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METHOD OF FORMING CHEMICAL MIXTURES

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2 Sheets-Sheet 1

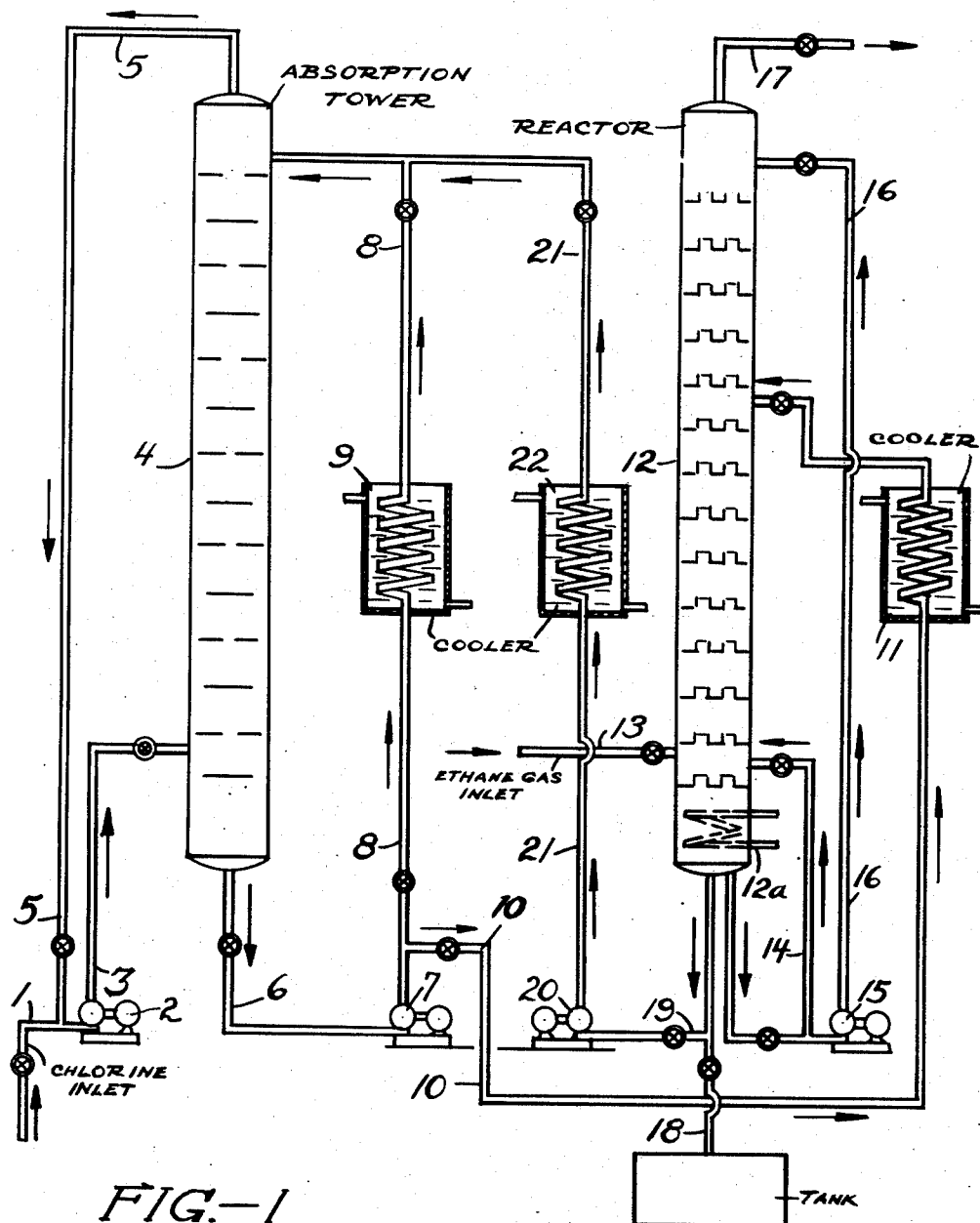


FIG.-1

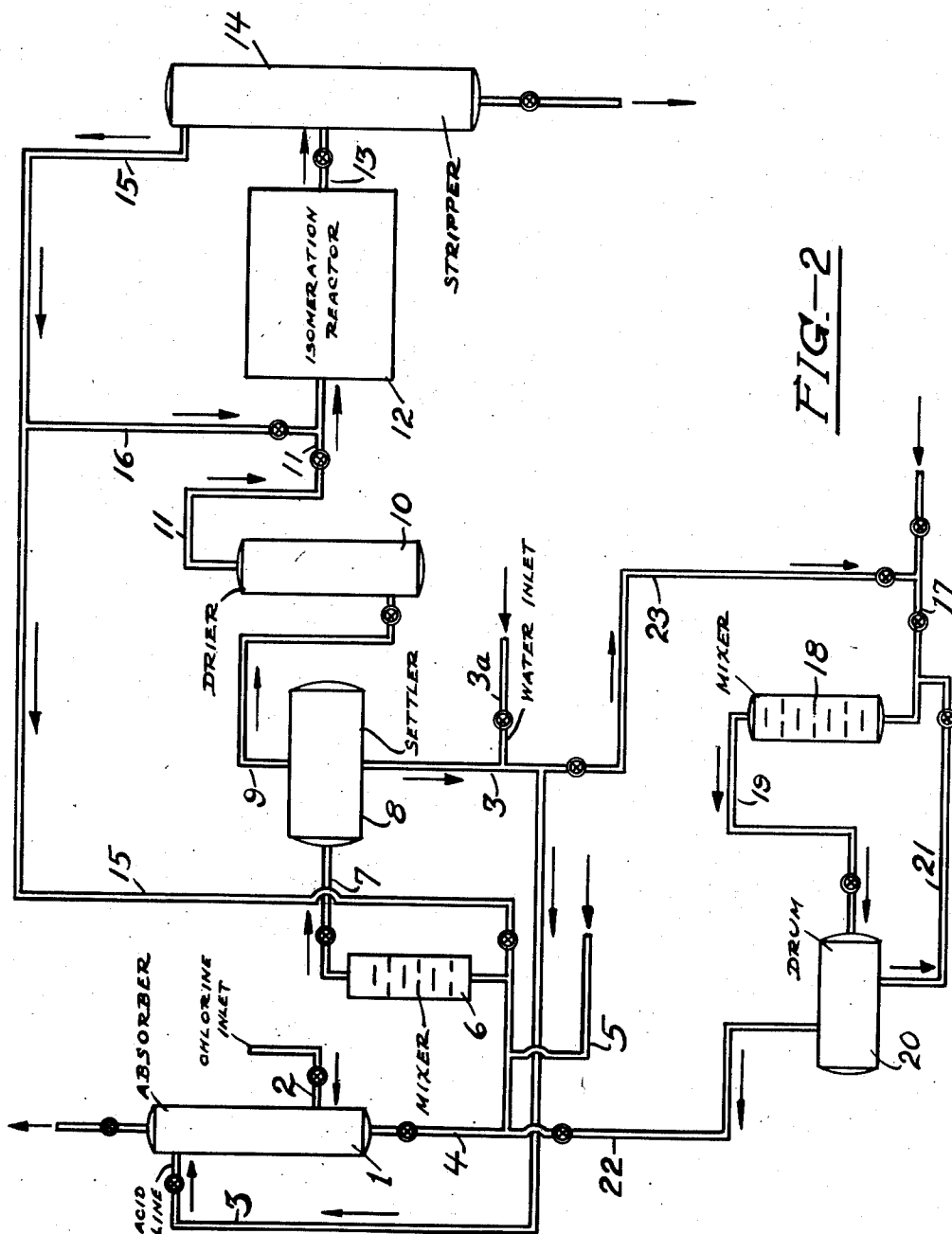
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## METHOD OF FORMING CHEMICAL MIXTURES

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2 Sheets-Sheet 2



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## UNITED STATES PATENT OFFICE

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## METHOD OF FORMING CHEMICAL MIXTURES

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9 Claims. (Cl. 260—683.5)

This invention relates to a method of forming mixtures of two or more compounds of carefully controlled proportions, and it has a particular relation to a method of introducing halogen into a hydrocarbon in such a manner that the danger of forming explosive mixtures is entirely eliminated.

It is known that certain mixtures of halogens and hydrocarbons, such as a mixture of chlorine and butane, may form mixtures which are spontaneously explosive when the proportion of halogen is too high. For example, in the isomerization of low molecular weight paraffin hydrocarbons in the presence of a catalyst, such as aluminum chloride, free chlorine is occasionally used as a promoter of the reaction. When free chlorine is introduced directly into a portion of the hydrocarbon, such as butane, which is generally done at temperatures of about 200° F. and below, means must be provided for avoiding concentrations of chlorine which are greater than about 10% in the absence of a catalyst or 5% in the presence of a catalyst in order that the danger may be entirely eliminated. However, so long as chlorine is introduced directly into the hydrocarbon phase, it will never be possible, in plant scale work, to absolutely avoid the possibility of the formation, to some extent, during the operation of at least a localized composition of an explosive nature. This could occur, for example, by mechanical failure of a check valve, allowing one fluid to be sucked back into the other, or by imperfect mixing of hydrocarbon and chlorine, also by a localized condensation of chlorine in case chlorine were added as a gas.

It is an object of the invention, therefore, to provide a method of introducing a halogen, such as chlorine or bromine, into a hydrocarbon without at any time incurring the danger of even localized formation of an explosive mixture. It is a further object of the invention to provide a means of forming mixtures of carefully controlled proportions, even when the danger of explosion is not present.

In accordance with the present invention, the halogen is first introduced into an inert medium to form a solution or mixture with the same, whereby the halogen is considerably diluted. This mixture is then contacted with the hydrocarbon, which absorbs the chlorine, at least in

part, from the mixture and the transfer medium is then separated from the hydrocarbon and may be used for further absorption of halogen. By preparing mixtures of halogen and an inert medium which sufficiently dilutes the halogen, it is never possible for the halogen to become concentrated in any portion of the hydrocarbon to an extent which would become dangerous.

The medium to be employed for the transfer of a halogen to a hydrocarbon may be either a liquid or a gas, and the halogen may be introduced into this medium either as a liquid or gas, as may be found most convenient. The medium must, of course, be chemically inert to both the halogen and the hydrocarbon with which it is to come in contact, and the medium should preferably be insoluble in the hydrocarbon and easily separated therefrom by gravity; although, in some cases, it might be desirable to use a medium soluble in the hydrocarbon and to remove the same from the hydrocarbon by distillation. A gaseous transfer medium will generally be used only when it is to come in contact with a liquid hydrocarbon, or when the medium and the hydrocarbon can be separated by condensation of one of the materials. If the medium is a liquid, it may be used for transferring halogen to either a gaseous or a liquid hydrocarbon.

The halogen, e. g., chlorine, may be conveniently contacted with the transfer medium in a packed tower, bubble tower, perforated plate tower, or some similar contacting device, and the contact between the mixture thus formed and the hydrocarbon may be accomplished in a similar apparatus if the hydrocarbon is a gas. If both the transfer medium and the hydrocarbon are liquids, a suitable vessel equipped with mixing facilities, such as mechanical agitators, mixing orifices, baffles, etc., may be used.

A medium which is particularly well suited for introducing chlorine into light hydrocarbons is aqueous hydrochloric acid. This material absorbs chlorine best when in concentrated form, but an acid of any strength may be used. For example, a solution containing about 9.8 gram mols of hydrogen chloride per 1000 grams of water dissolves approximately 0.13 gram mols of chlorine per 1000 grams of solution. Either gaseous or liquid chlorine may be contacted with the hydrochloric acid, and the mixture formed

may then be contacted with liquid butane, mixed and separated therefrom by gravity. This medium is of special value in isomerization processes, since small amounts of hydrogen chloride carried along by the butane after the chlorine absorption will not only have no harmful effect upon the subsequent isomerization reaction but will, in general, promote the reaction. In some cases, it might be desirable to use gaseous hydrogen chloride as the transfer medium in such a process, but in such a case the gas must be quite free from hydrocarbon when contacted with the chlorine.

Another material which serves as a satisfactory medium in the process described is water, which readily absorbs chlorine, especially under pressure, and which separates readily from gaseous or liquid hydrocarbons. The chlorine may be introduced into contact with water either as a gas or liquid and its solution may be handled for the transfer of chlorine to hydrocarbon in the same way as aqueous hydrochloric acid. As a special case in the use of water as a transfer medium, if a very high partial pressure of chlorine is employed in contacting the same with water, chlorine hydrate ( $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ ) will be formed and will separate from water as a separate phase. Thus, the chlorine may be contacted with water under superatmospheric pressure and if provision is made for settling, the chlorine hydrate may be taken off for use as a supply of chlorine for the hydrocarbon, while the remaining water is recirculated for the absorption of more chlorine. The chlorine hydrate, on contact with the hydrocarbon, such as butane, at a higher temperature will give up its chlorine and the water released can then be removed from the hydrocarbon.

Sulfuric acid, concentrated or diluted with water, is also well suited as a carrier for introducing chlorine into saturated hydrocarbons, such as butane, and when used in concentrated form may be of value in drying the material as well as in removing traces of harmful impurities, such as olefins, sulfur compounds and the like, which would seriously impair the activity of catalysts such as aluminum chloride in the isomerization reaction. The solubility of chlorine in 90% sulfuric acid at room temperature is 0.016 weight percent (0.029 gram/100 cc.) and increases to approximately 0.2 weight percent at approximately 33% strength and 0.3 weight percent at 16%, whereas in butane chlorine is soluble in all proportions. By using 80% acid in equal volumes with the hydrocarbon feed to insure thorough drying and saturating the acid with chlorine it is possible to introduce 0.05 gram of chlorine per 100 cc. of butane or 0.083 weight percent, based on the feed. This quantity is sufficient to replace normal process losses and at the same time has a good acid treating effect on the feed. If necessary to obtain larger chlorine introductions, it is permissible to either increase the rate of acid recirculation or to use weaker acid in which the solubility of chlorine is markedly increased. In general, strengths of the acid varying from about 55% to 100% are preferred for the process, although much weaker acids may be used. Acid of 80% to 100% strength will serve for drying and for acid treating to remove sulfur compounds, as well as for chlorine introduction. Weaker acids will serve also for introducing chlorine as well as for milder treating to remove olefins.

Among other liquid materials which may be used as transfer media in certain cases are car-

bon tetrachloride, hexachlorethane, chlorphenol, dichlorethyl ether, and the like.

Particular compounds for transferring the halogen will be chosen with due regard to the ease with which they may be separated from the hydrocarbon involved in a particular process. Chlorinated hydrocarbons are especially suitable in processes in which these materials are formed by reacting chlorine with hydrocarbons, the product of the reaction then serving as the transfer medium. For example, when chlorine is reacted with ethane to form ethyl chloride, a portion of the liquid product may be withdrawn and used to absorb chlorine in a separate absorbing device, and the solution of chlorine thus formed is then introduced into the reaction tower where it comes into contact with the gaseous ethane. The chlorine is then removed from the solution by the hydrocarbon and the remaining ethyl chloride forms a part of the product of reaction.

When the halogen is to be introduced into a liquid hydrocarbon, well known inert gases, such as nitrogen and carbon dioxide, may be employed as the medium. Apparatus suitable for scrubbing the halogen out of the gaseous mixture by the hydrocarbon will in such case be employed.

The process of the present invention may be applied generally to the introduction of halogens into hydrocarbons, such as the paraffins or olefins. If unsaturated hydrocarbons are used, a reactive material, such as hydrochloric acid, could not, in such case, be employed as the transfer medium.

The method of the present invention may be illustrated by a continuous process for the chlorination of ethane, illustrated by Figure 1 of the drawings. In this process, chlorine is pumped through line 1, pump 2 and line 3 into absorption tower 4, where it meets a downflowing stream of the reaction product ethyl chloride. Recirculation of unabsorbed chlorine is provided through line 5. The solution of chlorine formed in tower 4 is transferred by means of line 6, pump 7 and line 10 to reactor 12. Cooling means 11 may be introduced into line 10. A portion of the solution may be recycled to tower 4 through line 8 and cooler 9 to provide a more concentrated solution. In reactor 12 the downflowing stream of chlorine solution meets the upflowing ethane gas introduced into the reactor through line 13 and the chlorine is thus absorbed from the solution and reacted with the ethane. Heat for maintaining the proper temperature of the reaction is provided by a water coil 12a in the bottom portion of reactor 12. Circulation of the reacting liquids is provided by line 14, pump 15 and line 16, the latter re-entering the reactor in its upper portion. Unreacted hydrocarbon and by-product gases are removed from the top of the reactor through line 17. The reaction product is drawn off at the bottom through line 18, but a portion of the same is recycled to tower 4 by means of line 19, pump 20, line 21 and cooler 22, to provide a supply of the transfer medium.

The use of the present invention in an isomerization process, in which the chlorine is introduced as a promoter for the isomerization reaction, is illustrated in Figure 2 of the drawings. In this process concentrated aqueous hydrochloric acid is employed as the transfer medium. Chlorine gas is absorbed in a stream of concentrated hydrochloric acid solution in absorber 1, the chlorine being introduced through line 2. The hydrochloric acid solution is introduced through line 3 and is largely recycle material

from settler 8. The mixture formed in absorber 1 flows out through line 4 and meets a supply of liquid n-butane introduced through line 5 and these materials are mixed in mixer 6 for extraction of the dissolved chlorine from the hydrochloric acid. All products from mixer 6 pass out through line 7 to settler 8 where the hydrochloric acid separates by gravity from the butane layer and is recycled to absorber 1 through line 3. By properly adjusting the proportions of chlorine, hydrochloric acid and n-butane feed, the proper concentration can be obtained in the latter for optimum isomerization. The n-butane-chlorine solution is withdrawn through line 9 to drier 10 for removal of dissolved water, the drying being effected by contacting with a drying agent, such as concentrated sulfuric acid, or a solid dehydrating agent. Chlorine is only slightly soluble in sulfuric acid, so that the latter is quickly saturated, and as the acid is only infrequently removed from the system, losses of chlorine are negligible. The n-butane from drier 10, containing the correct amount of chlorine, is then sent through line 11 to isomerization reactor 12, where, in contact with anhydrous aluminum chloride at elevated temperature and pressure, the isomerization reaction is carried out. The isomerized product is removed through line 13 to stripper 14, where the hydrogen chloride formed in reactor 12 by reaction of the introduced chlorine with hydrocarbon is stripped out and returned through line 15 to mixer 6 for the purpose of maintaining the aqueous hydrochloric acid concentration at that point. A portion of the hydrogen chloride may be passed through line 16 to line 11 to maintain the proper concentration in the feed for the isomerization reactor. Any deficiency in water in the aqueous hydrochloric acid circulation system is made up by introducing the same through line 3a. Nearly 100% of the chlorine added is converted into hydrogen chloride in the isomerization process through reaction with the hydrocarbon. The isomerized hydrocarbon product containing a small amount of dissolved hydrogen chloride is removed from the bottom of stripper 14 and transferred to product finishing apparatus.

An alternative process may be carried out by using liquid chlorine and mixing the same with hydrochloric acid under pressure in mixer 18 (Figure 2), the resulting mixture being passed through line 19 to drum 20, where the unabsorbed liquid chlorine settles out and is returned to mixer 18 through line 21, while the hydrochloric acid containing dissolved chlorine is transferred to mixer 6 for mixing with incoming n-butane, as described above. The process is otherwise carried out as previously described, the recycle hydrochloric acid being brought back to mixer 18 through line 23.

Sulfuric acid may also be used as the transfer medium in place of hydrochloric acid in the above described example illustrated by Figure 2, by properly adjusting the rates of flow.

The following are typical requirements for a plant scale operation of the process described above and illustrated in Figure 2 in which 1000 barrels of isobutane are produced per day from 2500 barrels per day of n-butane feed. In this process, the chlorine added will be about 300 pounds per day and the concentration of chlorine required in the feed is about 0.06% by weight. The requirements are given for gaseous chlorine introduction (case A) and liquid chlorine intro-

duction (case B). These requirements are as follows:

	Case A	Case B
<b>5</b>		
Absorption stage:		
Concentration of recirculated HCl solution, wt. percent HCl.....	24.7	24.7
Pressure (atmospheres).....	1	8.75
Temperature of acid feed, °F.....	85	85
Temperature rise, °F.....	2	12
<b>10</b>		
Concentration of saturated chlorine-HCl solution:		
Pounds chlorine/cu. ft. solution.....	0.623	3.27
Grams chlorine/liter solution.....	10	52.6
<b>15</b>		
Extraction stage:		
Direction of flow.....	Concurrent	Concurrent
Rate of flow, gallons/minute:		
N-butane.....	73	73
HCl solution.....	2.5	0.5
Concentrations:		
Separated n-Butane, weight percent chlorine.....	0.06	0.06
<b>20</b>		
Spent HCl solution:		
Pounds chlorine/cu. ft. solution.....	0.006	0.00542
Grams chlorine/liter solution.....	0.089	0.087

The operating conditions in the above-described process are, of course, not limited to those given or shown in Figure 2, since these will be largely dictated by plant economics and the percentage of chlorine desired in the n-butane feed to the isomerization reactor. In the example shown, the concentration of chlorine in butane which is desired is 0.06% by weight. The conditions maintained in the isomerization reaction zone are the usual optimum operating conditions of 175-200° F. reaction temperature, using 40% aluminum chloride and 8% hydrogen chloride, both being weight percentages based on the n-butane feed for liquid phase reaction. All chlorine eventually leaves the system as hydrogen chloride.

This invention also applies to the vapor phase type of isomerization process employing a fixed bed reactor with throughputs of 0.3-1.2 volume/volume/hour at about 150-300 lbs. pressure and at temperatures of 200-375° F.

This invention is not to be limited in scope by any of the described examples which are given by way of illustration only, but is to be limited solely by the terms of the appended claims.

I claim:

1. In a catalytic hydrocarbon conversion process in which a halogen is used as a promoter of the reaction, the step which comprises mixing the halogen with a liquid inert material immiscible with the hydrocarbon feed for said conversion process, contacting the mixture so formed with the said hydrocarbon feed, separating the said inert material from the hydrocarbon and converting the hydrocarbon in the presence of a catalyst.

2. Process according to claim 1, in which the said inert material is an aqueous hydrochloric acid solution.

3. Process according to claim 1 in which the said inert material is sulfuric acid of 55 to 100% strength.

4. Process according to claim 1 in which the said inert material is sulfuric acid of 80 to 100% strength.

5. In a process of isomerizing butane by means of aluminum chloride as a catalyst, using chlorine as a promoter, the step which comprises mixing the chlorine with a concentrated aqueous solution of hydrochloric acid, contacting the mixture so formed with the butane feed for the isomerization process, separating the hydrochloric

acid solution from the butane and subjecting the butane to isomerization conditions in the presence of aluminum chloride.

6. In a catalytic hydrocarbon conversion process in which a halogen is used as a promoter of the reaction, the step which comprises mixing the halogen with aqueous sulfuric acid of 55 to 100% strength, contacting the mixture so formed with the said hydrocarbon feed, separating the said acid from the hydrocarbon and converting the hydrocarbon in the presence of a catalyst.

7. In a catalytic hydrocarbon conversion process in which a halogen is used as a promoter of the reaction, the step which comprises mixing the halogen with a fluid material chemically inert to halogen and the hydrocarbon feed for said conversion process and immiscible with said hy-

drocarbon feed, contacting the mixture so formed with the said hydrocarbon feed, separating the said inert material from the hydrocarbon and converting the hydrocarbon in the presence of a catalyst.

8. In a process for isomerizing butane by means of an aluminum chloride catalyst, using a free halogen as a promoter for the reaction, the step which comprises mixing the free halogen with sulfuric acid of 80% to 100% strength, contacting the mixture so formed with a butane feed for said isomerization process, separating the sulfuric acid from the butane, and isomerizing the butane in the presence of the said catalyst.

9. Process according to claim 8 in which the free halogen promoter is chlorine.

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