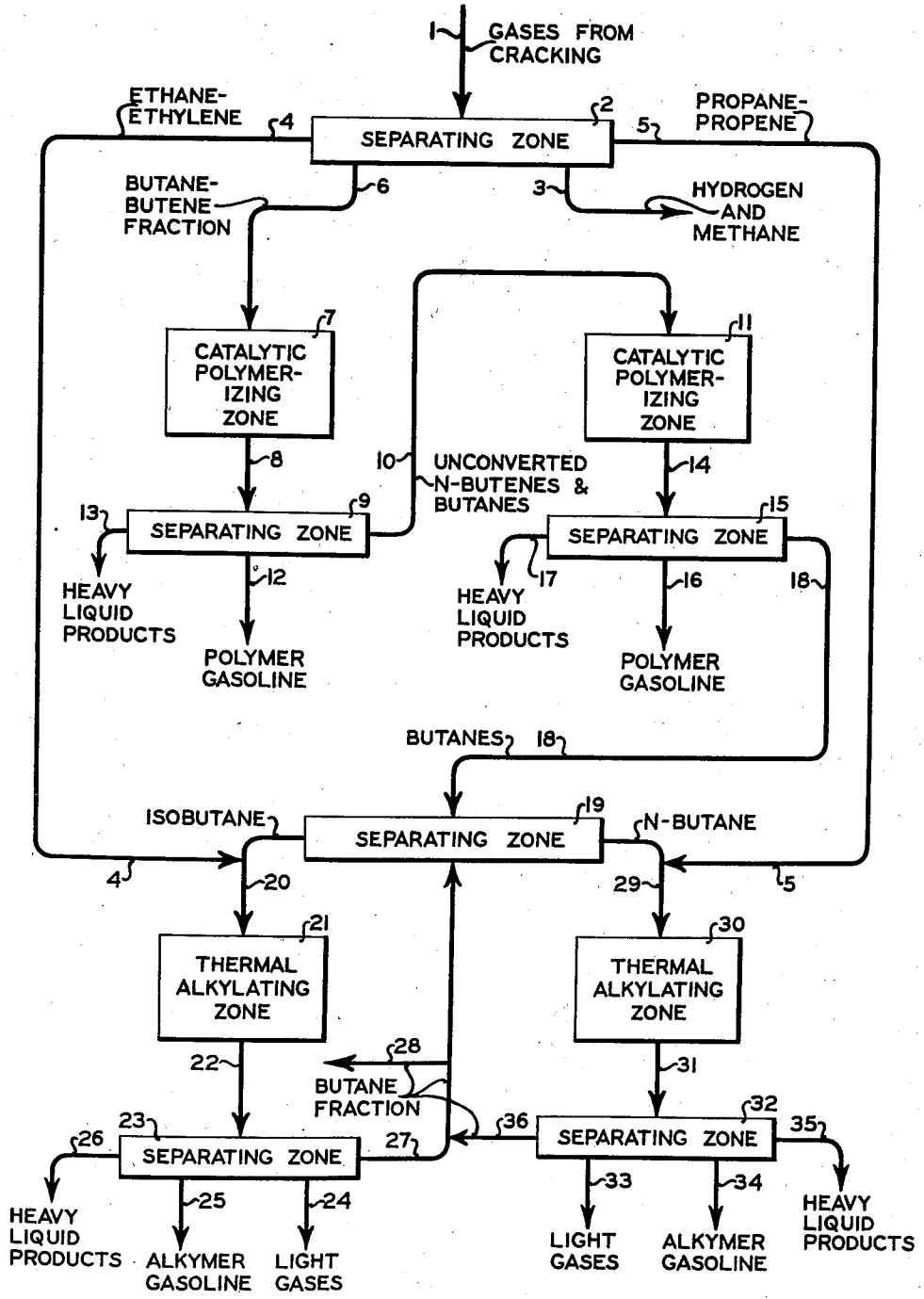
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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This invention relates to the production of high quality gasoline from gases containing olefins and paraffins of 2, 3 and 4 carbon atoms per molecule such as are formed during cracking of hydrocarbon oils including crude petroleum, gas oil, topped crude oil, and oils produced from coal or from other sources. The invention involves a series of steps which are so combined as to cooperate in a novel and advantageous manner to produce a desired result.

In one specific embodiment the present invention relates to a process for producing motor fuel of high antiknock value which comprises separating cracked gases into a mixture of methane and hydrogen, an ethane-ethylene fraction, a propane-propene fraction, and a butane-butene fraction; subjecting said butane-butene fraction to catalytic polymerization to convert isobutene and a portion of the normal butenes into polymers and to form an uncoverted fraction containing butanes and normal butenes; subjecting said unconverted fraction containing butanes and normal butenes to catalytic polymerization to yield polymers of normal butenes and a mixture of unconverted butanes; substantially separating said unconverted butanes into isobutane and normal butane: subjecting a mixture of said isobutane and said ethane-ethylene fraction to thermal alkylation to form a substantially saturated product containing an alkymer gasoline rich in neohexane; and subjecting a mixture of said normal butane and said propane-propene fraction to another thermal alkylating treatment to form a substantially saturated alkymer gasoline of good antiknock value.

In a further embodiment the present invention comprises a similar combination process in which the primary polymerizing step involves polymerization of isobutene contained in the butane-butene fraction charged thereto followed by a second polymerizing treatment for effecting substantially complete polymerization of remaining normal butenes into normally liquid polymers.

An essential feature of the invention is the separate or mixed polymerization of isobutene and normal butenes from a butane-butene fraction to form octenes hydrogenatable to octanes of high antiknock value followed by separation of the residual butanes and thermal alkylation of isobutane with ethylene and thermal alkylation of normal butane with propene to form substantially saturated alkymer gasolines of high antiknock value. With catalytic hydrogenation of the butene polymers, substantial proportions of the 2-, 3-, and 4-carbon atom hydrocarbons charged are converted into paraffinic motor fuel fractions of high antiknock value.

The invention is not in any individual step of the process per se, but rather in the advantageous combination of steps which co-operate to produce the desired final result, namely, conversion of a substantial proportion of the gases charged into a relatively high yield of normally liquid hydrocarbons boiling within the range of gasoline and suitable for use as aviation motor fuel.

The invention is of course not limited to the use of the charging stock consisting essentially of paraffins and olefins having 2, 3, and 4 carbon atoms per molecule, although the invention is primarily concerned with the treatment of such charging stock containing butanes and the olefins, ethylene, propene, and butenes. Suitable charging stock may be separated within the scope of the invention from a mixture of normally gaseous and normally liquid hydrocarbons wherein these desired 2, 3, and 4-carbon atom hydrocarbons are included in substantial quantities with other constituents of the mixture.

It is also within the scope of the invention, when desired, to hydrogenate the polymer gasolines formed in the respective polymerizing steps of the process. In most instances it is ordinarily preferable to separately hydrogenate the two polymer gasolines formed so that the respective products may be recovered separately without contaminating the hydrogenated product of the first polymerizing step with the hydrogenated product of the second polymerizing step, the latter product being of lower antiknock value.

As previously indicated, no novelty is claimed herein for any of the individual conversion steps of the process per se. To those familiar with the art, various polymerizing and hydrogenating catalysts suitable for use in different catalytic conversion steps of the process are well known, as well as the operating conditions of temperature, pressure, and time of contact which may be employed successfully with each of the different catalysts and which may be used in the thermal alkylating step of the process to effect the desired predominating reactions. It is therefore considered unnecessary to recite herein the various catalysts and/or specific operating conditions for conducting each of the steps of the process. Neither is the invention concerned with a specific method or methods whereby various satisfactory catalysts are produced. However, the following paragraphs will illustrate the operating conditions suitable in each of the process

steps when utilizing the particular catalyst specified.

In a primary polymerizing zone a butane-butene fraction (separated from a mixture of hydrogen and methane, an ethane-ethylene fraction, and a propane-propene fraction as hereinabove set forth, or obtained from any other source) is subjected to contact with sulfuric acid of between about 60 and about 70% concentration at a temperature between about 65° and 100° F. under a liquefying pressure to selectively absorb isobutene in the acid phase which is separated from the unconverted 4-carbon atom hydrocarbons comprising essentially butanes and normal butenes. The sulfuric acid containing absorbed isobutene is then subjected to a temperature of about 210° F. to form isobutene polymers and regenerate sulfuric acid. The resulting isobutene polymers containing a substantial proportion of di-isobutene are hydrogenatable to iso-octane of 100 octane number.

Alternatively in the primary polymerizing zone the butane-butene fraction separated from the cracked gas may be subjected to contact with a so-called solid phosphoric acid catalyst as described in U. S. Patent No. 1,993,513 and others to effect substantially selective polymerization of isobutene. A catalyst temperature between about 75° and 200° F. is generally suitable for polymerizing isobutene with substantially no polymerization of the normal butenes also contained in most butane-butene fractions. Suitable polymerizing pressure is within the approximate limits of 200 and 1500 pounds per square inch.

Sulfuric acid may also be employed in the primary polymerizing zone for effecting mixed polymerization of isobutene and normal butene to produce polymers hydrogenatable to paraffin hydrocarbons of high octane number. This type of polymerization may be effected conveniently by contacting the olefin-containing fraction with sulfuric acid of about 60 to about 70% concentration at a temperature within the approximate limits of 100° and 200° F. under a pressure of from substantially atmospheric to approximately 600 pounds per square inch. Under these conditions isobutene and normal butenes yield interpolymers or mixed polymers of relatively high octane number.

Mixed polymerization of isobutene and normal butenes may also be carried out in the primary polymerizing zone by subjecting the butane-butene fraction to contact with a so-called solid phosphoric acid catalyst, as described in United States Patent No. 1,993,513 and others, at a temperature between about 225° and 350° F. under a pressure between about 300 and 1500 pounds per square inch to convert isobutene and a substantial proportion of the normal butene into polymers containing octenes hydrogenatable to octanes of higher antiknock value.

The mixture of butanes and unconverted normal butenes separated from the products of the first polymerizing treatment is subjected to a second polymerizing treatment in the presence of solid phosphoric acid catalyst at a temperature between about 225° and about 550° F. under a pressure within the approximate limits of 100 and 1500 pounds per square inch to form a polymer gasoline which is separated from the unconverted isobutane and normal butane.

Branched chain octenes and higher butene polymers formed in the presence of sulfuric acid or of a solid phosphoric acid catalyst from isobutene, mixtures of isobutene and normal butene, or normal butenes are hydrogenated to substantially paraffinic products by means of hydrogen introduced from an outside source or separated from the gas charged to the process. Any suitable hydrogenating catalyst may be employed such as reduced nickel, nickel supported on a substantially inert carrier, mixtures of nickel and copper, as well as oxides or sulfides of chromium, molybdenum, tungsten, and vanadium. Hydrogenation of butene polymers in the presence of a mixture of nickel and diatomaceous earth is generally effected at a temperature of from about 150° to about 500° F. and under a pressure of from substantially atmospheric to approximately 2000 pounds per square inch although the use of higher pressure may occasionally be desirable.

Isobutane and normal butane remaining after the second polymerizing treatment are separated by fractionation. The isobutane fraction is commingled with the ethane-ethylene fraction separated from the gas charged and the resulting commingled mixture containing between about 1 and 10 mole per cent of ethylene is directed to a thermal alkylating zone maintained at a temperature between about 750° and about 1000° F. under a pressure in excess of about 1000 pounds per square inch but generally from about 1000 to about 4000 pounds per square inch to effect a substantial conversion of said isobutane and ethylene into a substantially saturated hydrocarbon mixture containing a relatively high yield of neohexane.

Normal butane also separated from the butane mixture remaining after the second polymerizing treatment is mixed with a propane-propene fraction in such an amount that the resulting commingled mixture contains from about 1 to about 10 mole per cent of propene after which the commingled gaseous hydrocarbons are subjected to thermal alkylation under substantially the same conditions of temperature and pressure used in the thermal alkylation of isobutane by ethylene as aforementioned. The product so formed from normal butane and the propane-propene fraction consists of substantially saturated liquid hydrocarbons of high antiknock value.

The accompanying drawing is a flow diagram illustrating one specific combination of steps by which the process of the invention may be carried out for producing motor fuel of high antiknock value from a normally gaseous hydrocarbon fraction comprising essentially paraffins and olefins having 2, 3, and 4 carbon atoms per molecule.

Referring to the drawing, a gaseous charging stock containing 2, 3, and 4 carbon atom olefins and paraffins as well as methane and hydrogen is supplied through line 1 to separating zone 2 which comprises absorbing, stripping, and fractional distilling equipment of conventional form designed to substantially separate said gaseous charging stock into a mixture of hydrogen and methane, an ethane-ethylene fraction, a propane-propene fraction, and a butane-butene fraction. Said mixture of hydrogen and methane is discharged from separating zone 2 through line 3 to storage, to hydrogenation of polymers as hereinafter set forth, or to any other use desired. The ethane-ethylene fraction, propane-propene fraction, and butane-butene fraction are directed through lines 4, 5, and 6, respectively, to further use as hereinafter described.

The butane-butene fraction separated from lighter gases in separating zone 2 and directed therefrom through line 6 is introduced to cata-

lytic polymerizing zone 7 in which substantially all of the isobutene and, when desired, a portion of the normal butenes, undergo polymerization to normally liquid polymers containing a substantial proportion of isomeric octenes. Catalytic polymerizing zone 7 comprises a reactor in which said butane-butene fraction is subjected to contact with sulfuric acid of between about 60% and about 70% concentration, the temperature and pressure being controlled so as to effect either selective polymerization of isobutene or mixed polymerization of one molecular proportion of isobutene with up to approximately an equal molecular proportion of normal butenes.

Substantially similar polymerization of butenes may be effected in the presence of solid phosphoric acid catalyst under a liquefying pressure. At a relatively low catalyst temperature between about 75° and 200° F., polymerization of isobutene is the predominant reaction while at a higher temperature between about 225° and 350° F. isobutene and approximately an equal molecular proportion of normal butenes undergo mixed polymerization.

The polymers formed in catalytic polymerizing zone 7 together with butanes and unconverted normal butenes are directed therefrom through line 8 to separating zone 9 which comprises fractional distilling equipment designed to separate a mixture of butanes and unconverted normal butenes from polymer gasoline containing a substantial proportion of isomeric octenes and smaller amounts of relatively heavy liquid products. Said mixture of butanes and unconverted normal butenes is directed from separating zone 9 through line 10 to a second catalytic polymerizing zone 11 hereinafter described. Polymer gasoline is withdrawn from separating zone 9 through line 12 to storage or it is directed to a hydrogenating treatment, not shown, to produce therefrom a substantially paraffinic motor fuel of high antiknock value containing a substantial proportion of isomeric octanes. Heavy liquid products boiling higher than octenes and generally higher than gasoline are withdrawn from separating zone 9 through line 13 to storage or to other use as desired.

The mixture of butanes and unconverted normal butenes introduced to catalytic polymerizing zone 11 as hereinabove set forth is therein subjected to contact with a solid phosphoric acid catalyst at a temperature between about 225° and 550° F. under a pressure within the approximate limits of 100 and 1500 pounds per square inch to convert said butenes into polymers which are in admixture with unconverted butanes. The polymerization products are directed from zone 11 through line 14 to separating zone 15 which comprises conventional fractionating equipment designed to separate butanes, polymer gasoline, and heavy liquid products. Said polymer gasoline is withdrawn from separating zone 15 through line 16 to storage or to subsequent hydrogenation, not shown, in order to form a substantially paraffinic product of high antiknock value suitable for use as aviation motor fuel. The heavy liquid products separated in zone 15 are discharged therefrom through line 17 to storage or to any use.

The mixture of unconverted butanes separated from normally liquid products in zone 15, as hereinabove set forth, is directed through line 18 to separating zone 19 in which isobutane and normal butane are substantially separated. The isobutane is directed from separating zone 19 through line 20, therein commingled with the ethane-ethylene fraction introduced by way of line 4 and thence subjected to contact in thermal alkylating zone 21 at a temperature between about 750° and 1000° F. under a pressure within the approximate limits of 1000 and 4000 pounds per square inch. In order to promote alkylation and to avoid excessive ethylene polymerization, it is preferable that not more than from about 1 to about 10 mole per cent of ethylene be present in the hydrocarbon mixture being charged to alkylation. The ethylene-containing fraction may be commingled with the isobutane prior to its introduction to the alkylating zone but to assist in diminishing the ethylene polymerization and to dissipate the heat liberated during alkylation, it is preferable that the ethylene-containing mixture or the hydrocarbon mixture containing both ethylene and isobutane be added in relatively small increments throughout the length of the alkylating zone.

The products of the above indicated thermal alkylation which contain substantial proportions of branched chain hexanes, as neohexane, and higher boiling paraffins are directed from zone 21 through line 22 to separating zone 23 which comprises fractional distilling equipment of conventional form designed for separately recovering from the products light gases, an unconverted butane fraction, alkymer gasoline, and heavy liquid products. From separating zone 23 light gases, alkymer gasoline, and heavy liquid products are withdrawn to storage or to further use through line 24, 25, and 26, respectively. The unconverted butane fraction comprising essentially isobutane and small amounts of normal butane formed during the thermal alkylating treatment is withdrawn from separating zone 23 through line 27, and at least a portion of said unconverted butane fraction is conducted therethrough to butane separating zone 19 already mentioned, the remainder of said unconverted butane fraction being discharged from line 27 through branch line 28 to storage or to other desired use.

Normal butane substantially separated from iso butane in zone 19 is directed through line 29, therein commingled with the propane-propene fraction of the cracked gas conducted thereto by way of line 5, and the resulting commingled mixture is subjected to thermal alkylation in zone 30 at a temperature between about 750° and 1000° F. under a pressure within the approximate limits of 1000 and 4000 pounds per square inch. Propene polymerization in zone 30 is substantially avoided by limiting to between about 1 and about 10 mole per cent the propene content of the hydrocarbon mixture charged thereto. The propane-propene fraction may be commingled with the normal butane prior to introduction to alkylating zone 30, but to assist in diminishing propene polymerization and in dissipating the heat liberated during alkylation, it is preferable that the propane-propene fraction or hydrocarbon mixture containing propene be admitted in relatively small increments throughout the length of the alkylating zone. The products of this second thermal alkylating treatment which contains substantial proportions of branched chain heptanes and higher boiling paraffins, are directed from alkylating zone 30 through line 31 to separating zone 32 which comprises fractional distilling equipment of conventional form designed for separating the products into light gases, alkymer gasoline, heavy liquid products, and an unconverted butane fraction. predominantly normal

butane. Said light gases, alkymer gasoline, and heavy liquid products are discharged from zone 32 to storage or directed to other use by way of lines 33, 34, and 35, respectively. Said unconverted butane fraction is directed from separating zone 32 through line 36 to line 27 and thereby directed to butane separating zone 19. From line 27 a portion of the unconverted butanes being directed therethrough is discharged through branch line 28 to storage or to other use as desired.

The following example is introduced to show results which may be expected in one specific operation of the process although with no intention of unduly limiting the generally broad scope of the invention:

A mixture of gases formed during cracking of gas oil and having the composition indicated in the following table, is separated into a mixture of hydrogen and methane, an ethane-ethylene fraction, a propane-propene fraction, and a butane-butene fraction.

TABLE

Analysis of gas from cracking

	Mole per cent
Hydrogen	5.2
Methane	13.5
Ethylene	8.2
Ethane	14.7
Propene	8.8
Propane	12.9
i-Butane	8.4
i-Butene	5.7
n-Butene	9.1
n-Butane	10.3
Pentane and higher	3.2

The butane-butene fraction obtained from the above indicated cracked gas is subjected to contact with sulfuric acid of 68% concentration at 65° F. under a pressure of 100 pounds per square inch to selectively absorb isobutene in the acid phase. After separation from unconverted butanes and normal butenes, the sulfuric acid containing absorbed isobutene is subjected to a temperature of about 210° F. to form isobutene polymers and to regenerate the sulfuric acid. The remaining mixture of butanes and normal butenes is subjected to contact with a calcined composite of pyrophosphoric acid and diatomaceous earth at 400° F. under a pressure of 600 pounds per square inch to substantially polymerize said butenes into normally liquid mono-olefins easily separable by fractional distillation from isobutane and normal butane. The polymers thus formed separately from substantially isobutene and normal butenes in the two polymerizing steps are hydrogenated separately to give substantially saturated motor fuel fractions to 100 and 85 octane number, respectively.

The unconverted isobutane and normal butane remaining after the second polymerizing treatment are separated by fractional distillation. Isobutane is commingled with the ethane-ethylene fraction, and normal butane is commingled with the propane-propene fraction. These commingled mixtures are separately subjected to thermal alkylation at 925° F. and 975° F., respectively, under a pressure of 3,500 pounds per square inch to form substantially saturated products. Alkylation products which form from isobutane and ethylene contain a substantial proportion of isomeric hexanes, particularly neohexane; while the reaction mixture which forms from normal butane and propene is rich in isomeric heptanes. By recycling the unconverted butanes to further separation into isobutane and normal butane and alkylation of these paraffins with ethylene and propene, respectively, substantially all of the olefinic hydrocarbons and butanes contained in the cracked gas are converted into high antiknock gasoline suitable for use as aviation motor fuel.

Neither the foregoing example nor the drawing should be interpreted as restricting the broader aspects of the invention as defined in the appended claims. Certain alternatives and refinements which are not illustrated in the drawing will be readily apparent to those familiar with the art, in view of the advantageous combination illustrated, and falling within the scope of the broad concepts of the invention. For example, the invention contemplates the elimination, when desired, of the second polymerizing step, particularly when the molal ratio of isobutenes to normal butenes in the charging stock is of the order of 1 or more to 1 and an octane number of less than 98 to 100, or thereabouts, in the hydrogenated polymer gasoline is satisfactory under prevailing market conditions. In such instances, all of the normal butenes, as well as the isobutene, may be polymerized in the first polymerizing step, the resulting unconverted normally gaseous fractions therefrom, which will consist predominantly of butanes, being separated into essentially isobutane and essentially normal butane, the isobutane being supplied with the ethane-ethylene fraction to one of the thermal alkylating steps and the normal butane being supplied with the propane-propene fraction to the other alkylating step.

In the preferred embodiment of the invention, although the 2 and 3-carbon atom fractions supplied to the alkylating steps include both olefins and paraffins, a high ratio of butanes to olefins is preferably maintained in the mixture supplied to each alkylating step in order to retard polymerization of the olefins. This may ordinarily be accomplished by recycling unconverted butanes as described, but during the early part of the operation before a cycle of unconverted butanes of sufficient quantity is established, and during normal operation, in case the quantities of residual isobutane and normal butane do not exceed, respectively, the quantities of ethylene and propylene recovered from the initial charging stock mixture on a molal basis. The desired high ratio of butanes to olefins may be maintained either by removing regulated quantities of the 2 and/or 3-carbon atom gases from the system and supplying only a portion of these gases to the alkylating steps or by supplying isobutane or normal butane or both to the respective alkylating steps from an external source.

I claim:

1. A process for producing more valuable products from a hydrocarbon mixture containing olefins and paraffins of 2, 3 and 4 carbon atoms to the molecule, which comprises fractionating the mixture to separate therefrom a C_2 fraction, a C_3 fraction and a C_4 fraction, subjecting the C_4 fraction to butene polymerizing conditions and separating resultant butene polymers from residual butanes, separating the latter into an isobutane fraction and a normal butane fraction, commingling the isobutane fraction with said C_2 fraction and subjecting the mixture to alkylation to react ethylene with isobutane, commingling said normal butane fraction with said C_3 frac-

tion and subjecting the mixture thus formed to independent alkylation treatment to react normal butane with propene.

2. The process as defined in claim 1 further characterized in that the polymerization treatment is performed in stages, isobutene being polymerized in the first stage and normal butenes in the second stage.

3. The process as defined in claim 1 further characterized in that the polymerization treatment is catalytic while the alkylation treatments are thermal.

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