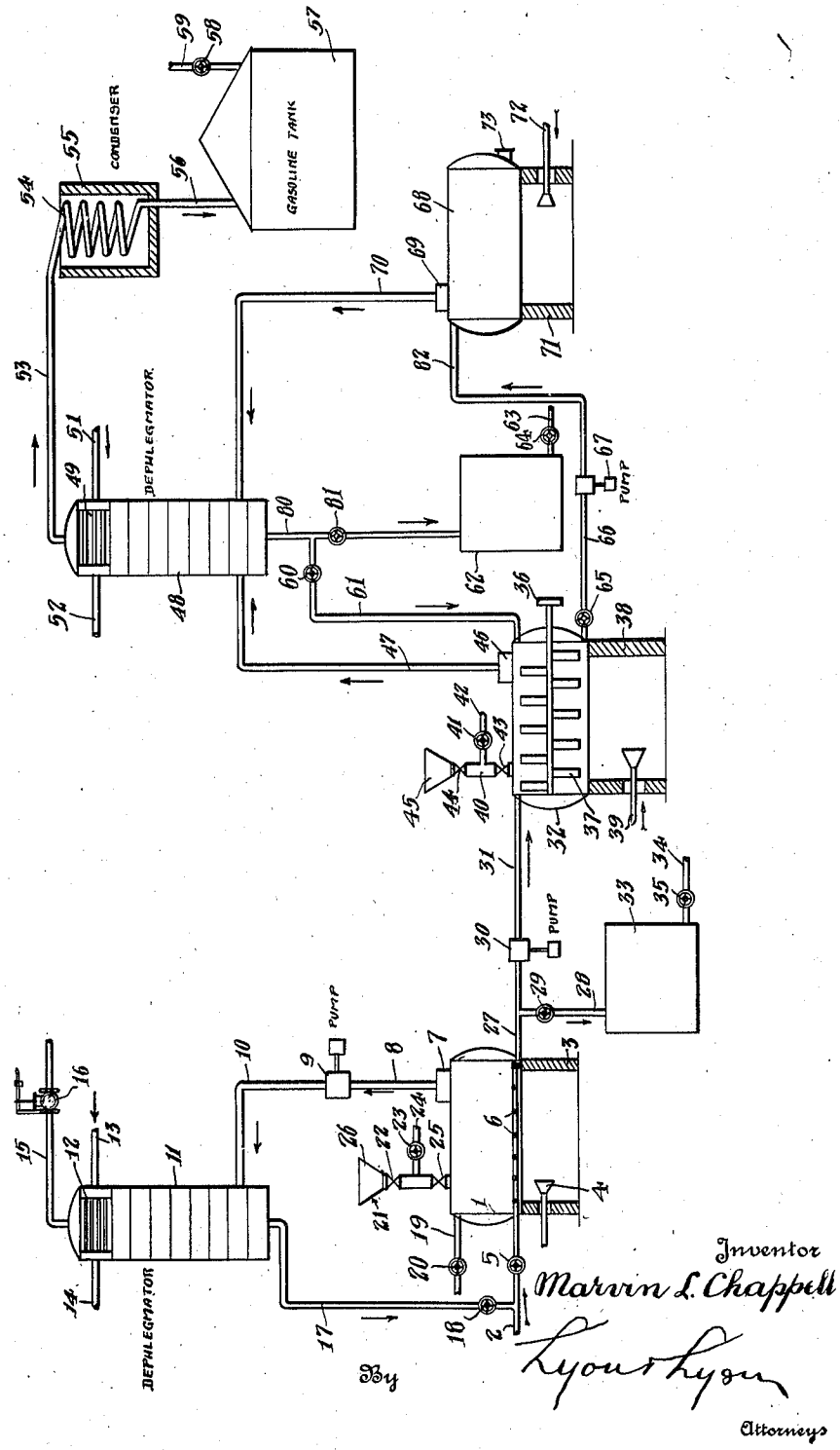
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PROCESS OF TREATING HYDROCARBONS WITH A CHLORINATED HYDROCARBON IN THE PRESENCE OF A METALLIC HALIDE

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PROCESS OF TREATING HYDROCARBONS WITH A CHLORINATED HYDROCARBON IN THE PRESENCE OF A METALLIC HALIDE

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This invention relates to the treatment of hydrocarbon oils, and is of particular value for the treatment of hydrocarbon oils high in carbocyclic compounds such as petroleum oils found in California, Texas, Mexico, Russia, and other places; or oils derived by the distillation of any petroleum hydrocarbon of the carbocyclic series, which may be shale oils or coal tar oils, with a metallic halide such as aluminum chloride, iron chloride, and the like, in the anhydrous form, and refers particularly to a continuous, batch, or intermittent process of treating hydrocarbon oil with a metallic halide of which aluminum chloride is preferred, in the presence of a chlorinated hydrocarbon gas of the paraffin series.

It is well known in the science of chemistry that a chlorinated hydrocarbon, such as methyl or ethyl chloride will react with an oil of the aromatic series to produce a methyl or ethyl aromatic oil, such as methyl benzol and the like; this reaction being known as the Friedel-Crafts synthesis to which reference is hereby made to Weyl, Die Methoden der Organischen Chemie, Volume 1, page 297.

I have discovered that this reaction may also be applied to the petroleum oils, particularly those containing oils of the carbocyclic series, preferably a distillate, which will react with a chlorinated gas of the aliphatic series, in the presence of aluminum chloride at a temperature of approximately 212° F. Such carbocyclic oils may be of the naphthenic type or other similar types of the carbocyclic series. The reaction between the said carbocyclic oils and the said chlorinated hydrocarbon gas results in the condensation of the hydrocarbon radical of the chlorinated gas and the carbocyclic oil with the evolution of HCl. The following represents the type of reaction which takes place, in which the CH_3 radical may be any other radical of the aliphatic series such as C_2H_5, C_3H_7 and the like, and the R radical represents any hydrocarbon with a ring structure such as a naphthene, a polynaphthene, aromatic oils, etc.:

$$CH_3Cl + RH + AlCl_3 = CH_3R + HCl + AlCl_3.$$

I have further discovered that this condensed hydrocarbon produced by the action of a carbocyclic oil and a chlorinated hydrocarbon in the presence of aluminum chloride at a temperature of approximately 212° F. may be further reacted upon by a further addition of aluminum chloride at a temperature ranging from 300° F. to 650° F. to form gasoline or naphtha and a higher boiling oil.

An object of the present invention is to provide a process for treating hydrocarbon oil, preferably distillate, with aluminum chloride in which the said hydrocarbon oil and aluminum chloride are agitated together by means of a chlorinated hydrocarbon gas of the aliphatic series at a temperature sufficient to cause a chemical reaction therein with the evolution of HCl and the formation of a condensed oil; transferring said condensed oil to a second reaction chamber and mixing therewith a further addition of aluminum chloride, maintaining in said second reaction chamber a temperature greater than 300° F., commingling the said polymerized oil and aluminum chloride for a sufficient period of time and at a sufficient temperature to cause a reaction therein with the production of naphtha or gasoline and a higher boiling hydrocarbon oil.

Another object of the present invention is to provide a continuous or intermittent process for treating hydrocarbon oils of the carbocyclic series with aluminum chloride in the presence of a chlorinated hydrocarbon gas to produce therein a condensation of the said carbocyclic oil and the hydrocarbon radical of the chlorinated gas for a stock suitable for the manufacture of lubricating oil.

Another object of the invention is to produce a gasoline or motor fuel and a stock suitable for the manufacture of lubricating oil from a high boiling hydrocarbon oil of the carbocyclic series and a hydrocarbon gas derived from oil wells or natural methane gas wells by the catalytic action of a metallic halide in two steps, the first step being a condensation reaction and taking place at a temperature of approximately 212° F. with the evolution of HCl, the second step being conducted at higher temperatures with the addition of a further amount of aluminum chlo-

ride under atmospheric or superatmospheric condition for the production of gasoline or motor fuel and a higher boiling oil suitable for the production of a lubricating oil stock.

Another object of the invention is to provide a process in which the unconverted chlorinated hydrocarbons may be separated from the HCl produced by the reaction and returned to the system.

In accordance with the process of the present invention hydrocarbon gases, preferably those derived from oil wells or natural gas wells, are chlorinated by well known methods, for example by the addition of or contact with chlorine gas alone or in the presence of chlorides, and then introduced into a body of high boiling hydrocarbon oils, preferably containing a large amount of hydrocarbons of the carbocyclic series to which has been added a metallic halide, preferably aluminum chloride, in amounts ranging from $\frac{1}{10}$ to as high as $\frac{5}{10}$ pounds per gallon of high boiling hydrocarbon oil. This mixture is maintained at the reaction temperature suitable for condensation of said constituents as heretofore stated, the oil being continuously agitated by means of a continuous introduction of the said chlorinated gas. The products of reaction consisting of the condensed oil and the hydrocarbon radical of the said chlorinated gas are continuously or intermittently pumped to a second reaction chamber. The evolved gases consisting of HCl and the chlorinated gas are pumped into a fractionating column at a sufficient pressure and reduced to a sufficiently low temperature so that the chlorinated hydrocarbon will liquefy and may be drawn off from the bottom of the fractionating system and returned to the system. The HCl is evolved from the top of said fractionating system and may be converted to chlorine gas by well known processes such as the Deacon. The condensed hydrocarbon oil which may be continuously or intermittently introduced into the second reaction chamber is agitated with a further addition of aluminum chloride which may range from $\frac{2}{10}$ to as high as $\frac{3}{4}$ of a pound of anhydrous aluminum chloride per gallon of oil introduced. In said reaction chamber, the temperature ranging from 300° F. to as high as 650° F. is maintained, depending upon the products desired and the product treated. In case a small amount of gasoline is desired and a larger amount of lubricating stock, a smaller amount of aluminum chloride is introduced into said reaction chamber. This said reaction chamber for the production of gasoline from a condensed oil, is preferably carried at a pressure of approximately 15 pounds gauge, and the gasoline produced therein together with higher boiling hydrocarbons are vaporized and carried into a dephlegmating tower provided with a cooling medium or planer at the top, where said higher boiling hydrocarbons are condensed and return to the reflux line. The refluxed oil may be used for the manufacture of a lubricating oil stock or may be returned to the reaction chamber for further reaction with aluminum chloride, or said refluxed oil after being returned to the reaction chamber together with the aluminum chloride may be introduced into a still and therein vaporized for the removal of all carbonaceous material and then returned again to the reaction chamber for further action with aluminum chloride for the production of gasoline.

The reaction between the condensed hydrocarbon oil and the aluminum chloride in the reaction chamber provided with a mechanical stirrer may be modified for the production of the desired products by regulating the heat and pressure and quantity of metallic halide employed. For example, if it is desired to obtain a gasoline or naphtha having a high percentage of low boiling hydrocarbon oils, a higher pressure and temperature is maintained in the reaction chamber than would be employed for the production of a higher boiling gasoline or naphtha stock.

The process of the present invention may be carried out with the major object, the production of gasoline or motor fuel and coke, or the major object may be to produce a smaller percentage of gasoline and a higher boiling hydrocarbon oil suitable for the manufacture of lubricating oils and the like, or the process may be carried out for the manufacture of a stock suitable for the manufacture of lubricating oil alone.

The process of the present invention is preferably continuous but may be operated intermittently or in batch lots.

Various further objects and advantages of the present invention will be understood from a description of the preferred process of treating a hydrocarbon oil in the presence of a chlorinated hydrocarbon gas employing the present invention. For this purpose, there is hereafter set forth a specific example of one form of process which embodies the invention. The process is described as it is carried out in the apparatus illustrated in the accompanying drawing.

The drawing represents a diagrammatic elevation in vertical section of the complete apparatus.

Referring to the drawing, 1 indicates generally a reaction chamber which is preferably mounted over a suitable heating means, such as the furnace 3 having the burner 4. The reaction chamber 1 is also provided with a charger 21 for introducing aluminum chloride into the reaction chamber, said charger 21 including a hopper 26, two spaced valves 22 and 25, a line 24 controlled by a valve 23, line 24 leading to a source of aluminum chloride, not shown, for the introduction of aluminum

chloride in a liquid or dissolved state, controlled by said valve 23.

The reaction chamber 1 is also preferably provided with an oil charging line 19 and a residual draw-off line 27 with a branch line 28 controlled by a valve 29. The branch line 28 leads to a tank 33. The tank 33 is provided with a draw-off line 34 controlled by a valve 35. The draw-off line 27 leads to the suction side of a pump 30 and discharges into a line 31 which is connected to a second reaction chamber 32 provided with a mechanical stirrer 36. The mechanical stirrer 36 is provided with paddles 37 so that the products undergoing reaction may be kept in a constant agitation.

The reaction chamber 1 is provided on the top with a dome 7 which is connected to a line 10 leading to the suction side of pump 9, which discharges into line 10. The line 10 is connected to a dephlegmator 11 which is provided with a planer or condenser 12. 13 is a line which leads to a source of cooling medium, such as liquefied ammonia, or other fluids for obtaining very low temperatures, not shown, and 14 is a line leading from the condenser or planer 12 to carry off the supply of cooling medium introduced. 15 is a line connected to the top of the dephlegmator 11 controlled by pressure regulating valve 16 and leading to a source, not shown, for conducting the HCl formed in the process to a suitable apparatus for the production of chlorine, such as the Deacon process. The dephlegmator 11 is connected at the bottom by a line 17, controlled by a valve 18, and also connected to the line 2 which is used for conducting the condensed liquefied, chlorinated hydrocarbon into the line 2 which enters reaction chamber 1 along the bottom controlled by valve 5. The line 2 leads to a source of chlorinated hydrocarbon of the paraffin series, not shown, and enters the reaction chamber 1, as heretofore stated, along the bottom and contains perforations, as indicated at 6, so that the introduced chlorinated gases may agitate the admixture within the reaction chamber 1.

The second reaction chamber 32, into which the condensed oils are conducted from the reaction chamber 1, is provided with a charger 40 for introducing aluminum chloride into the reaction chamber, said charger 40 including a hopper 45, two space valves 43 and 44, a line 42 controlled by a valve 41, line 42 leading to a source of aluminum chloride, not shown, for the introduction of aluminum chloride in a liquid or dissolved state.

The reaction chamber 32 is also provided with a dome 46 on the top to which is connected a line 47 leading to a dephlegmator 48. Interposed in the top of said dephlegmator 48 is a planer or condenser 49 connected to a line 51 which leads to a source of water or other liquid cooling medium, not shown. A line 52 is connected to said condenser or planer 49 for conducting away the cooling medium to a place not shown. Connected at the top of said dephlegmator 48 is a line 53 leading to a condenser 54, interposed in a condenser box 55, where the gasoline vapors are condensed to a liquid and passed through line 56 into the gasoline receiving tank 57. Gasoline receiving tank 57 contains a line 59 in the top and a valve 58 to regulate the pressure on the system.

Connected at the bottom of said dephlegmator 48 is a drain line 80 controlled by a valve 81, which line 80 leads to a tank 62. Said tank 62 is provided with a draw-off line at the bottom 63, controlled by a valve 64. The draw-off line 80 which leads from the bottom of said dephlegmator 48 is also connected to a branch line 61 controlled by a valve 60 and is connected to reaction chamber 32 at the top. A line 61 may be employed when desired to conduct the refluxed oil from the dephlegmator 48 back into the reaction chamber when it is desired to obtain a high percentage yield of gasoline, and in case a large percentage of lubricating stock is desired, the valve 60 is closed and the entire amount of refluxed oil is conducted into the storage tank 62.

Connected at the bottom of the reaction chamber 32 is a line 66 controlled by a valve 65 which leads to the suction side of a pump 67, which discharges into the line 82. The line 82 is connected to a still 68 at the top, so that the products of reaction from the reaction chamber 32 may be introduced into said still and there converted into vapors which pass through the dome 69 interposed upon the top of said still 68, into a line 70 and from there into the dephlegmator 48. The still 68 is mounted over a furnace 71 provided with a burner 72. The said still 68 is also provided with a man-hole 73 at the bottom, so that the coke accumulating from any distillation may be removed.

The preferred process as carried out with the apparatus thus described is as follows Hydrocarbon oil, preferably one containing considerable hydrocarbons of the carbocyclic series, is introduced into reaction chamber 1, preferably continuously, and a chlorinated hydrocarbon gas, preferably mainly of the paraffin series, is introduced continuously through the line 2, entering the reaction chamber 1 through the perforations in said pipe, thereby agitating and producing an intimate contact between the oil and gas. Preferably the chlorinated hydrocarbon gas is obtained by chlorinating natural gas. There is also preferably continuously introduced through the charger 21, aluminum chloride at the rate of .1 to as high as .5 pound per gallon of oil entering said reaction chamber. A temperature above 60° F., and pref-

erably approximately 212° F. is maintained in the reaction chamber 1 and causes a portion of the chlorinated hydrocarbon gas to react with the hydrocarbon oil (principally the carbocyclic oil) while HCl is evolved. The hydrogen chloride gas HCl passes upwardly through dome 7 into line 8 and into pump 9 along with that part of the chlorinated hydrocarbon which did not combine. The said HCl and chlorinated hydrocarbon gas are compressed by means of the pump 9 and enter the dephlegmator 11 where they are cooled to such a temperature that the unacted upon chlorinated hydrocarbon gas is condensed to a liquid and is returned to the reaction chamber through the bottom of the dephlegmator 11 into pipe 17 and back to the reaction chamber 1. The HCl gas, on account of its very low boiling point, is not liquefied and is therefore separated from the chlorinated hydrocarbon and is drawn off from the dephlegmator 11 at the top through the line 15 controlled by the pressure regulating valve 16 and then conducted to a place, not shown, for the manufacture of chlorine gas.

The hydrocarbon oil after being reacted upon as heretofore stated by the chlorinated hydrocarbon gas with the formation of condensed products, is continuously drawn off through the line 27 into the suction side of a pump 30 which discharges into a second reaction chamber 32 through the line 31, or in case it is desired to make a lubricating oil stock, the condensed oil coming from reaction chamber 1 is run through line 28 into the tank 33 and thereafter manufactured into high grade lubricating oil by processes well known. This condensed oil may also be employed as a charging stock of a thermal cracking process.

In case, however, it is desired to convert a part or all of the condensed stock coming from reaction chamber 1 into gasoline or motor fuel, said pump 30 discharges the condensed product into the reaction chamber 32. Aluminum chloride, in portions varying from as low as .2 to as high as ¾ of a pound per gallon of oil charged into the reaction chamber 32, is introduced through the charger 40, either in the form of a solid or in a dissolved solution. The reaction chamber 32 is carried at a temperature ranging from 300° to as high as 650° F., and preferably under a pressure of approximately 15 pounds gage, depending upon the product treated and the products desired. In case a high percentage of low boiling hydrocarbons is desired a higher temperature and a higher pressure are employed. The converted oil in the form of vapor and consisting principally of gasoline, higher boiling hydrocarbons and aluminum chloride passes through the line 47 into the dephlegmator 48 where the aluminum chloride and higher boiling hydrocarbons are condensed and may be returned to the system through the line 80 and then into the line 61, valve 81 being closed, and valve 60 open. In case it is desired to produce a small amount of higher boiling stock suitable for the manufacture of lubricating oil or other purposes, the said reflux coming from the dephlegmator 48 is permitted to pass down the line 80 and into the tank 62, valve 81 being open and valve 60 closed.

The gasoline or motor fuel produced by the action of aluminum chloride in reaction chamber 32, after passing through the dephlegmator 48, passes into the line 53 from the top of said dephlegmator 48 and then into the condenser 54 where said low boiling hydrocarbons or gasoline stock is condensed and passed into the gasoline receiving tank 57, the pressure on the system being controlled by the valve 58, which is connected into the line 59.

The aluminum chloride residuum along with some of the higher boiling hydrocarbon oil are continuously withdrawn from the reaction chamber 32 through line 66 controlled by valve 65 into the suction side of the pump 67, which discharges into the line 82 connected to the still 68 at the top, so that when it is desired to obtain as high a yield as poscible of stock suitable for motor spirits or gasoline, the reflux from dephlegmator 48 is permitted to flow back through pipe 80 into line 61 and thereafter into the reaction chamber 32 where it is again reacted upon by the aluminum chloride. By means of this still 68, the carbonaceous matter resulting from the aluminum chloride reaction may be continuously removed from the hydrocarbon oils as produced.

The chlorinated hydrocarbon gas employed in this process may be any chlorinated hydrocarbon of the aliphatic or paraffin series such, for example as methane, ethane, butane, pentane etc., of the general formula C_nH_{2n+2}, and the high boiling hydrocarbon, any oil containing compounds of the carbocyclic series, such as naphthanes, polynaphthenes, aromatic oils, etc., represented by the formulas C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, and C_nH_{2n-6}. However, it is to be understood that the high boiling petroleum oils may be one of the mixed base type, by which is meant a naphthenic oil containing as much as 50 per cent. of hydrocarbons of the aliphatic or other series. In the second step of the process where the oils are again reacted upon by a further addition of aluminum chloride at higher temperatures for the decomposing reaction and the formation of gasoline, the aluminum chloride not only decomposes the condensed oil but also the other oils of any other series that may be present therein.

It is also to be understood that the condensation reaction between the chlorinated gas and the hydrocarbon oil or its content

of carbocyclic oil may not be quantitive, since, in some cases, as low as 10 per cent of the carbocyclic oil may be only reacted upon by the chlorinated gas, and in other cases as high as 98 per cent.

An important feature of the present process is the production of gasoline or lubricating oils using in part fixed gases such as methane, which hitherto have not been utilized for that purpose.

While the process herein described is well adapted for carrying out the objects of the present invention, it is understood that various modifications may be made without departing from the invention and the invention includes all such modifications and changes as come within the scope of the appended claims.

I claim:

1. A method of treating hydrocarbon oil containing hydrocarbons of the naphthenic type which comprises treating said oils with a chlorinated gas of the aliphatic series in the presence of a metallic halide at temperatures suitable for the production of a condensation reaction therein between the hydrocarbons of the naphthenic type and the chlorinated hydrocarbon, introducing a further amount of metallic halide raising the temperature sufficiently to produce a decomposing reaction between said metallic halide and oils for the production of gasoline, withdrawing metallic halide residue into a still, separating said metallic halide residue and tarry constituents by a distillation operation, returning the high boiling oil distilled therefrom back to the reaction chamber to be further reacted upon by metallic halide for the further production of gasoline.

2. A method of treating hydrocarbon oil containing hydrocarbons of the naphthenic type which comprises treating said oils with a chlorinated gas of the aliphatic series in the presence of a metallic halide at temperatures suitable for the production of a condensation reaction therein between the hydrocarbons of the naphthenic type and the chlorinated hydrocarbon in a reaction zone, withdrawing said condensed oil together with the unacted upon oil into a second reaction zone, introducing a further amount of metallic halide into said reaction zone and raising the temperature sufficiently therein to produce a decomposing reaction between said metallic halide and oils for the production of gasoline and a high boiling oil, withdrawing said high boiling oils and metallic halide residue into a still, separating said metallic halide residue and tarry constituents by a distillation operation, returning the higher boiling oils to a separate condenser to be utilized for the manufacture of lubricating oil stock.

3. A method of treating hydrocarbon oil containing hydrocarbons of the naphthenic type which comprises treating said oil with a chlorinated gas of the aliphatic series in the presence of aluminum chloride at temperatures suitable for the production of a condensation reaction therein between the hydrocarbon of the naphthenic type and the chlorinated hydrocarbon, introducing a further amount of aluminum chloride, raising the temperature sufficiently to produce a decomposing reaction between said aluminum chloride and oils for the production of gasoline, withdrawing the aluminum chloride residue into a distillation zone, separating said aluminum chloride residue and tarry constituents by a distillation operation in such zone, and returning the high boiling oil distilled therefrom back to the reaction chamber to be further reacted upon by aluminum chloride for the further production of gasoline.

4. In a method of treating hydrocarbon oils, the steps of forming a mixture of hydrocarbon oil containing hydrocarbons of naphthenic type with a metallic halide in a reaction zone, passing a stream of chlorinated light aliphatic paraffins into the oil-halide mixture undergoing reaction in a reaction zone, whereby condensation and polymerization reactions result therein between the hydrocarbons of the naphthenic type and the chlorinated hydrocarbons, vaporizing from such mixture hydrogen chloride and that part of the chlorinated paraffins which do not react in said reaction zone, separating said unacted upon chlorinated paraffins from said hydrogen chloride, returning said separated unacted upon chlorinated paraffins to the reaction zone, and separately removing polymerized and condensed hydrocarbon oil from said reaction zone.

5. A method of treating hydrocarbon oil containing hydrocarbons of the naphthenic type, which comprises treating said oil with a gas containing chlorinated hydrocarbons of the aliphatic series in the presence of aluminum chloride at temperatures suitable for the production of a condensation reaction therein between the hydrocarbon of the naphthenic type and the chlorinated hydrocarbons, introducing a further amount of aluminum chloride, raising the temperature sufficiently to produce a decomposing reaction between said aluminum chloride and oils for the production of gasoline, withdrawing the aluminum chloride residue into a distillation zone, and separating said aluminum chloride residue and tarry constituents by a distillation operation in such zone.

6. In a method of treating hydrocarbon oils, the steps of forming a mixture of hydrocarbon oils containing hydrocarbons of the naphthenic type with a metallic halide in a reaction zone, passing a stream of hydrocarbon oil well gases containing chlorinated light aliphatic paraffins into the oil-halide

mixture undergoing reaction in a reaction zone, whereby condensation and polymerization reactions result therein between the hydrocarbons of the naphthenic type and the chlorinated hydrocarbons, vaporizing from such mixture hydrogen chloride and that part of the chlorinated paraffins which do not react in said reaction zone, separating said unacted upon chlorinated paraffins from said hydrogen chloride, and separately removing polymerized and condensed hydrocarbon oil from said reaction zone.

7. A method of treating hydrocarbon oils containing hydrocarbons of the naphthenic type, which comprises treating said oils with a hydrocarbon oil well gas containing chlorinated hydrocarbons of the aliphatic series in the presence of aluminum chloride at temperatures suitable for the production of a condensation reaction therein between the hydrocarbons of the naphthenic type and the chlorinated hydrocarbon in a reaction zone, withdrawing said condensed oil together with the unacted upon oil into a second reaction zone, introducing a further amount of aluminum chloride into said reaction zone, raising the temperature sufficiently therein to produce a decomposing reaction between said aluminum chloride and oil for the production of gasoline and a high boiling oil, withdrawing said high boiling oil and aluminum chloride residue into a still, and separating said aluminum chloride residue and tarry constituents by a distillation operation.

8. A method of treating hydrocarbon oils containing hydrocarbons of the naphthenic type, which comprises treating said oils with a hydrocarbon oil well gas containing chlorinated hydrocarbons of the aliphatic series in the presence of aluminum chloride at temperatures suitable for the production of a condensation reaction therein between the hydrocarbons of the naphthenic type and the chlorinated hydrocarbon in a reaction zone, withdrawing said condensed oil together with the unacted upon oil into a second reaction zone, introducing a further amount of aluminum chloride into said reaction zone, raising the temperature sufficiently therein to produce a decomposing reaction between said aluminum chloride and oil for the production of gasoline and a high boiling oil, discharging gasoline vapors from said reaction zone, and separately discharging said high boiling oil and aluminum chloride residue from said reaction zone.

Signed at Los Angeles, Calif., this 5 day of January 1927.

MARVIN L. CHAPPELL.