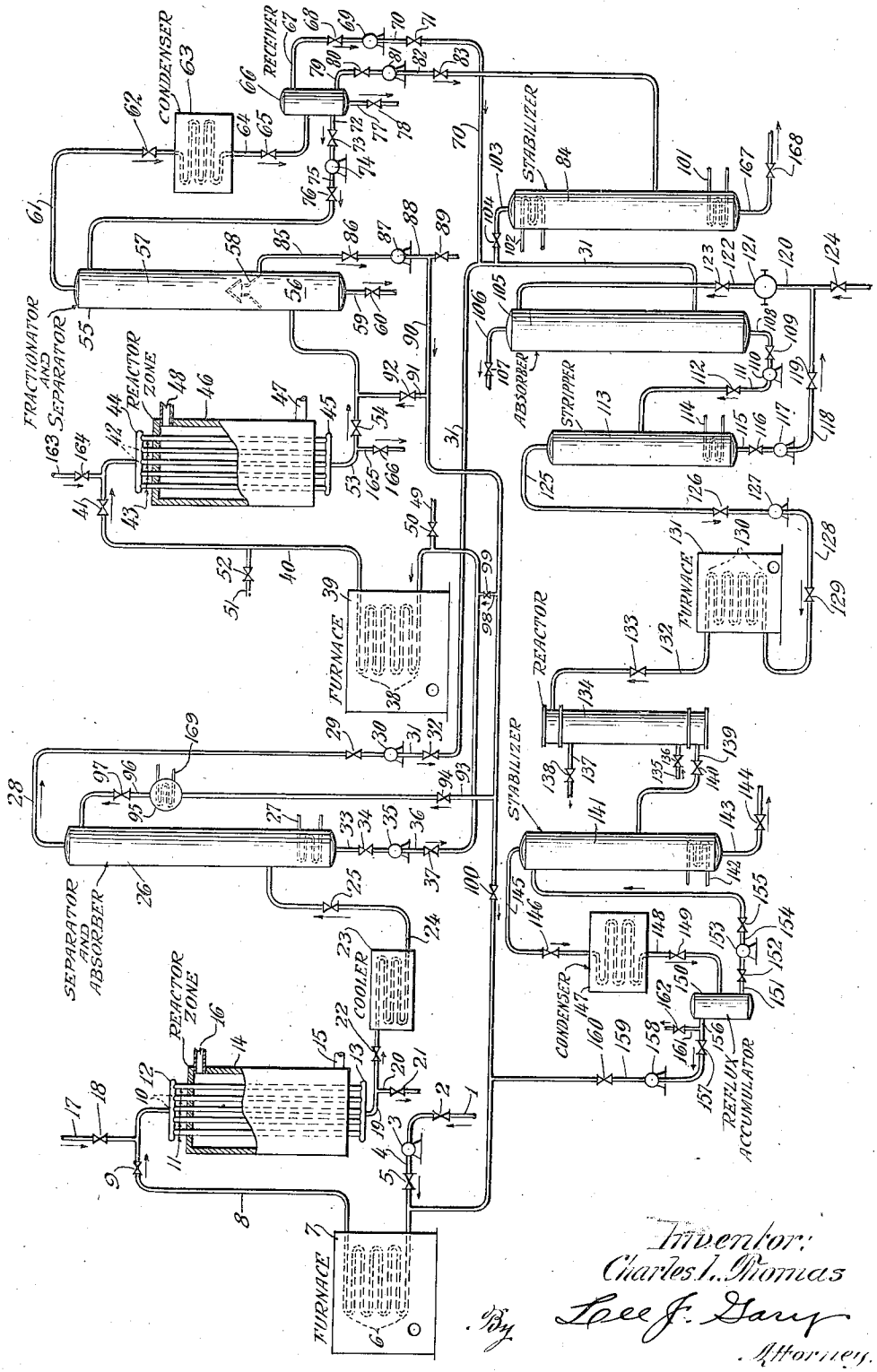
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CATALYTIC TREATMENT OF HYDROCARBONS

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CATALYTIC TREATMENT OF HYDROCARBONS

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16 Claims. (Cl. 196—10)

This invention relates particularly to the catalytic treatment of hydrocarbon oils and is more specifically concerned with a process involving a succession of closely cooperating steps for effecting the conversion of hydrocarbon oils into optimum yields of high antiknock gasoline.

The invention provides for dehydrogenating hydrocarbon oils in the presence of a catalyst to produce substantial quantities of liquid olefinic hydrocarbons followed by catalytic cracking of the resulting liquid products and polymerization of the normally gaseous olefinic hydrocarbons produced in both the dehydrogenation and the catalytic cracking steps. In addition, the invention provides for subjecting the residual gases, left after the removal of olefins in the polymerization step, to dehydrogenation in commingled state with the charging stock in order to dehydrogenate the paraffins to olefins and thereby increase the amount of available normally gaseous olefinic hydrocarbons in the charge to the polymerizers.

It has been found that hydrocarbon oils previously subjected to dehydrogenation respond more readily to catalytic cracking than either paraffinic or aromatic hydrocarbons because in properly controlled dehydrogenation substantial quantities of liquid olefinic hydrocarbons may be produced. Furthermore, it has been found that the catalytic cracking reaction may be carried out at a lower temperature when the charge has been previously subjected to dehydrogenation and there is less deposition of carbon on the catalyst because of the lower temperatures employed. It is known, also, that in catalytic cracking relatively large yields of normally gaseous olefinic hydrocarbons are produced which, when subjected to polymerization, polymerize to form a gasoline of relatively high octane number. Therefore, the main object of this invention is to carry out the three operations in a combination of steps designed to produce an optimum yield of gasoline of relatively high antiknock value.

Within the broad concepts of this invention dehydrogenation refers to the breaking of carbon-to-hydrogen bonds resulting in the splitting off of hydrogen from the molecule and the formation of a molecule containing a double bond, such as for example, an olefin from a paraffin hydrocarbon. Catalytic cracking refers primarily to the breaking of the carbon-to-carbon bonds resulting in the formation of two or more molecules of lighter hydrocarbons than the original. Polymerization refers to the joining together of two or more molecules of an unsaturated, and particularly an olefinic hydrocarbon to form one molecule of a heavier hydrocarbon.

In one specific embodiment the present invention comprises subjecting vaporized hydrocarbon oil to contact with a dehydrogenating catalyst under selected conditions of temperature and pressure in a primary step, separating fixed gases from the dehydrogenated products, subjecting the liquid dehydrogenated products in the vapor state to contact with a cracking catalyst under selected conditions of temperature and pressure in a second step, subjecting the conversion products from said second step to separation and fractionation to separate gas, gasoline, and heavier hydrocarbons, recovering the gasoline as a product of the process, subjecting the gas from said second step, together with the gas from said first step, to polymerization in the third step, separating residual gases from the product obtained from said third step, and subjecting said residual gases to dehydrogenation in commingled state with the charging stock in said first step.

The outline of the process given in the preceding paragraph will be amplified in the following description to indicate its important features in greater detail by describing the characteristic operations in connection with the attached diagrammatic drawing. The drawing illustrates one specific form of apparatus in which the process of the invention may be conducted. It is not drawn to any absolute or relative scale and the design and relative sizes of the individual units may be varied within reasonably wide ranges without departing from the broad scope of the invention.

Referring to the drawing, charging stock for the process, preferably comprising a hydrocarbon oil heavier than gasoline, is introduced through line 1 containing valve 2 to pump 3 which discharges through line 4 containing valve 5 into heating coil 6. The oil subjected to heating in coil 6 is substantially completely vaporized therein and raised to the desired temperature by means of heat supplied from a suitable furnace 7. In order to suppress the pyrolytic cracking reaction when vaporizing the charging stock, it is preferred that relatively short heating times be employed in heating coil 6, relatively low superatmospheric pressures, and relatively high heat input rates. The vaporized charging stock is discharged from heating coil 6 and is directed through line 8 containing valve 9 to catalytic reactor 10.

Preferably and in the case here illustrated, catalytic reactor 10 comprises a plurality of small

diameter reactor tubes 11 connected in parallel between upper and lower headers 12 and 13 and is disposed within a heating or cooling zone 14. Since dehydrogenation is an endothermic reaction (requiring heat), in order to obtain best results some form of heating must be employed in zone 14. It has been found that best results are usually obtained when employing fluid heating means, preferably comprising hot combustion gases, which may be introduced to zone 14 through duct 15, passed in indirect heat exchange relationship with the vapors passing through reactor tubes 11, after which they are discharged from the upper portion of zone 14 through duct 16.

In catalytic reactions, such as dehydrogenation, the deposition of carbon on the catalysts is relatively rapid and tends to decrease their activity. In order to obtain best results, relatively short periods of operation are preferably employed, i. e., the catalysts are subjected to contact with process vapors for a relatively short time and are then reactivated in approximately the same length of time. In this case it is preferred that a plurality of reactors be employed, each disposed within a separate heating or cooling zone, and in order to make the operation continuous reactivation may be accomplished in some of the reactors while the others are processing.

Although I have found it advantageous to employ a reactor of the type described above, various other kinds of reactors may be employed, such as, for example, the chamber type, without departing from the broad scope of the invention.

The hydrocarbon vapors introduced to header 12 of reactor 10 are directed through reactor tubes 11 and are subjected to contact therein with a suitable dehydrogenating catalyst under selected conditions of temperature and pressure.

Catalysts are preferably employed which have been found to be highly efficient in the catalytic dehydrogenation of hydrocarbon oil vapors to produce optimum yields of olefinic liquid hydrocarbons. The preferred catalysts for effecting dehydrogenation are those consisting of activated aluminum oxide supporting about 20% or less of chromium sesquioxide. These catalysts are preferably produced by the preliminary reduction of chromium trioxide left as a residue after the ignition of salt such as adsorbed chromium nitrate, $Cr(NO_3)_3$, or the precipitation of chromium trihydroxide, $Cr(OH)_3$, upon alumina granules. The process, however, is not limited to this particular composition of dehydrogenating catalysts but may employ other composite catalysts of a refractory character, such as, for example, alumina or silica or any inert refractory material supporting compounds and preferably oxides selected from the group comprising compounds and oxides of the elements in the left hand column of groups 4, 5, and 6 in the periodic table. The catalysts which are alternately utilizable are not exactly equivalent in their reaction and are not to be considered as absolute substitutes one for the other. This fact will be more or less apparent to those conversant with the practical aspects of catalysis.

In the particular case here illustrated, when the catalysts are reactivated the flow of hydrocarbon vapors is stopped and suitable reactivating gas mixtures at an elevated temperature and containing regulated quantities of oxygen are introduced to catalytic reactor 10 through line 17 containing valve 18 and line 8. Reactivating gases pass through reactor tubes 11 and due to oxidation the carbon deposited upon the catalysts disposed therein is caused to burn. The resulting mixture of combustion gases and reactivating gases is discharged from reactor 10 through line 19 and line 20 containing valve 21 to storage for further use as the reactivating gas mixture, or a portion or all may be cooled and recirculated as the reactivating gas mixture, or the whole may be discharged to the atmosphere as desired. When reactivating, an exothermic reaction takes place and, therefore, suitable means must be employed to dissipate this heat of reaction. In this case, it is preferred to employ cooled combustion gases which are supplied to zone 14 through duct 15, passed in indirect heat exchange relationship with the flow of reactivating gases in the reactor tubes, and are discharged therefrom through duct 16.

The dehydrogenated products are discharged from header 13 of reactor 10 through line 19 and are directed through valve 22 to cooler 23 wherein they are cooled to a temperature sufficiently low to substantially arrest the thermal cracking reaction which would otherwise take place, if the products were allowed to remain for a prolonged time under the conditions employed in the catalytic dehydrogenation reaction. Cracking obviously does not take during dehydrogenation because of the relatively short contact times employed. The cooled dehydrogenated products are discharged from cooler 23 through line 24 and are directed through valve 25 into separator and absorber 26. The dehydrogenated products introduced to separator and absorber 26 are preferably separated into a fraction substantially free of normally gaseous hydrocarbons and a fraction composed of said normally gaseous hydrocarbons. This may be accomplished by introducing cooled reflux condensate produced as subsequently described to the upper portion of separator and absorber 26 through line 96 and by subjecting the bottoms to reboiling. In the particular case here illustrated, reboiler coil 27, to which steam or some suitable heating medium is supplied, is used for reboiling in the lower portion of vessel 26; however, various other forms of reboilers may be employed, as is apparent to those skilled in the art, and it is not intended that this invention should be limited to the particular form of apparatus herein described.

Although separator and absorber 26 is preferably operated to remove all of the normally gaseous hydrocarbons, it may be desirable at times to separate only hydrogen and methane, in which case the balance of the normally gaseous hydrocarbons would be commingled with the liquid recovered as bottoms in this step. In any case, the fixed gases separated in separator and absorber 26 are withdrawn from the upper portion thereof through line 28 and are directed through valve 29 to compressor 30 by means of which they are discharged through line 31 containing valve 32 into absorber 105 and treated as subsequently described. The liquid hydrocarbons collected in the lower portion of separator and absorber 26 comprising normally liquid hydrocarbons and, when desired, condensed and dissolved normally gaseous hydrocarbons, are withdrawn from the lower portion thereof through line 33 and are directed through valve 34 to pump 35 which discharges through line 36 containing valve 37 to heating coil 38.

The dehydrogenated products introduced to heating coil 38 are raised to the desired reaction temperature, which is preferably high enough to

maintain all of the materials in the vapor state, by means of heat supplied from a suitable furnace 39. The heated vapors are discharged from heating coil 38 through line 40 and are directed through valve 41 to reactor 42. Preferably and as illustrated, the design of reactor 42 is similar to reactor 10 and comprises a plurality of relatively small diameter reactor tubes 43 connected in parallel between upper and lower headers 44 and 45, respectively, and is disposed within a heating or cooling zone 46. Although catalytic cracking and dehydrogenation differ in many respects, the operating conditions and the means employed for obtaining these conditions are usually very similar. It follows that the preferred method for heat exchange within reactor zone 46 is by fluid heating means which may be accomplished by introducing hot combustion gases through duct 47, passing the same in indirect heat exchange relationship with the vapors in reactor tubes 43 and discharging the cooler combustion gases through duct 48.

When desired, steam may be introduced to the charge of catalytic reactor 42 to assist in vaporizing and in reducing the effective pressure on the hydrocarbon vapors. This may be accomplished by introducing steam to the dehydrogenated products either before their introduction to heating coil 38 through line 49 containing valve 50 or after they have been vaporized in heating coil 38, through line 51 containing valve 52, in which case superheated dry steam is preferably employed.

The hydrocarbon vapors introduced to header 44 of reactor 42 are contacted with a cracking catalyst disposed within reactor tubes 43 under selected conditions of temperature and pressure and are discharged therefrom through line 53 containing valve 54, preferably cooled by commingling with the same a suitable cooling medium introduced as subsequently described in order to suppress the thermal cracking reaction, and introduced to separating zone 56 within combined fractionator and separator 55.

The preferred catalysts for effecting catalytic cracking consist in general of pellets or granules of specially prepared silica-alumina masses, the ratio of the constituents being varied to suit requirements depending upon the stock to be treated and the operating conditions employed. As a rough average, good results are usually obtained, for example, when employing silica with 15% alumina. This percentage is varied for best results under specific conditions over a relatively wide range, for example, from 2% to 50%, or alumina may be employed as the major constituent and silica as the minor constituent, the amount of silica composited with the alumina being varied over substantially the same range, that is, 2% to 50%. Catalysts of this character may be initially prepared in any of several different manners and subsequently dried. The preferred catalyst is prepared by precipitating silica from a solution of sodium silicate by acidifying with acid, such as, for example, hydrochloric acid, subsequently treating and washing the silica to remove substantially all of the alkali metal ions, suspending the purified silica gel in a solution of aluminum salts, and depositing the alumina upon the suspended silica by the addition of volatile basic precipitants, such as, for example, ammonium hydroxide, ammonium carbonate, or ammonium sulfide. After the alumina has been deposited upon the purified hydrated silica gel the material is dried, formed into pellets, when desired, and calcined at a temperature of from approximately 850 to 1000° F. The process, however, is not limited to this particular composition of cracking catalysts but may employ other composite catalysts of a refractory character, such as, for example, silica with compounds of the group comprising zirconia, vanadia, alumina-zirconia, alumina-thoria, and other catalysts, such as acid treated clays may be employed. The catalysts referred to above are not exactly equivalent in their reaction and are not to be considered as absolute substitutes one for the other, which fact will be more or less apparent to those conversant with the practical aspect of catalysis.

In catalytic cracking, as in dehydrogenation, while the hydrocarbon vapors are in contact with the catalyst, carbon deposits upon the catalyst decreasing its activity and necessitates relatively frequent reactivation. Therefore, in the case of catalytic cracking as in the case of dehydrogenation, it is preferred that a plurality of reactors be employed each disposed within a separate heating or cooling zone in order that they may be separately processed and reactivated and in order that the process may be carried out continuously. When reactivating the catalysts disposed within reactor 42 a suitable reactivating gas mixture at an elevated temperature and containing regulated quantities of oxygen is introduced to catalytic reactor 42 through line 163 containing valve 164 and line 40. The carbon deposited upon the catalysts disposed within reactor tubes 43 is caused to burn by oxidation with air introduced with the reactivating gas mixture. The resulting gases are discharged from reactor 42 through line 53 and are directed through line 165 containing valve 166 to storage or recirculated or discharged to the atmosphere as desired. In order to dissipate the heat evolved during the reactivation, suitable cooling means, preferably comprising cooled combustion gases, are introduced through duct 47, passed in indirect heat exchange relationship with the flow of reactivating gases in the reactor tubes 43 and are discharged therefrom through duct 48.

Preferably and as illustrated in the accompanying drawing, vessel 55 comprises a separating zone 56 in its lower portion and a fractionating zone 57 separated from said separating zone by means of reflux trapout tray 58. However, other means may be employed to accomplish the same purpose, such as, for example, separate vessels.

The commingled materials in line 53 are subjected to separation in separating zone 56 wherein the residual liquids are separated from the vaporous components. The residual liquids are discharged from the lower portion of zone 56 through line 59 and are directed through valve 60 to cooling and storage or elsewhere as desired. The vaporous components are introduced to fractionating zone 57 in combined separator and fractionator 55 wherein fractionated vapors in the gasoline boiling range are separated from higher boiling hydrocarbons.

Fractionated vapors of the desired end boiling point are withdrawn from the upper portion of fractionating zone 57 through line 61 and are directed through valve 62 to cooler and condenser 63. The resulting gas-containing distillate, together with undissolved and uncondensed gases discharged from condenser 63, are directed through line 64 and valve 65 to receiver 66. Undissolved and uncondensed gases collected and

separated in receiver 66 are withdrawn from the upper portion thereof through line 67 and are directed through valve 68 to pump 69 which discharges through line 70 containing valve 71 into line 31 by means of which they are introduced into absorber 105 in commingled state with the gases removed from the upper portion of separator and absorber 26. Water collected in the lower portion of receiver 66, resulting from condensing the steam employed in the process, is withdrawn therefrom through line 77 containing valve 78. Regulated portions of the distillate collected in receiver 66 are directed through line 72 containing valve 73 to pump 74 from which they are discharged through line 75 containing valve 76 to the upper portion of fractionating zone 57 for refluxing and cooling the upper portion thereof. The remaining distillate collected in receiver 66 is directed from the lower portion thereof through line 79 and valve 80 to pump 81 which discharges said distillate through line 82 containing valve 83 into stabilizer 84.

The heavier hydrocarbons separated from the fractionated vapors in fractionating zone 57 and comprising a fraction whose average boiling point is above that of said fractionated vapors, are condensed as reflux condensate therein and collected on trapout tray 58. The reflux condensate is withdrawn from fractionating zone 57 through line 85 and is directed through valve 86 to pump 87. Pump 87 discharges through line 88 and a portion or all of said reflux condensate may be directed through valve 89 to cooling and storage or elsewhere as desired. Preferably, however, the reflux condensate in line 88 is directed through line 90 and a portion commingled with the conversion products in line 53 for use as cooling oil, as previously described, this being accomplished by directing the reflux condensate in line 90 through line 91 containing valve 92. The remainder of the reflux condensate in line 90 is preferably directed through line 93 containing valve 94 to sub-cooler 95 wherein the reflux condensate is cooled to the desired temperature by means of a suitable cooling medium introduced to a cooling coil 169 in sub-cooler 95. The cooled reflux condensate is discharged from sub-cooler 95 through line 96 containing valve 97 into the upper portion of separator and absorber 26 to act as an absorption medium, as previously described. On the other hand, instead of introducing reflux condensate to conversion in the second step as an absorption oil, all or a portion of the reflux condensate subjected to conversion in the second step may be introduced to heating coil 38 by way of line 90, line 98, valve 99, and line 36. A portion of the reflux condensate in line 90 may, when desired, be directed through valve 100 for subsequent treatment in commingled state with the hydrocarbon oil introduced to heating coil 6.

Provision is made, in the case here illustrated for removing dissolved gases over those required to produce a distillate of the desired vapor pressure by liberating the same from the distillate in stabilizer 84. Provision is made for reboiling the distillate in the lower portion of stabilizer 84 by passing a suitable heating medium through close coil 101, and provision is made for cooling the upper portion of the stabilizer by passing a suitable cooling medium through closed coil 102. The stabilized distillate collected in the lower portion of stabilizer 84 is removed therefrom through line 167 and is directed through valve 168 to cooling and storage or elsewhere as desired.

The gases liberated from the distillate in stabilizer 84 are directed from the upper portion thereof through line 103 containing valve 104 and introduced to absorber 105 by way of line 31 in commingled state with the gases from separator and absorber 26 and the gases liberated in receiver 66.

The function of absorber 105 is to recover desirable high boiling components, including substantially all of the readily polymerizable olefins, such as butenes and propenes, from the gaseous products supplied to this zone by adsorption of said high boiling components by a suitable absorption medium. In the particular case here illustrated, the absorber oil is introduced to the upper portion of absorber 105 by way of line 122 and passes downward through absorber 105 countercurrent to the ascending gases with which it is intimately contacted by suitable means, such as bubble trays, or the like, not illustrated. The resulting enriched absorber oil collects in the lower portion of absorber 105 and the unabsorbed gases are released from the upper portion of the absorber through line 106 and valve 107. The enriched absorber oil is withdrawn from the lower portion of absorber 105 through line 108 and is directed through valve 109 to pump 110 which discharges through line 111 containing valve 112 into stripper 113.

Provision is made in stripper 113 for stripping the enriched absorber oil of the dissolved normally gaseous hydrocarbons, and this may be accomplished by reboiling the distillate collected in the lower portion of stripper 113 by means of a suitable closed heating coil 114 to which steam or some suitable heating medium is supplied. The stripped absorber oil is withdrawn from the lower portion of stripper 113 through line 115 and is directed through valve 116 to pump 117 which discharges through line 118 containing valve 119 into line 120 by means of which it is introduced to sub-cooler 121. The cooled absorber oil is discharged from sub-cooler 121 through line 122 containing valve 123 into the upper portion of absorber 105, as previously described. Additional absorber oil, required as makeup in absorber 105, may be introduced from an outside source through valve 124 in line 120.

The stripped gases liberated in stripper 113 are withdrawn from the upper portion thereof through line 125 and are directed through valve 126 to compressor 127 which discharges through line 128 containing valve 129 into and through heating coil 130. The charge in passing through heating coil 130 is raised to the optimum temperature for initiating the polymerization of the olefins by means of heat supplied from a suitable furnace 131.

The heated charge is discharged from heating coil 130 into line 132 and is directed through valve 133 into a suitable reactor 134 containing polymerizing catalysts. Among preferred catalysts are precalcined mixtures of phosphoric acids and absorbents, the latter preferably being of a siliceous character and comprising such materials as certain clays of the montmorillonite and bentonite type, (either raw or acid treated), kieselguhr, precipitated silica, and other siliceous and refractory materials. Granular catalysts may be prepared by making a paste, for example, of kieselguhr and a major portion by weight of ortho or pyrophosphoric acid, calcining the mix-

ture at temperatures of from 570 to 750° F. to produce a cake, grinding and sizing the cake to produce particles of a convenient size, usually from 4 to 20 mesh, and, if necessary, subjecting the sized particles to the action of superheated steam at about 110° F. and atmospheric pressure to bring the active catalytic acid to the state of hydration corresponding to maximum efficiency. The above procedure may be modified by extruding and forming the original pasty material and calcining the preformed particles.

The reaction of polymerization of olefins is exothermic, and in order to secure best results, means must be provided for extracting evolved heat to prevent excessive temperature rise in the catalyst zone. The polymerizing catalyst is preferably contained in banks of tubes of relatively small diameter which are surrounded by a cooling medium, (such as evaporating water), in suitably constructed reactors, such as that shown under 134 in the diagrammatic drawing. Preferably and as shown in the accompanying diagrammatic drawing, water is introduced to reactor 134 through line 135 and valve 136, and the steam produced within the reactor is withdrawn from the upper portion thereof through line 137 and valve 138.

Although only one reactor is shown in the accompanying diagrammatic drawing, a plurality of reactors connected in series, may be employed to obtain the desired contact time, and otherwise connected so that individual reactors may be segregated when the catalyst has become spent in order to replace such spent catalyst while employing other reactors in which the catalyst has sufficient activity to maintain operation.

The reaction products from reactor 134, comprising polymers and residual gases, are withdrawn from the lower portion thereof and directed through line 139 containing valve 140 to stabilizer 141. Provision is made in stabilizer 141 for removing residual gases over and above the amount required for obtaining the desired vapor pressure on the polymer product. Provision is made for reboiling the distillate contained in the lower portion of stabilizer 141 by means of a suitable closed heating coil 142 to which steam of some suitable heating medium is supplied. The stabilized distillate of the desired vapor pressure is withdrawn from the lower portion of stabilizer 141 through line 143 and is directed through valve 144 to cooling and storage or further treatment, not shown.

Residual gases liberated in stabilizer 141 are withdrawn from the upper portion thereof through line 145 and are directed through valve 146 to condenser 147. Light distillate, comprising liquefied normally gaseous hydrocarbons, together with undissolved and uncondensed gases, is discharged from condenser 147 through line 148 and is directed through valve 149 to reflux accumulator 150. Reflux accumulated in reflux accumulator 150 is withdrawn from the lower portion thereof through line 151 and is directed through valve 152 to pump 153 which discharges through line 154 containing valve 155 into the upper portion of stabilizer 141 for cooling and refluxing therein. The gaseous hydrocarbons collected in reflux accumulator 150 are directed through line 156 and valve 157 to compressor 158 which discharges through line 159 containing valve 160 into line 90 by means of which the gaseous hydrocarbons are introduced to line 4 wherein they are commingled with the charging stock prior to heating coil 6. When desired, regulated amounts of gaseous hydrocarbons withdrawn from reflux accumulator 150 may be directed through line 161 containing valve 162 to storage or to the atmosphere as desired.

The preferred range of operating conditions which may be employed in an apparatus such as illustrated and above described to accomplish the desired results is approximately as follows:

The primary heater to which the charging stock is supplied may employ an outlet temperature ranging, for example, from 800 to 1200° F. and a superatmospheric pressure of from 20 to 100 pounds or more per square inch. Substantially the same conditions of temperature and pressure are maintained on the process vapors introduced to the catalytic dehydrogenation reactor as are employed on the outlet of the heating coil to which the charging stock is supplied. The separator and absorber may employ a superatmospheric pressure substantially the same as that on the outlet of the catalytic dehydrogenation reactor. The furnace to which the dehydrogenated products are introduced may employ an outlet temperature ranging, for example, from 800 to 1200° F. and a superatmospheric pressure of from 20 to 100 pounds or more per square inch. However, this process permits the utilization of lower temperatures than would otherwise be employed if the cracking step was not preceded by the dehydrogenation step. Substantially the same conditions of temperature and pressure may be employed in the catalytic cracking reactor as are employed on the outlet of the heating coil to which the dehydrogenated products are supplied. The conversion products discharged from the catalytic cracking reactor are preferably cooled to a temperature ranging, for example, from 600 to 800° F. or at least to a temperature sufficiently low to substantially arrest any thermal cracking reaction. The combined fractionator and separator may utilize a pressure substantially the same as that employed at the outlet of the catalytic cracking reactor. The stabilizer, absorber, and stripper may utilize a superatmospheric pressure ranging, for example, from 50 to 200 pounds or more per square inch. The heating coil and communicating polymerizing reactor to which the normally gaseous hydrocarbons are introduced may employ a temperature ranging, for example, from 240 to 420° F. and a superatmospheric pressure in the approximate range of 200 to 500 pounds or more per square inch. The stabilizer to which the polymerization reaction products are supplied may employ a superatmospheric pressure ranging, for example, from 100 to 250 pounds or more per square inch.

As an example of one specific operation of the process as it may be accomplished in an apparatus such as illustrated and above described is approximately as follows:

Charging stock comprising a 36.7° A. P. I. gravity Midcontinent gas-oil was subjected to contact in the vapor state with an alumina-chromia dehydrogenating catalyst at a temperature of approximately 932° F. and under a superatmospheric pressure of approximately 40 pounds per square inch. The dehydrogenated products were treated for the removal of fixed gases and the resulting dehydrogenated products subjected to contact in the vapor state with a silica-alumina catalyst at a temperature of approximately 900° F. and under a superatmospheric pressure of approximately 30 pounds per square inch. The conversion products were cooled to ap-

proximately 650° F. by commingling reflux condensate produced as hereinafter described with the same. The conversion products, together with the cooling oil, were subjected to separation for the removal of liquid residue and the vaporous materials subjected to fractionation to separate fractionated vapors of the desired end boiling point from the heavier hydrocarbons. The fractionated vapors, including normally gaseous hydrocarbons, were subjected to condensation and the resulting distillate and undissolved and uncondensed gases collected and separated in a receiver. The heavier hydrocarbons were condensed as reflux condensate in the fractionating zone and a portion utilized as cooling oil to the conversion products discharged from the catalytic cracking step and the balance employed as an absorption oil to the gas separation step following the dehydrogenation reaction. Gasoline was subjected to stabilization to remove a portion of the normally gaseous hydrocarbons in order to reduce the vapor pressure of the gasoline product. The normally gaseous hydrocarbons obtained from the stabilization step, together with the receiver gases and the fixed gases removed in the separator and absorber following the dehydrogenation step, were subjected to absorption for the removal of hydrogen and methane. Normally gaseous hydrocarbons were recovered from the stripper substantially free from hydrogen and methane and were subjected to polymerization in the presence of a solid phosphoric acid polymerizing catalyst at a temperature of approximately 450° F. and under a pressure of approximately 300 pounds per square inch. The polymerized products were subjected to stabilization and the gaseous hydrocarbons recovered therefrom, comprising substantially paraffinic hydrocarbons were subjected to dehydrogenation in commingled state with the hydrocarbon oil charging stock. This operation yielded approximately 82% of 81 octane number gasoline by volume of the charge, the balance being attributed normally to gas and loss, and a minor yield of approximately 4% liquid residue.

I claim as my invention:

1. A process for producing gasoline of high anti-knock value from hydrocarbon oils heavier than gasoline, which comprises vaporizing the hydrocarbon oil charging stock, subjecting the vapors to contact with a dehydrogenating catalyst under dehydrogenating conditions of temperature and pressure in a primary step, separating fixed gases from the dehydrogenated products, subjecting the dehydrogenated liquid products in the vapor state and under cracking conditions of temperature and pressure to contact with a cracking catalyst in a second step, separately recovering gas, gasoline, and heavier hydrocarbons from the conversion products produced in said second step, removing said gasoline as a product of the process, subjecting said heavier hydrocarbons to substantial further conversion by returning them in part to said first step and in part to said second step, subjecting said fixed gases, together with the gases produced in said second step, to contact with a polymerizing catalyst under conditions selected to effect substantially complete polymerization of the olefins in a third step, separating residual gases from the polymer gasoline produced in said third step and recovering the latter as a product of the process, and subjecting said residual gases to dehydrogenation in commingled state with the charging stock.

2. A process for producing gasoline of high antiknock value from hydrocarbon oils heavier than gasoline, which comprises vaporizing the hydrocarbon oil charging stock, subjecting the vapors to contact with a dehydrogenating catalyst consisting essentially of an inert refractory material supporting a compound selected from the group consisting of compounds of the elements in the left hand columns of groups 4, 5, and 6 of the periodic table under dehydrogenating conditions of temperature and pressure in a primary step, separating fixed gases from the dehydrogenated products, subjecting the dehydrogenated liquid products in the vapor state and under cracking conditions of temperature and pressure to contact with a cracking catalyst in a second step, separately recovering gas, gasoline, and heavier hydrocarbons from the conversion products produced in said second step, removing said gasoline as a product of the process, subjecting said heavier hydrocarbons to substantial further conversion by returning them in part to said first step and in part to said second step, subjecting said fixed gases, together with the gases produced in said second step to contact with a polymerizing catalyst under conditions selected to effect substantially complete polymerization of the olefins in a third step, separating residual gases from the polymer gasoline produced in said third step and recovering the latter as a product of the process, and subjecting said residual gases to dehydrogenation in commingled state with the charging stock.

3. A process for producing gasoline of high antiknock value from hydrocarbon oils heavier than gasoline, which comprises vaporizing the hydrocarbon oil charging stock, subjecting the vapors to contact with a dehydrogenating catalyst consisting essentially of an inert refractory material supporting a compound selected from the group consisting of compounds of the elements in the left hand columns of groups 4, 5, and 6 in the periodic table under dehydrogenating conditions of temerature and pressure in a primary step, separating fixed gases from the dehydrogenated products, subjecting the dehydrogenated liquid products in the vapor state and under cracking conditions of temperature and pressure to contact with a cracking catalyst consisting essentially of silica and a member of the group consisting of alumina, zirconia, vanadia, alumina-zirconia, and alumina-thoria in a second step, separately recovering gas, gasoline, and heavier hydrocarbons from the conversion products produced in said second step, removing said gasoline as a product of the process, subjecting said heavier hydrocarbons to substantial further conversion by returning them in part to said first step and in part to said second step, subjecting said fixed gases, together with the gases produced in said second step, to contact with a polymerizing catalyst under conditions selected to effect substantially complete polymerization of the olefins in a third step, separating residual gases from the polymer gasoline produced in said third step and recovering the latter as a product of the process, and subjecting said residual gases to dehydrogenation in commingled state with the charging stock.

4. A process for producing gasoline of high antiknock value from hydrocarbon oils heavier than gasoline, which comprises vaporizing the hydrocarbon oil charging stock, subjecting the vapors to contact with a dehydrogenating cata-

lyst consisting essentially of an inert refractory material supporting a compound selected from the group consisting of compounds of the elements in the left hand columns of groups 4, 5, and 6 in the periodic table under dehydrogenating conditions of temperature and pressure in a primary step, separating fixed gases from the dehydrogenated products, subjecting the dehydrogenated liquid products in the vapor state and under cracking conditions of temperature and pressure to contact with a cracking catalyst consisting essentially of silica and a member of the group consisting of alumina, zirconia, vanadia, alumina-zirconia, and alumina-thoria in a second step, separately recovering gas, gasoline, and heavier hydrocarbons from the conversion products produced in said second step, removing said gasoline as a product of the process, subjecting said heavier hydrocarbons to substantial further conversion by returning them in part to said first step and in part to said second step, subjecting said fixed gases, together with the gases produced in said second step, to polymerization in the presence of a phosphoric acid-containing catalyst under conditions selected to effect substantially complete polymerization of the olefins in a third step, separating residual gases from the polymer gasoline produced in said third step and recovering the latter as a product of the process, and subjecting said residual gases to dehydrogenation in commingled state with the charging stock.

5. A process for producing gasoline of high anti-knock value from hydrocarbon oils heavier than gasoline, which comprises vaporizing the hydrocarbon oil charging stock, subjecting the vapors to contact with an alumina-chromia dehydrogenating catalyst at a temperature of from 800 to 1200° F. and under a pressure of from substantially atmospheric to 100 pounds per square inch in a primary step, separating fixed gases from the dehydrogenated products, subjecting the dehydrogenated liquid products in the vapor state and at a temperature of from 800 to 1200° F. and under a pressure of from substantially atmospheric to 100 pounds per square inch to contact with a silica-alumina cracking catalyst in a second step, separately recovering gas, gasoline, and heavier hydrocarbons from the conversion products produced in said second step, removing said gasoline as a product of the process, subjecting said heavier hydrocarbons to substantial further conversion by returning them in part to said first step and in part to said second step, subjecting said fixed gases, together with the gases produced in said second step to polymerization in the presence of a phosphoric acid-containing catalyst at a temperature of from 250 to 450° F. and at a superatmospheric pressure of from 100 to 500 pounds per square inch in a third step, separating residual gases from the polymer gasoline produced in said third step and recovering the latter as a product of the process, and subjecting said residual gases to dehydrogenation in commingled state with the charging stock.

6. A process for producing gasoline of high anti-knock value from hydrocarbon oils heavier than gasoline, which comprises vaporizing said hydrocarbon oil, subjecting the resulting vapors to contact with a dehydrogenating catalyst under dehydrogenating conditions of temperature and pressure in a primary step, cooling the dehydrogenated products, introducing the cooled dehydrogenated products to a separator and absorber wherein fixed gases are removed from the dehydrogenated liquid products, vaporizing said dehydrogenated liquid products, subjecting the vaporized dehydrogenated liquid products to contact with a cracking catalyst under cracking conditions of temperature and pressure in a second step, cooling the conversion products with reflux condensate produced as hereinafter set forth, introducing said conversion products, together with the cooling oil, to a separating zone wherein liquid residue is separated from the vaporous components, removing and recovering said liquid residue as a product of the process, subjecting said vaporous components to fractionation to separate fractionated vapors of the desired end boiling point from heavier hydrocarbons whose average boiling point is above that of said fractionated vapors, condensing said heavier hydrocarbons as reflux condensate in the fractionating zone and introducing it in part to said separator and absorber as absorber oil and in part to said conversion products, condensing and recovering said fractionated vapors to form distillate and gas, separating normally gaseous hydrocarbons in excess of those required to make the desired vapor pressure from the distillate, recovering the stabilized distillate as a product of the process, subjecting said gases, together with said fixed gases produced in said primary step, to contact with a polymerizing catalyst under polymerizing conditions of temperature and pressure in a third step, separating residual gases from the polymer product, and returning said residual gases to the dehydrogenation step for conversion in commingled state with said hydrocarbon oil charging stock.

7. A process for producing gasoline of high antiknock value from hydrocarbon oils heavier than gasoline, which comprises vaporizing said hydrocarbon oil, subjecting the resulting vapors to contact with a dehydrogenating catalyst consisting essentially of an inert refractory material supporting a compound selected from the group consisting of compounds of the elements in the left hand columns of groups 4, 5, and 6 in the periodic table under dehydrogenating conditions of temperature and pressure in a primary step, cooling the dehydrogenated products, introducing the cooled dehydrogenated products to a separator and absorber wherein fixed gases are removed from the dehydrogenated liquid products, vaporizing said hydrogenated liquid products, subjecting the vaporized dehydrogenated liquid products to contact with a cracking catalyst under cracking conditions of temperature and pressure in a second step, cooling the conversion products with reflux condensate produced as hereinafter set forth, introducing said conversion products, together with the cooling oil, to a separating zone wherein liquid residue is separated from the vaporous components, removing and recovering said liquid residue as a product of the process, subjecting said vaporous components to fractionation to separate fractionated vapors of the desired end boiling point from heavier hydrocarbons whose average boiling point is above that of said fractionated vapors, condensing said heavier hydrocarbons as reflux condensate in the fractionating zone and introducing it in part to said separator and absorber as absorber oil and in part to said conversion products, condensing and recovering said fractionated vapors to form distillate and gas, separating normally gaseous hydrocarbons in excess of those required to make the desired vapor pressure from the distillate,

recovering the stabilized distillate as a product of the process, subjecting said gases, together with said fixed gases produced in said primary step, to contact with a polymerizing catalyst under polymerizing conditions of temperature and pressure in a third step, separating residual gases from the polymer product, and returning said residual gases to the dehydrogenation step for conversion in commingled state with said hydrocarbon oil charging stock.

8. A process for producing gasoline of high antiknock value from hydrocarbon oils heavier than gasoline, which comprises vaporizing said hydrocarbon oil, subjecting the resulting vapors to contact with a dehydrogenating catalyst consisting essentially of an inert refractory material supporting a compound selected from the group consisting of compounds of the elements in the left hand columns of groups 4, 5, and 6 in the periodic table under dehydrogenating conditions of temperature and pressure in a primary step, cooling the dehydrogenated products, introducing the cooled dehydrogenated products to a separator and absorber wherein fixed gases are removed from the dehydrogenated liquid products, vaporizing said dehydrogenated liquid products, subjecting the dehydrogenated liquid products in the vapor state and under cracking conditions of temperature and pressure to contact with a cracking catalyst consisting essentially of silica with a member of the group consisting of alumina, zirconia, vanadia, alumina-zirconia, and alumina-thoria in a second step, cooling the conversion products with reflux condensate produced as hereinafter set forth, introducing said conversion products, together with the cooling oil, to a separating zone wherein liquid residue is separated from the vaporous components, removing and recovering said liquid residue as a product of the process, subjecting said vaporous components to fractionation to separate fractionated vapors of the desired end boiling point, from heavier hydrocarbons whose average boiling point is above that of said fractionated vapors, condensing said heavier hydrocarbons as reflux condensate in the fractionating zone and introducing it in part to said separator and absorber as absorber oil and in part as cooling to said conversion products, condensing and recovering said fractionated vapors to form distillate and gas, separating normally gaseous hydrocarbons in excess of those required to make the desired vapor pressure from the distillate, recovering the stabilized distillate as a product of the process, subjecting said gases, together with said fixed gases produced in said primary step, to contact with a polymerizing catalyst under polymerizing conditions of temperature and pressure in a third step, separating residual gases from the polymer product, and returning said residual gases to the dehydrogenation step for conversion in commingled state with said hydrocarbon oil charging stock.

9. A process for producing gasoline of high anti-knock value from hydrocarbon oils heavier than gasoline, which comprises vaporizing said hydrocarbon oil, subjecting the resulting vapors to contact with a dehydrogenating catalyst consisting essentially of an inert refractory material supporting a compound selected from the group consisting of compounds of the elements in the left hand columns of groups 4, 5, and 6 in the periodic table under cracking conditions of temperature and pressure in a primary step, cooling the dehydrogenated products, introducing the cooled dehydrogenated products to a separator and absorber wherein fixed gases are removed from the dehydrogenated liquid products, vaporizing said dehydrogenated liquid products, subjecting the dehydrogenated liquid products in the vapor state and under dehydrogenating conditions of temperature and pressure to contact with a cracking catalyst consisting essentially of silica with a member of the group consisting of alumina, zirconia, vanadia, alumina-zirconia, and alumina-thoria in a second step, cooling the conversion products with reflux condensate produced as hereinafter set forth, introducing said conversion products, together with the cooling oil, to a separating zone wherein liquid residue is separated from the vaporous components, removing and recovering said liquid residue as a product of the process, subjecting said vaporous components to fractionation to separate fractionated vapors of the desired end boiling point from heavier hydrocarbons whose average boiling point is above that of said fractionated vapors, condensing said heavier hydrocarbons as reflux condensate in the fractionating zone and introducing it in part to said separator and absorber as absorber oil and in part as cooling to said conversion products, condensing and recovering said fractionated vapors to form distillate and gas, separating normally gaseous hydrocarbons in excess of those required to make the desired vapor pressure from the distillate, recovering the stabilized distillate as a product of the process, subjecting said gases, together with said fixed gases produced in said primary step, to polymerization in the presence of a phosphoric acid-containing catalyst under conditions selected to effect substantially complete polymerization of the olefins in a third step, separating residual gases from the polymer product, and returning said residual gases to the dehydrogenation step for conversion in commingled state with said hydrocarbon oils.

10. A process for producing gasoline of high anti-knock value from hydrocarbon oils heavier than gasoline, which comprises vaporizing said hydrocarbon oil, subjecting the resulting vapors to contact with an alumina-chromia dehydrogenating catalyst at a temperature of from 800 to 1200° F. and under a pressure of from substantially atmospheric to 100 pounds per square inch in a primary step, cooling the dehydrogenated products, introducing the cooled dehydrogenated products to a separator and absorber wherein fixed gases are removed from the dehydrogenated liquid products, vaporizing said dehydrogenated liquid products, subjecting the vaporized dehydrogenated liquid products at a temperature of from 800 to 1200° F. and under a pressure of from substantially atmospheric to 100 pounds per square inch to contact with a silica-alumina cracking catalyst in a second step, cooling the conversion products with reflux condensate as hereinafter set forth, introducing said conversion products, together with the cooling oil, to a separating zone wherein liquid residue is separated from the vaporous components, removing and recovering said liquid residue as a product of the process, subjecting said vaporous components to fractionation to separate fractionated vapors of the desired end boiling point from heavier hydrocarbons whose average boiling point is above that of said fractionated vapors, condensing said heavier hydrocarbons as reflux condensate in the fractionating zone and introducing it in part to said separator and absorber as ab-

sorber oil and in part as cooling to said conversion products, condensing and recovering said fractionated vapors to form distillate and gas, separating normally gaseous hydrocarbons in excess of those required to make the desired vapor pressure from the distillate, recovering the stabilized distillate as a product of the process, subjecting said gases, together with said fixed gases produced in said primary step, to polymerization in the presence of a phosphoric acid-containing catalyst at a temperature of from 250 to 450° F. and at a superatmospheric pressure of from 100 to 500 pounds per square inch in a third step, separating residual gases from the polymer product, and returning said residual gases to the dehydrogenation step for conversion in commingled state with said hydrocarbon oils.

11. A process such as claimed in claim 10 wherein a portion of the reflux condensate is commingled with the hydrocarbon charging oil prior to the vaporizing step.

12. A process such as claimed in claim 10 wherein an aqueous fluid is introduced to the dehydrogenated liquid products prior to the vaporizing step.

13. A process such as claimed in claim 10 wherein superheated steam is commingled with the vaporized dehydrogenated liquid products.

14. A hydrocarbon oil conversion process which comprises subjecting the oil, together with normally gaseous paraffins of at least 3 carbon atoms to the molecule, to catalytic dehydrogenation to produce normally gaseous and normally liquid olefins, separating from the resultant products an olefinic gas and an olefinic liquid, cracking the latter in the presence of a cracking catalyst to produce gasoline and additional gaseous olefins therefrom, subjecting said olefinic gas and additional gaseous olefins produced by the cracking to polymerization to form normally liquid hydrocarbons boiling in the gasoline range, separating the last-named hydrocarbons from residual gases, and supplying at least a portion of the residual gases to the dehydrogenation step as said normally gaseous paraffins.

15. A hydrocarbon oil conversion process which comprises subjecting the oil, together with normally gaseous paraffins of at least 3 carbon atoms to the molecule, to catalytic dehydrogenation to produce normally gaseous and normally liquid olefins, separating from the resultant products an olefinic gas and an olefinic liquid, cracking the latter in the presence of a cracking catalyst to produce gasoline and additional gaseous olefins therefrom, separating the gasoline and additional gaseous olefins from conversion products heavier than gasoline, returning at least a portion of said heavier products to the dehydrogenation step, subjecting said olefinic gas and additional gaseous olefins produced by the cracking to polymerization to form normally liquid hydrocarbons boiling in the gasoline range, separating the last-named hydrocarbons from residual gases, and supplying at least a portion of the residual gases to the dehydrogenation step as said normally gaseous paraffins.

16. A hydrocarbon oil conversion process which comprises subjecting the oil, together with normally gaseous paraffins of at least 3 carbon atoms to the molecule, to catalytic dehydrogenation to produce normally gaseous and normally liquid olefins, separating from the resultant products an olefinic gas and an olefinic liquid, cracking the latter in the presence of a cracking catalyst to produce gasoline and additional gaseous olefins therefrom, separating the gasoline and additional gaseous olefins from conversion products heavier than gasoline, returning separate portions of said heavier products to the dehydrogenation and cracking steps, subjecting said olefinic gas and additional gaseous olefins produced by the cracking to polymerization to form normally liquid hydrocarbons boiling in the gasoline range, separating the last-named hydrocarbons from residual gases, and supplying at least a portion of the residual gases to the dehydrogenation step as said normally gaseous paraffins.

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