a process of treating a hydrocarbon mixture containing C_4 or higher secondary and tertiary olefins.

Another object is to provide an improved process of separately converting both the normal and the tertiary base olefins of at least 4 carbon atoms in a mixture containing the same.

Another object is to provide an improved process of preparing conjugated diolefins such as butadiene, piperylene, isoprene, etc.

Another object is to reduce the cost of preparation of aliphatic conjugated C_4, C_5 or C_6 diolefins and thereby the cost of synthetic rubber prepared therefrom.

Numerous other objects of this invention will appear as this description proceeds.

This invention may be more fully understood by reference to the accompanying drawings wherein Fig. 1 portrays a flow diagram of the process of the present invention in its preferred form; and Fig. 2 portrays diagrammatically one form of apparatus which has been found useful in carrying out the process of the present invention.

As used herein, the term "halogen" denotes chlorine, bromine or iodine, and the term "hydrogen halide" ordinarily indicates hydrogen chloride or hydrogen bromide, although it may indicate hydrogen iodide or hydrogen fluoride where suitable reaction conditions are used. Likewise, unless the context requires otherwise, specific reference to a given halogen such as chlorine or compound thereof or process involving the same is intended to include other halogens as alternative or equivalent. While chlorine and hydrogen chloride are generally employed because of their cheapness and availability, this does not necessarily means that chlorine is always preferred since occasions may arise where another halogen is preferred because of its superior reactivity or special properties for a particular use. Thus the use of bromine and hydrogen bromide is frequently more advantageous than the use of chlorine and hydrogen chloride.

As will be more fully brought out below, my invention seeks to separately convert the secondary and the tertiary C_4 or higher olefins present in a mixture containing the same to classes of compounds which may be readily separated from each other, the secondary olefins being converted to dichlorolefins and the tertiary olefins being converted to tertiary alkyl chlorides. These are readily separated from each other and any other material and are then converted to desirable materials, the dichlorolefins preferably being converted to diolefins by dehydrohalogenation and the tertiary alkyl chloride (where it

contains at least 5 carbon atoms) preferably being converted to branched chain diolefins.

If a mixture comprising normal butene and isobutene be chlorinated and the resulting mixture dehydrochlorinated, the butadiene obtained by dehydrochlorination of the normal dichlorbutane will be contaminated with various decomposition products obtained by dehydrochlorination of the tertiary dichlorbutane. If a mixture comprising normal and tertiary pentenes is chlorinated and the mixture dehydrochlorinated, the aliphatic straight chain diolefin (piperylene) derived from the normal pentene is contaminated with the branched chain diolefin (isoprene) derived from the tertiary pentene. The same is true of the hexenes.

Since synthetic rubber manufacture demands pure aliphatic conjugated diolefins, i. e., pure butadiene, pure piperylene, pure isoprene, etc., a process involving chlorination and dehydrochlorination of mixtures containing both normal and tertiary C_4 or higher olefins such as is outlined in the preceding paragraph is wholly unsuitable. It is the aim of the present invention to provide a process overcoming these difficulties.

The secondary olefins are characterized by the grouping R—CH=CH— and consist of two types, namely, the normal olefins (characterized by straight chain configuration) and the secondary iso olefins (having branched chain structure). The tertiary base olefins are characterized by the grouping

$$R_2C=C\diagup\diagdown$$

In the case of C_4 olefins, there are only two possibilities, namely the normal butenes and isobutene which is tertiary. In the case of C_5 and higher olefins, if secondary iso olefins are encountered in the refinery stream treated by my process they behave like the normal olefins except that they form branched chain diolefins which are recovered along with the straight chain diolefins derived from the normal olefins. For example, in the case of pentenes, if (as is unlikely) the secondary isopentene 3-methylbutene-1 be present in the pentene stream treated by my process, it forms isoprene which is recovered along with the piperylene.

While my invention is particularly applicable to a hydrocarbon stream wherein the C_4 or higher olefins consist of normal and tertiary olefins, it is applicable to a stream wherein the olefins consist of secondary iso and tertiary olefins, or normal, secondary iso and tertiary olefins.

Briefly stated, my invention involves reacting a hydrocarbon mixture containing C_4 or higher secondary and tertiary base olefins with a hydrogen halide under conditions such that substantially all of the tertiary base olefins selectively react with the hydrogen halide to form tertiary alkyl halides. The reaction mixture thus obtained (in which the secondary olefins are substantially unchanged) is then halogenated under such conditions that substantially all of the secondary olefins are converted by additive halogenation to secondary dihalogen derivatives, while the other components of the reaction mixture, including the tertiary alkyl halides, are substantially unaffected. The resulting mixture is then fractionated to recover a fraction of the secondary dihalogenated derivatives and a second fraction of the tertiary alkyl halides. These materials may then be employed for the preparation of other compounds. Thus the secondary dihalogenated derivatives are preferably subjected to dehydrohalogenation to remove two molecules of hydrogen halide (a portion of which may be recycled for use in carrying out the initial step of the process and another portion of which may be converted to elemental halogen for use in the halogenation step) and thereby form a conjugated diolefin. Monochlorolefin recovered from the dehydrochlorination step may be recycled for dehydrohalogenation.

A process such as just described, with chlorine as the halogen, is portrayed in the flow sheet of Fig. 1 of the drawings.

As applied to a predominantly C_4 hydrocarbon raw material containing saturated and monoolefinic hydrocarbons, or the olefins only, the olefins present comprising normal butenes and isobutene, the reaction mixture is first reacted with anhydrous hydrogen chloride to convert the isobutene to tertiary butyl chloride, which compound does not react further to any appreciable extent with chlorine under the conditions used in the subsequent chlorination. The mixture is then chlorinated to convert the n-butenes and particularly butene-2 to dichlorbutanes and particularly 2,3-dichlorbutane. The reaction mixture is then fractionated to separate the dichlorbutane and the tertiary butyl chloride, which have widely separated boiling points, from one another and from any other material. The dichlorbutane fraction is then dehydrohalogenated to remove two molecules of HCl and form 1,3-butadiene. The tertiary butyl chloride may be utilized in several ways, for example: for conversion by dehydrochlorination to pure isobutene; for the production of diisobutylene which can be hydrogenated to isooctane, as component of 100 octane aviation gasoline; for production of high octane motor fuels by acid alkylation of suitable aliphatic, olefinic, acetylenic or aromatic hydrocarbons; for production of valuable organic chemicals, such as tertiary butyl alcohol. Any tri- or higher chlorides of butane or polymers of these recovered as by-products in the process may be utilized as intermediates, as solvents, etc. HCl recovered from the dehydrohalogenation of the dichlorbutanes or from the dehydrohalogenation of the tertiary butyl chloride may be recycled for reaction with isobutylene and also for regeneration of chlorine to be used in the chlorination of the normal butenes.

In a modification of the foregoing process, the butene stream may be reacted with hydrogen fluoride to convert the isobutene to tertiary butyl fluoride, followed by chlorination or bromination of the n-butenes to the corresponding dihalogen derivatives and fractionation to separate the tertiary butyl fluoride. Tertiary butyl fluoride is a particularly valuable alkylating agent for the production of high octane fuels by alkylation of hydrocarbons.

As applied to a predominantly C_5 hydrocarbon stream, a corresponding series of steps may be employed. The initial reaction with HCl produces tertiary amyl chloride from the tertiary base pentenes namely 2-methylbutene-1 and 2-methylbutene-2. The subsequent additive chlorination converts the normal pentene content to straight chain dichlorpentanes, namely the 2,3 and 1,2 substituted products. After separation, the straight chain dichlorpentanes are converted to piperylene by dehydrochlorination. As before, the separation of the dichlorpentane fraction and the tertiary amyl chloride fraction is readily effected because of the widely separated boiling

points. The tertiary amyl chloride may be dehydrohalogenated to form tertiary base C_5 olefins, namely, 2-methylbutene-2 and 2-methylbutene-1, or may be utilized for the production of isoprene by conversion to 2,3-dichlor-2-methylbutane which upon dehydrohalogenation yields isoprene. The tertiary amyl chloride may be converted to 2,3-dichlor-2-methylbutane either by substitutive chlorination or by dehydrohalogenation followed by additive chlorination. Alternatively, the tertiary amyl chloride may be hydrolyzed to form tertiary amyl alcohol, or may be used for polymerization or alkylation reactions, as an intermediate, etc.

If desired, in the case of a C_4 hydrocarbon stream containing C_4 olefins, the stream may be first subjected to catalytic isomerization in such manner as to convert any butene-1 to butene-2 so that upon chlorination an increased proportion of the preferred 2,3-dichlorobutane is formed. In the case of a C_5 stream containing C_5 olefins, the stream may be isomerized in such manner as to convert C_5 olefins largely to 2-methylbutene-2 (the equilibrium isomerization reaction mixture containing approximately 50% of 2-methylbutene-2). The necessary isomerization conditions for either type of isomerization are known to those skilled in the art. The resulting C_5 mixture is reacted with HCl to convert the 2-methylbutene-2 and any 2-methylbutene-1 present to tertiary amyl chloride and the reaction mixture is subjected to chlorination, followed by fractionation, as before, to separately recover the tertiary amyl chloride and the dichlorpentanes.

The invention is applicable to all possible mixtures of C_4, C_5, C_6, C_7, and higher olefins, with or without C_4, C_5, C_6, C_7 and higher paraffins, and containing both secondary and tertiary olefins. The invention may be employed to produce all possible straight or branched chain aliphatic conjugated diolefins, either in essentially pure form or in the form of all possible mixtures of the straight and/or branched chain diolefins. Thus the invention may be employed to produce straight-chain diolefins, as for example butadiene, piperylene, etc., or branched chain diolefins, as for example: isoprene, 2,3-dimethylbutadiene, etc., either in pure form or as a concentrate thereof, or to produce mixtures of any of the straight chain diolefins or mixtures of any of the branched chain diolefins or, under certain circumstances, mixtures of straight chain diolefins with branched chain diolefins. It is particularly applicable to the production of pure or concentrated straight chain diolefins on the one hand and branched chain diolefins on the other hand.

Preferably the initial hydrocarbon stream treated in accordance with the present invention is free from hydrocarbons other than olefins or paraffins, such as diolefins, cyclic hydrocarbons, aromatics, naphthenes, etc., having been previously treated to remove such hydrocarbons.

Care must be taken in the treatment of the initial stream with hydrogen chloride to use such conditions that it adds preferentially to the tertiary olefin content thereof. This reaction may be conducted in the liquid or vapor phase, preferably the former, using sufficient pressure to maintain the liquid phase. Temperatures may be from about −80° C. to about 100° C. The reaction proceeds in the absence of catalyst, though catalysts which speed up the reaction with the tertiary olefins without causing reaction of the hydrogen chloride with the secondary olefins may be employed. It is preferred to use anhydrous HCl and to have the reaction mixture free from water. The time of contact should be so limited that the HCl does not appreciably attack the secondary olefin content. The amount of HCl may vary from theoretical required to combine with the tertiary olefin content up to about a 10% excess thereover. Too large an excess may induce additive reaction with the secondary olefins.

The conditions for the additive chlorination reaction should be such that chlorine adds preferentially to the secondary olefin content to form the dichloride without appreciably reacting with the tertiary monochloride, or any paraffins present, by substitutive chlorination. Liquid phase chlorination is preferred, although in some cases vapor phase chlorination may be employed. The pressure should be such that the liquid phase is maintained. The temperature should be maintained at the lowest economically practicable level in order to avoid decomposition reactions and induced substitutive chlorination. Temperatures ranging from about −20° C. to about 50° C., and preferably in the neighborhood of 0° C. are desirable. The heat of the chlorination is preferably continuously abstracted throughout the reaction preferably by circulating a liquid cooling medium through heat exchange surfaces or by refrigeration where compressed gases are available for expansion. The reaction is preferably conducted in the anhydrous state though in some cases small amounts of water or aqueous alkali may be present to absorb any HCl evolved. Ordinarily no catalyst is used, although mild catalysts which do not catalyze substitutive chlorination of the tertiary monochloride present may be used. Preferably the chlorination is conducted in the dark or in the absence of radiations which induce substitutive chlorination.

Where the tertiary monochloride fraction is chlorinated in production of branched chain diolefins therefrom, this substitutive chlorination is carried out under different conditions from the additive chlorination just described. For this reaction a relatively active chlorine-substitution catalyst such as antimony chloride or iodine should be used. The conditions for carrying out such a chlorination in the liquid phase are well-known to those skilled in the art. In order to avoid excessive formation of the tri- and higher chlorides, the chlorination is preferably terminated before all of the monochloride has been converted to the dichloride, whereupon the mixture is fractionated and the monochloride returned. Alternatively the substitutive chlorination may be conducted in the absence of a catalyst but in the presence of suitable light radiation, at such a temperature that the dihalide as formed condenses out and is removed from the reaction zone so that it is not further reacted upon to form tri- and higher chlorides.

The dehydrochlorination step to produce the diolefins may be carried out in accordance with conditions set forth below or in accordance with known conditions for catalyzed dehydrochlorination. As set forth below, I prefer to conduct this step in an open stainless steel tube without any added catalyst and, in the case of C_4, at temperatures of from about 500° to about 750° C. As progressively heavier materials are treated the temperature should be progressively lowered in order to avoid excessive decomposition and side reactions. When operating in the preferred temperature range the contact time should be so controlled that it is shorter at the higher temperatures and longer at the lower temperatures. The

reaction may be expedited either by use of reduced pressure or by the reduction of partial pressure of the material being decomposed by the introduction of an inert diluent.

The process outlined above effects great economy, particularly in the case of C_4 hydrocarbons, by preventing waste of expensive chlorine since it eliminates the chlorination of the tertiary base olefins by first reacting the tertiary base olefins with dry HCl under such conditions that they are substantially completely converted to tertiary alkyl chlorides while the secondary olefins either do not or only slightly react with the HCl. In addition, the subsequent chlorination is carried out under such conditions that direct addition of chlorine to the secondary olefins takes place with a minimum of substitutive chlorination of the saturated hydrocarbons or of the tertiary alkyl chloride. The latter in particular is unaffected by chlorine at low temperatures in the liquid phase and in the absence of active catalysts or light.

Moreover the process further reduces the cost of producing the conjugated diolefins by permitting ready recovery and utilization of all other products such as the tertiary alkyl chlorides, tri- and higher halogenated paraffins and polymers thereof, etc., for production of useful materials such as high octane motor fuels, organic chemicals, etc. The recovery and recycling of the hydrogen chloride for use both as such and after partial conversion to chlorine effects a further reduction in the cost of operation.

The process is advantageous because it permits the easy separation of the tertiary alkyl chlorides and the secondary dichlorides from each other and from other components so that each may be further individually processed.

The process is further advantageous because side reactions are kept to a minimum thereby making possible more economical production of products of high purity and because the process is capable of control in a convenient and economical manner to yield the desired products. The need for expensive and difficult fractionation or extraction methods to separate the tertiary base olefins from the hydrocarbon stream is eliminated. Moreover less heat is generated during the chlorination step of the process than would be liberated were the hydrocarbon stream chlorinated directly with the tertiary base olefins present; consequently, heat exchange requirements are less, there is less chance of side reactions occurring, and better control is possible using the process of the present invention.

In one embodiment, the invention comprises reacting dry hydrogen chloride under suitable conditions with vaporized C_4 hydrocarbons consisting essentially of n- and iso-butane, n-butenes (largely butene-2), and isobutylene in such a way that the isobutylene reacts to form tertiary butyl chloride, whereas the n-butenes and butanes do not react to any appreciable extent. Prior to this treatment the C_4 stream is preferably enriched in butene-2 and depleted in butene-1 by means of a catalytic isomerization process in known manner to such an extent that the n-butenes present are largely butene-2. The reaction mixture containing the tertiary butyl chloride and any excess HCl in liquid phase is then chlorinated in such a way that chlorination takes place to form dichlorbutane practically completely by direct addition to the n-butenes, without any appreciable substitutive chlorination of the n- and iso-butane, tertiary butyl chloride or the desired dichlorbutane products. This may be accomplished by chlorinating in a fractionating tower which is packed with inert carbon or stoneware Raschig rings or other suitable packing in such a way that the infeed is introduced as a liquid, either under sufficient pressure to maintain liquid phase or at a low enough temperature to maintain liquid phase at atmospheric pressure, into the column packing at a point nearer the bottom than the top of the column. The chlorine is introduced, in molar quantity equal to that of the n-butenes present, into the column packing with provision for good dispersion at a point near that at which the C_4 stream is introduced. The tertiary butyl chloride and the dichloro derivatives tend to pass down the column and collect in the kettle whereas the unreacted butanes and any excess of chlorine and HCl pass off the top of the column, the chlorine and HCl being completely removed by scrubbing or further fractionation and the butanes being returned to the refinery for further processing. The reflux column should be long enough to permit complete reaction of the n-butenes with the chlorine before they reach the top of the column and thereby prevent unreacted n-butenes from passing out with the overhead butane stream. The chlorination may be conducted at temperatures ranging from about −10 to about 50° C. depending upon the pressure and other factors.

The chlorination may be conducted in other ways, for example by passing the chlorine directly into the liquified C_4 hydrocarbons with abstraction of the heat of reaction, being careful to stop the chlorination before or when the addition reaction is substantially completed in order to avoid substitutive reactions. However this involves the use of staggered intermittent or batch operation or other special provisions for continuous operation which is not so convenient or efficient as the continuous process outlined above.

During chlorination, a catalyst, such as sulfuryl chloride either added as such or formed in situ by the introduction of sulfur dioxide which forms sulfuryl chloride by reaction with the free chlorine; may be present in the chlorination zone, though use of a catalyst is unnecessary.

The chlorinated material is removed continuously from the chlorination apparatus and sent to a fractionating column where the mono-, di-, tri-, and higher chlorinated derivatives of n- and iso-butane are separated by distillation. The dichlorides, principally 2,3-dichlorobutane, are then sent to the dehydrohalogenation furnace where the crude butadiene is produced by liberation of two moles of HCl per mole of the 2,3-dichlorbutane. Also, one mole of HCl is liberated from 2,3-dichlorbutane to form 2-chlorbutene-3, which is subsequently removed by fractionation or scrubbing and recycled to the furnace to liberate another mole of HCl to form butadiene. The tertiary butyl chloride can be dehydrohalogenated to isobutylene or treated in any other desired manner.

The following example illustrates the foregoing process applied to a C_4 hydrocarbon stream.

Example 1

A vaporized refinery C_4 stream is catalytically isomerized to convert the butene-1 substantially to butene-2. The isomerized material has the following composition, expressed in mole percentages: butene-2, 7.6; butene-1, 0.4; isobutylene, 0.5; n-butane, 64; isobutane, 21; propane, 6; and propylene 0.5. This material is then reacted

with hydrogen chloride either in the liquid or in vapor phase, the hydrogen chloride being added in slight excess (not exceeding 10%) of the equimolar amount required to react with the isobutylene. If this step is to be carried out in the liquid phase, as is preferred, the C_4 stream is compressed to a pressure of from about 50 to about 150 lbs. per sq. in. (depending upon the external atmospheric temperature) and cooled to the surrounding atmospheric temperature to produce the liquid phase. This liquid phase is contacted with the dry hydrogen chloride which is pumped into a suitable reactor or absorber in countercurrent fashion, the liquid hydrocarbons flowing downward over suitable contact material and the hydrogen chloride flowing upward from the point of introduction at the bottom. Under these conditions, the hydrogen chloride reacts almost instantaneously with the isobutylene without the presence of a catalyst and very little of the n-butenes react since the reaction of hydrogen halide with normal olefins is very slow in the absence of a suitable catalyst.

The reaction just described may alternatively be carried out in the vapor phase by passing the isomerized C_4 stream, to which dry HCl has been added in 10% excess over the molar concentration of isobutylene, over a suitable catalyst such as porous $BaCl_2$ or $MgCl_2$ at 50–120° C. in which case substantially all of the isobutylene but practically none of the butene-2 will be reacted. However, liquid phase addition reaction of HCl is preferable because it is desirable to carry out the subsequent additive chlorination of butene-2 in the liquid phase in order to minimize substitutive chlorination reactions. Moreover, in order to avoid corrosion difficulties, it is desirable to compress the isomerized C_4 stream before rather than after the addition of the HCl, for in the former case the reaction mixture containing slight excess HCl can be introduced directly into the chlorinator without removal of HCl, which would be necessary were it to be taken into an ordinary compressor for introduction as liquid phase into the chlorinator. Otherwise a compressor of expensive corrosion resistant construction would be required.

The reaction mixture from the foregoing step is then chlorinated. This chlorination may be conducted continuously in a modified fractionator type reactor packed with inert carbon or stoneware Raschig rings or similar corrosion resistant material, the liquid C_4 stream containing isobutyl chloride and hydrogen chloride being introduced into the column somewhat below the mid-point and the chlorine being introduced at several points nearby with provision for diffuse introduction of the chlorine to prevent serious local overheating. The molar quantity of chlorine introduced should equal or only very slightly exceed the molar quantity of n-butenes present in the C_4 stream in order to insure that the reaction proceeds principally by addition to n-butenes and to minimize substitutive chlorination. Since it is desirable to chlorinate in the liquid phase rather than in the vapor phase in order to avoid substitutive chlorination, it is necessary to refrigerate the chlorinator if the reaction is carried out at atmospheric pressure. Ordinarily, this is too expensive unless compressed gases are available which have to be expanded before using in other parts of the process, in which case they may be used for refrigerating the chlorinator. Thus the vaporization of the C_4 stream before passage through the isomerization reactor can be used for this purpose.

Ordinarily if it is necessary to rely for cooling the chlorinator upon cooling water available at the refinery, the temperature of which may be as high as 46° C., it will be necessary to carry out the chlorination reaction under pressure to keep the C_4 hydrocarbons in the liquid phase. Thus for a head temperature of the chlorinator ranging approximately from −10 to 46° C., the pressure required to maintain liquid phase will range approximately from atmospheric to about 110–120 lbs. sq. in. Use of the lowest temperature and pressure economically possible is desirable in order to keep substitutive chlorination at a minimum. It is advantageous to remove the heat of chlorination as by circulation of cooling liquid around or through the chlorinator column, or in other suitable manner to prevent development of excessive temperatures and pressures and any possibility of an explosion. The cooling medium is preferably introduced at the top section of the column first and subsequently in series to other cooling coils or jackets arranged along the column from top to bottom so that the head of the column is the coolest point.

In the chlorination process, the introduced C_4 stream tends to flow downward as reflux until it contacts the chlorine when the heat of reaction causes it to vaporize and pass upward through the column. The mono- and dichlor derivatives, which have higher boiling points, pass downward through the column and collect in the kettle, thereby being removed from further contact with chlorine, eliminating the possibility of additional chlorination by substitution to form higher chlorides. The liquid phase absorbs the heat of chlorination and aids in rapidly transmitting this heat to the external cooling means, thus avoiding local overheating which may result in flashing or explosions. The column is so designed and built that the mono- and dichlorbutane derivatives, substantially free of C_4 hydrocarbons, collect in the kettle, the n-butenes are substantially completely chlorinated to the dichlor derivatives before they reach the head of the column; and the C_4 hydrocarbons that leave the head of the column are free of chlorinated products, the latter being higher boiling. This can be readily accomplished since the boiling points of the various possible compounds are as follows:

Compound	Boiling point, °C.
2,3- and 1,2-dichlorbutanes	114–124
Monochlorbutene isomers	64 and 84
Tertiary butyl chloride	51–52
n-Butane	−0.5
Isobutane	−11.8
Chlorine	−33.7
Propane	−44.5
Propene	−47.0
Hydrogen chloride	−83.7

Any higher chlorides have higher boiling points and hence concentrate in the kettle. Similarly, any C_3 or lighter hydrocarbons, hydrogen chloride, or unused chlorine pass off at the top of the chlorinator with the C_4 hydrocarbons. Since the amount of hydrogen chloride and chlorine present in this C_4 stream is very small, this fraction is given an alkali wash to remove these corrosive compounds before returning it to the refinery for further processing.

The product collected in the kettle is removed and distilled, preferably under reduced pressure to prevent decomposition, to recover substantially pure separate fractions of monochlorbutanes, dichlorbutanes, and monochlorbutenes, and separate

out the heavy ends. Because of the low chlorination temperature, very little monochlorbutene is formed. The monochlorbutane fraction is largely tertiary butyl chloride since there is very little substitutive chlorination to form other monochlor isomers. The tertiary butyl chloride can be readily decomposed by heating to 260° C. in the vapor phase which converts it practically completely to isobutylene and hydrogen chloride.

The cut boiling in the range of 114–124° C. and which consists essentially of 1,2- and 2,3-dichlorbutanes is decomposed thermally in a stainless steel or other suitable steel or metal tube to yield butadiene and hydrogen chloride.

Alternatively a cut boiling in the range of 64–163° C. containing all the monochlorbutene and dichlorbutane isomers can be taken and similarly dehydrochlorinated to produce butadiene which is fairly pure since there is very little 2,2-dichlorbutane present to form non-conjugated diolefins and very little other chlorinated compounds which would form other impurities in the butadiene.

The dehydrochlorination may be conducted thermally in a stainless steel tube at 600° C. For example, essentially pure 2,3-dichlorbutane may be thus decomposed with a contact time of 0.22 second with 33.4% and 3.8% of theoretical conversion of initial material per pass to 1,3-butadiene and 1,2-butadiene, respectively, or 85.8% and 9.8% of theoretical conversion to 1,3-butadiene and 1,2-butadiene, respectively, based on the material completely decomposed per pass. Undecomposed dichlorbutane, and the monochlorbutene present, may be recycled for more complete conversion to 1,3-butadiene and hydrogen chloride. The 1,3-butadiene is separated from the conversion products as by fractionation or scrubbing and purified by suitable chemical or solvent extraction processes. The 1,2-butadiene isolated may be isomerized practically completely to 1,3-butadiene by known methods to improve the yield of 1,3-butadiene. The hydrogen chloride is recycled and partially converted to chlorine.

In another embodiment, the invention is applied to C_5 olefins or a C_5 olefins-rich refinery stream. If the primary purpose is to produce piperylene, the initial catalytic isomerization is omitted. If isoprene principally is sought, the stock is first catalytically isomerized to produce trimethylethylene (2-methylbutene-2) in approximately a one to one ratio of n-pentenes to trimethylethylene.

Whether or not the initial catalytic isomerization step is employed, the C_5 hydrocarbon stream is now reacted in the liquid phase with hydrogen chloride added in molar concentration equal to that of the tertiary base olefin, 2-methyl-butene-2 and 2-methylbutene-1, to produce tertiary amyl chloride, practically no secondary, normal or iso pentenes reacting.

The resulting mixture is now chlorinated in the liquid phase so that normal pentane dichlorides are produced by additive reaction with n-pentenes only. Secondary iso pentene (3-methylbutene-1) is normally absent from the C_5 refinery stream. The mixture is then fractionated to recover separate fractions of the tertiary amyl chloride, the normal pentane dichlorides and of the unreacted pentanes. The normal pentane dichlorides are then dehydrochlorinated thermally or by means of organic or inorganic bases to form a mixture composed principally of piperylene, monochlorpentenes and uncracked dihalides, from which the piperylene is separated by fractionation or scrubbing and purified by chemical or selective solvent extraction methods. The tertiary amyl chloride is chlorinated in the liquid phase with a catalyst such as $SbCl_5$ or iodine, or in the vapor phase in the presence of ultraviolet light or intense sunlight at a temperature low enough that the dichloride condenses out when it forms and is quickly drained or removed from the reaction chamber, thus avoiding substitutive chlorination to higher chlorine derivatives. Alternatively the tertiary amyl chloride may be dehydrohalogenated and the tertiary olefin material (trimethylethylene) so formed subjected to liquid phase additive chlorination to form the dichloride. This additive chlorination should be conducted at a sufficiently low temperature, say about 0° C., to prevent dehydrochlorination of a portion of the dichloride initially formed to 3-chloro-3-methylbutene-1 with liberation of HCl which adds to trimethylethylene to form isoamyl chloride which does not dehydrochlorinate to isoprene. If desired, water or weak aqueous alkali may also be present, the mixture preferably being stirred to maintain an emulsion, to absorb any HCl liberated by any such dehydrochlorination and thereby prevent its addition to trimethylethylene. This addition prevents to that extent the desired formation of the dichloride by additive chlorination of the trimethylethylene. Similar precautions must be used in additively chlorinating any of the tertiary olefins. The dichlor derivative of trimethylethylene formed by either of the foregoing procedures is largely 2,3-dichlor-2-methylbutane, and is easily separated from the tertiary amyl chloride and from the hydrogen chloride by fractionation or scrubbing. The dichlor derivative is then dehydrochlorinated thermally or by means of organic or inorganic bases to form principally isoprene and uncracked halides, from which the isoprene is separated by fractionation or scrubbing and purified by chemical or selective solvent extraction methods.

Instead of converting the tertiary amyl chloride produced in either of the foregoing ways to isoprene, it may be used as such or as a starting material for other organic chemicals. It may be converted to a tertiary base olefin. Either the chloride or the olefin may be used for polymerization, alkylation or other syntheses.

The foregoing application of the invention is illustrated by the manufacture of piperylene and isoprene from a C_5 hydrocarbon stream in accordance with the following example.

Example 2

The refinery C_5 olefin stream has the following composition, expressed in mole percentages: pentene-1, 39; pentene-2, 30.5; 2-methylbutene-2, 30.5; 2-methylbutene-1, 0.0; 3-methylbutene-1, 0.0. This is treated with dry hydrogen chloride in such a way that the hydrocarbon stream in liquid phase passes downwardly through the upwardly passing dry gaseous hydrogen chloride, the absorber being filled with suitable contact material. The molar concentration of the dry hydrogen chloride should be equal to that of the 2-methylbutene-2, with which it reacts to form tertiary amyl chloride. This HCl addition reaction may be carried out at from 0 to 5 lbs. per sq. in. gauge for the temperature range of 0 to 46° C. in order to retain the C_5 hydrocarbons in the liquid phase. The mixture of C_5 olefins and tertiary amyl chloride is now chlorinated by additive chlorination in the dark and in the liquid phase either in a fractionator type chlorinator

as in Example 1 with adequate cooling to remove the heat of chlorination or in a kettle type chlorinator with or without a mild catalyst such as sulfuryl chloride but with adequate cooling. The pressure should be such as to maintain the C_5 olefins in the liquid phase during chlorination. Pressures of from 0 to 5 pounds per square inch gauge are necessary for temperatures ranging from 0 to 46° C. to maintain liquid phase during this additive chlorination. The reaction mixture may then be fractionated to separate the several components thereof. Since the amylenes boil in the range of 34–38° C., the tertiary amyl chloride at 85–88° C., and the dichlor derivatives of normal pentane at 139–178° C. at atmospheric pressure, separation of these materials by fractionation is readily effected. The dichlorpentane fraction is then dehydrohalogenated at 500 to 600° C. at contact times of the order of a few tenths of a second to produce substantially pure piperylene. Reduced pressure or the presence of an inert diluent favors the reaction. The piperylene, which boils at 43° C., is separated by fractionation and purified.

The tertiary amyl chloride is now chlorinated in liquid phase to 2,3-dichlor-2-methylbutane by substitutive reaction with chlorine gas, using a catalyst such as antimony chloride or iodine. Chlorination is allowed to proceed until the final weight is 1.22 times the initial weight, exclusive of catalyst, when the reaction is substantially completed. The 2,3-dichlor-2-methylbutane, which has a boiling point of 137° C., is separated from the other constituents by distillation and subjected to dehydrohalogenation to produce isoprene. Ordinarily the fraction boiling from 137 to 175° C. contains all of the dichlor isomers of pentane which produce isoprene upon dehydrohalogenation, conditions for which are substantially the same as those indicated above for dehydrohalogenation of the dichlor derivatives of n-pentane.

Example 3

Example 2 is duplicated except that the stream of C_5 olefins is first subjected to catalytic isomerization to convert the C_5 olefins largely to trimethylethylene by passing them in the vapor phase at 450° C. over calcined alumina, forming an equilibrium mixture containing approximately 50 percent trimethylethylene. The composition of the resulting C_5 stream, expressed in mole percentages is: pentene-1, 28; pentene-2, 22; 2-methylbutene-2, 50; 2-methylbutene-1, none; and 3-methylbutene-1, 0.0. This material is then treated in liquid phase with dry hydrogen chloride as in Example 2, to produce tertiary amyl chloride from the 2-methylbutene-2. The resulting mixture is then subjected to treatment as in Example 2 to additively chlorinate the normal pentenes to the dichlorides and is then fractionated to recover separate fractions of the dichlorides and of the tertiary amyl chloride. The dichloride fraction is then dehydrohalogenated as in Example 2 to form piperylene. The tertiary amyl chloride is chlorinated as before to 2,3-dichlor-2-methylbutane which may be dehydrochlorinated as before to form isoprene or used in any other desired manner.

Referring to Fig. 2 of the drawings, hydrocarbon feed stock containing both tertiary base and secondary olefins of at least C_4, with or without saturated hydrocarbons, is charged to the system via line 1. The feed may, for example, consist of refinery cracked gases or effluent from thermal polymerization processes. The hydrocarbon stream first passes in the vapor phase through isomerization unit 2, which may be bypassed by line 3ª where isomerization is not desired, and thence via line 3 through cooler 4, which cools the gases to a temperature suitable for compression, and via line 5 through pump 6 which compresses them, into heat exchanger or cooler 7 for condensation to liquid. The liquid hydrocarbons then are introduced into the absorber or contact tower 8 in which they flow downward over packing, dry gaseous hydrogen halide being introduced through line 9 by pump 10 into reactor 8 somewhat below the mid-point at sufficient pressure to overcome that of the hydrocarbon.

The hydrocarbon stream containing the tertiary halide and the slight excess of hydrogen halides passes via line 12 into fractionator-type halogenation reactor 13 below and near the mid-point. Halogen is introduced via line 14 and pump 15 near the point at which the hydrocarbon stream is introduced. Additive chlorination of the normal olefins takes place in the column 13. The saturated hydrocarbons, excess hydrogen halide, and any unused halogen pass out the top of the column by line 16 into scrubber 17 into which alkaline solution is introduced by way of line 18 through spray nozzle 19 in order to scrub out hydrogen halide and free halogen, the wash liquid collecting at the bottom of scrubber 17 from which it is recycled via line 20 and pump 22, spent alkali wash liquid being withdrawn through line 21. The condensed distillate forms a layer above the aqueous alkali layer and is withdrawn via line 24 through drier 25 which may contain activated alumina for desiccant, after which part of it is returned to column 13 as reflux via line 26, the remainder being withdrawn through line 27 to be sent back to the refinery for further processing.

The mono-, di- and higher halides pass downward through tower 13 and pass via line 28 into fractionator 29 in which the monohalides are fractionated off and pass out through line 30 into the vaporizer and dehydrohalogenation or cracking coil 31 in cracking furnace 32 where they are dehydrohalogenated. The cracked products pass into the separator 33 in which the hydrogen halide is fractionated from the teritary base olefin and leaves through line 34 to be eventually recycled back to the reactor 8 or to the Deacon equipment. The tertiary base olefin leaves through line 35.

The di- and heavier halides leave fractionator 29 through line 36 and enter fractionator 37 where the halides heavier than the dihalides are separated and leave via line 38 and the dihalides pass via line 39 and pump 40 into vaporizer and cracking coil 41 in the cracking furnace 42 from which the cracked products consisting largely of conjugated diolefins and hydrogen halide pass into the low temperature fractionator 43 from which the hydrogen halide leaves via line 44 to be recycled or passed to the Deacon equipment. The diolefins and uncracked dichlor derivatives and monochlor monoolefins pass via line 45 to fractionator 46 where the diolefins are separated from the unconverted halides and pass off via line 47. The unconverted halides leave via line 49 and are recycled back to coil 41 for further dehydrohalogenation. Higher halides and polymerized materials, such as tars, formed in the cracking operation are removed by any suitable means and not recycled. For example, a tar trap may be in-

serted in the line leading from coil 41 to column 43, or these heavy materials may be separated out as a heavy fraction in column 46. If the low temperature fractionation carried out in 43 is too expensive because of lack of compressed refinery or other gases available for expansion to produce refrigeration, the effluent from coil 41 may be scrubbed with suitable organic or inorganic bases or water, which may be removed from the diolefins and uncracked halides by fractionation or physical separation, respectively. The hydrogen halide may then be recovered from the water or organic hydrogen halide addition compound by concentration and dehydration or by suitable decomposition of the addition compound, respectively. The mixture of diolefins and uncracked dihalides may then be dried, if water washed, and fractionated to separate the diolefins from the uncracked material. Alternatively, the effluent from the cracking coil 41 may be scrubbed with dihalide charge stock from line 39 in a countercurrent scrubber to separate the hydrogen halide from the diolefins and organic halides present.

The solution of the diolefins and monochlorolefins present is then sent to fractionator 46 from which the diolefins pass off through line 47 and the dichlor and monochlor monolefins derivatives leave through line 49 and are recycled to cracking coil 41.

The line 50 serves to collect the hydrogen halide liberated from the various sources available, and may be connected to line 52 for recycling to reactor 8 and/or to line 55 whence it is introduced by pump 54 into Deacon reactor 61 for regeneration of halogen. Air or oxygen is taken through line 56 and pump 57 into preheated coil 58 inside furnace 59 and thence via line 60 into reactor 61 which may consist of a gas-tight enclosed checkerwork-type reaction chamber in which the hyddrogen halide is burned to halogen and water over a Deacon-type catalyst, using known operating conditions. The reaction products pass from the reactor 61 via line 62 into condenser and separator 63 in which the water is removed via line 64 as an aqueous solution of hydrogen halide, halogen, and hypohalogenous acid. This solution may be treated for recovery of hydrogen halide and halogen.

The gases from separator 63 pass through line 65 into drier 66 wherein activated alumina may be used as a desiccant, thence via line 67 into low temperature fractionator 68, whence the halogen passes via line 70 for recycling to chlorinator 13. The mixture of uncondensed gases consisting of O_2, N_2, hydrogen halide and a little free halogen leave 68 via line 71 and pass into lower temperature fractionator 72 in which the hydrogen halide and slight halogen residue are separated and removed via line 73 whence they may be passed through expansion coils to provide part of the refrigeration requirements of condenser 63 and fractionator 68 before being returned to line 50 for recycling. The O_2, N_2 and any other other gases boiling at a lower temperature than the hydrogen halide leave via line 74. These cold gases may be utilized for producing part of the refrigeration of the separation process. Compression of the dried gases in line 67 before introduction into fractionator 68 permits fractionation at higher temperatures in 68 and 72, thus reducing expensive refrigeration requirements.

Where HI is the hydrogen halide used, the I_2 formed in 61 would condense largely in separator 63 and very little or no I_2 vapor would pass via line 67 to fractionator 68. In such case fractionator 68 may be eliminated.

Instead of a distillation process for separating hydrogen halide and halogen from the Deacon reactor effluent, suitable selective solvent or absorption extraction processes may be used. Other processes for regeneration of the halogen from the hydrogen halide such as, for example, the electrolytic process, etc., may be used instead of the Deacon process if desirable.

Ordinarily the C_5 olefin-containing stream is free from the secondary isopentene, 3-methylbutene-1 (isopropylethylene) since this pentene is not commonly encountered in refinery C_5 streams. This may be because of its thermodynamic instability, because of its ready isomerization to other pentenes (chiefly trimethylethylene) in the refinery processes to which the C_5 stream has been subjected, or because of its low boiling point (20° C.) which causes it to weather off. Therefore the C_5 olefins usually encountered consist of normal pentenes (pentene-1 or pentene-2) and tertiary base pentenes (2-methylbutene-1 or 2-methylbutene-2). If this secondary isopentene, 3-methylbutene-1, be present in the stream it is unaffected in the treatment with HCl but adds chlorine in the additive chlorination step to form 1,2-dichloro-3-methylbutane which evidently isomerizes to 2,3-dichloro-2-methylbutane, which upon subsequent dehydrochlorination yields isoprene which contaminates the piperylene. Ordinarily since 3-methylbutene-1 content never exceeds more than a small percentage, the extent of contamination of piperylene with isoprene derived therefrom is negligible. If, however, it is desired to preclude such formation of isoprene, the initial stream may be readily freed from any 3-methylbutene-1 by fractionation in view of its low boiling point, or the 3-methylbutene-1 may be isomerized to other pentenes by initial isomerization of the stream. Since the initial concentration of 3-methylbutene-1 is normally very low or practically nil, a fractionation or other special treatment of the C_5 olefins to remove it may not be economically justifiable, particularly since it is possible to purify the piperylene by a chemical or solvent extraction process if extremely pure piperylene is required.

This invention may also be applied to the production of aliphatic conjugated C_6 or higher diolefins, preferably of the butadiene series, from hydrocarbon mixtures comprising both secondary and tertiary base olefins of C_6 or higher. However because of the relatively large number of isomers which are neither tertiary base nor normal secondary olefins but branched chain or iso secondary olefins, modifications may be required to produce relatively pure straight chain diolefins since the secondary iso olefins do not add hydrogen halide rapidly as compared to the tertiary base olefins but rather are reserved for additive halogenation along with the normal olefins. Therefore upon additive halogenation both normal and iso dihalogenated derivatives are produced. Upon fractionation separate fractions of the teritary monochlorides and of the normal and secondary iso dihalides are obtained. Upon dehydrohalogenation of the dihalide mixture, a mixture of normal and iso diolefins is formed in which the iso diolefin content may amount to as much as 27% in the case of C_6 diolefins. Upon conversion of the tertiary monochloride mixture to the dihalogenated derivatives and dehydro-

halogenation there is obtained a mixture of branched chain conjugated diolefins containing very little or no normal diolefins. Small amounts of alkylacetylene or non-conjugated diolefins may be formed and are preferably removed by chemical or solvent extraction procedures when required in order to produce pure conjugated diolefin concentrates rich in only a few or one of the possible conjugated diolefin isomers.

For example, a C_6 olefin or olefin-paraffin mixture may contain as many as thirteen C_6 olefin isomers several of which have cis and trans modifications having different physical properties. All of these isomers have boiling points lying within the range of 41–74° C. The only olefin or paraffin hydrocarbons having less than or more than six carbon atoms which lies within this range is 4,4-dimethylpentene-1 (boiling point 71.8° C.). Neither this heptene nor 3,3-dimethylbutene-1 (boiling point 41° C.) occurs in more than traces in refinery streams, indications being that dimethyl substituted olefins having two methyl substituents on a single carbon atom are thermodynamically less stable than other C_6 or higher olefins and are therefore less likely to survive cracking or dehydrogenation reactions used in the refinery. It is desirable to eliminate 3,3-dimethylbutene-1 completely since dihalides thereof upon dehydrohalogenation are not converted to diolefins except possibly by molecular arrangement.

I prefer to take first a C_6 cut starting at approximately 45° C. and ending at about 60° C., thereby eliminating the possibility of contamination by high boiling pentenes such as 2-methylbutene-2 (boiling point 38.6° C.), in this way the cut will contain in addition to any paraffins in this range all of the secondary iso C_6 olefins and one of the tertiary C_6 olefins, as follows:

Secondary iso olefins:	B. P. °C.
4-methylpentene-1	54
4-methylpentene-2 (trans)	55
4-methylpentene-2 (cis)	58
3-methylpentene-1	54
Tertiary olefins:	
2,3-dimethylbutene-1	56

Such a fraction is then treated as before in liquid phase at low temperature with HCl in such manner as to cause reaction with the tertiary olefin to form 2-chloro-2,3-dimethylbutane without appreciably affecting the secondary iso olefins, and is then additively chlorinated as before to convert the secondary iso olefins to the corresponding dichloro derivatives. The mixture is then fractionated as before preferably under reduced pressure. The dichloro derivative fraction is then dehydrochlorinated to give a diolefin mixture consisting principally of 2-methylpentadiene-2,4 (B. P. 76° C.) and containing smaller amounts of 3-methylpentadiene-1,3 (B. P. 78° C.) as well as smaller amounts of alkylacetylenes and non-conjugated diolefins which are preferably removed.

The 2-chloro-2,3-dimethylbutane is subjected to substitutive chlorination or otherwise converted largely to 2,3-dichloro-2,3-dimethylbutane which is dehydrochlorinated to produce largely 2,3-dimethylbutdiene-1,3 as well as small amounts of alkyl acetylenes, non-conjugated diolefins and other decomposition products which may be removed.

A second cut of the C_6 hydrocarbons boiling in the range of from about 60° C. to about 71° C. may be taken, which includes all of the normal secondary hexenes and all of the remaining tertiary hexenes except 2,3-dimethylbutene-2 which may be more readily separately recovered and treated to produce pure 2,3-dimethylbutadiene. The hexenes in this second cut are:

Tertiary olefins:	B. P. °C.
2-methylpentene-1	62
2-methylpentene-2	67
3-methylpentene-2 (cis)	66
3-methylpentene-2 (trans)	68
2-ethylbutene-1	66
Secondary normal olefins:	
Hexene-1	64
Hexene-2 (cis, trans mixture)	68
Hexene-3 (cis, trans mixture)	67

This second fraction is then treated as before with HCl to convert the tertiary olefins substantially completely to the monohalogenated derivatives without appreciable conversion of the normal hexenes, followed by additive chlorination to convert the normal hexenes to their respective dichlorinated derivative. Upon fractionation as before the fraction of dihalogenated derivatives obtained is dehydrohalogenated to form normal hexadienes comprising largely hexadiene-1,3 (B. P. 73° C.) and hexadiene-2,4 (low-boiling, 76° C., high-boiling 79° C.) and small amounts of decomposition products. The product may be fractionated and subjected to chemical or solvent extraction to recover pure hexadiene-1,3 and hexadiene-2,4. The monohalogenated derivative fraction is converted to the dihalogenated derivatives either by catalytic substitutive chlorination or by dehydrochlorination and additive chlorination, the dichlorinated derivatives being separated by fractionation and dehydrochlorinated to form conjugated diolefins, consisting largely of 2-methylpentadiene-1,3 (B. P. 76° C.) and 3-methylpentadiene-1,3 (B. P. 78° C.) together with a smaller amount of 2-ethylbutadiene-1,3 (B. P. 72–74° C.). Separation of these diolefins from alkylacetylene, non-conjugated diolefins, and other contaminants is effected by fractionation and chemical or solvent extraction methods. Separation of the individual diolefins, other than a 2-ethylbutadiene concentrate is difficult because of the closeness of their boiling points.

A third C_6 cut boiling in the range of from about 71° C. to about 76° C. will include 2,3-dimethylbutene-2 (B. P. 74° C.) and exclude heptanes and heptenes, the one having the closest boiling point being 3,3-dimethylpentene-1 (B. P. 77° C.) which is one of the least common heptene isomers. The 2,3-dimethylbutene-2 may be converted to the corresponding dihalogenated derivative by carefully controlled addition halogenation at low temperature in the liquid phase, or by addition of HCl to form 2-chloro-2,3-dimethylbutane followed by catalyzed substitutive chlorination to form dichlorinated derivatives, largely 2,3-dichloro-2,3-dimethylbutane, which are then dehydrochlorinated to give largely 2,3-dimethylbutadiene-1,3, which is then purified to remove contaminants.

Alternatively, though less preferably, the 2,3-dimethylbutene-2 may be included in the second cut by extending the boiling range therefor to an upper limit of about 76° C. Upon treatment with HCl, this tertiary hexene is converted to the monohalogenated derivative and after separation with the other monohalogenated tertiary derivatives and conversion to the dihalogen derivative followed by dehydrochlorination yields 2,3-dimethylbutadiene-1,3 in admixture with the other

branched chain diolefins discussed above in connection with the second cut. Because of its boiling point (70° C.) this diolefin may be separated from the other diolefins derived from the other tertiary hexenes, although production of pure 2,3-dimethylbutadiene-1,3 is difficult because the other possible isomers boil in the range 72–78° C., making sharp separation difficult.

Similarly, from C_7 and higher streams, one skilled in the art can by the practice of my invention produce C_7 or higher aliphatic conjugated diolefins of high individual purity or at most containing only a few very similar diolefin isomers in the individual fraction.

From the foregoing it will be seen that my invention offers numerous advantages over prior processes of making diolefins from olefin-containing streams. My process is markedly advantageous for example over a process wherein a C_4 or higher stream containing both tertiary and secondary C_4 or higher olefins, with or without C_4 or higher paraffins, is halogenated directly to form the dihalides which are then separated and dehydrohalogenated to yield a composite mixture containing aliphatic conjugated diolefins, since such a process in the case of C_4 results in contamination of the butadiene with the decomposition products of the dichloride of isobutene, in the case of C_5 yields a mixture of piperylene and isoprene and in the case of C_6 or higher produces a conglomerate mixture of straight and branched chain C_6 or higher diolefins.

My invention is susceptible of numerous modifications in the illustrative disclosure above without departing from the inventive thought. For example, in some cases it may be desirable to subject the mixture after the halogenation step, without fractionation, to dehydrohalogenation, thereby converting the tertiary monohalides to olefin and the secondary dihalides to diolefin, and to then separate the olefin and diolefin from one another in any suitable way. In this way contamination of the diolefin derived from the secondary or normal olefin content with the diolefin derived from the tertiary olefin content is avoided.

I claim:

1. The process which comprises reacting in liquid phase a hydrocarbon mixture containing both tertiary base and secondary olefins of at least four carbon atoms per molecule with anhydrous hydrogen chloride at a temperature within the range of −80 to 100° C. and thereby effecting addition of the hydrogen chloride preferentially to substantially all of the tertiary base olefin content with the formation of tertiary alkyl chloride without appreciable reaction with the secondary olefin content, and reacting in the absence of light the resulting mixture of tertiary alkyl chloride and secondary olefin with substantially anhydrous chlorine at a temperature within the range of −20 to 50° C. and at a pressure sufficient to maintain a liquid phase of the secondary olefin, thereby effecting the addition of the chlorine to substantially all of the secondary olefin with the formation of the secondary alkyl dichloride without appreciable reaction with the tertiary alkyl chloride, and separately recovering from the effluent of the chlorination by fractional distillation the tertiary alkyl chloride and the secondary alkyl dichloride.

2. The process as defined in claim 1 wherein the tertiary base olefin is isobutylene and the secondary olefin is butene-2.

3. The process which comprises reacting in the absence of light a mixture containing a tertiary alkyl chloride and a secondary olefin with substantially anhydrous chlorine at a temperature within the range of −20 to 50° C. and at a pressure sufficient to maintain a liquid phase of the secondary olefin, thereby effecting the addition of the chlorine to substantially all of the secondary olefin with the formation of the secondary alkyl dichloride without appreciable reaction with the tertiary alkyl chloride.

4. The process as defined in claim 3 wherein the tertiary alkyl chloride is tertiary butyl chloride, and the secondary olefin is butene-2.

5. The process which comprises reacting in the absence of light a mixture containing isobutyl chloride and butene-2 with substantially anhydrous chlorine at a temperature of approximately 0° C. and at a pressure sufficient to maintain a liquid phase of the secondary olefin, thereby effecting the addition of chlorine to substantially all of the butene-2 with the formation of 2,3-dichlorobutane without appreciable reaction with the isobutyl chloride.

6. The process as defined in claim 3 wherein the chlorination is effected with simultaneous fractional distillation of lower boiling constituents from the chlorides.

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