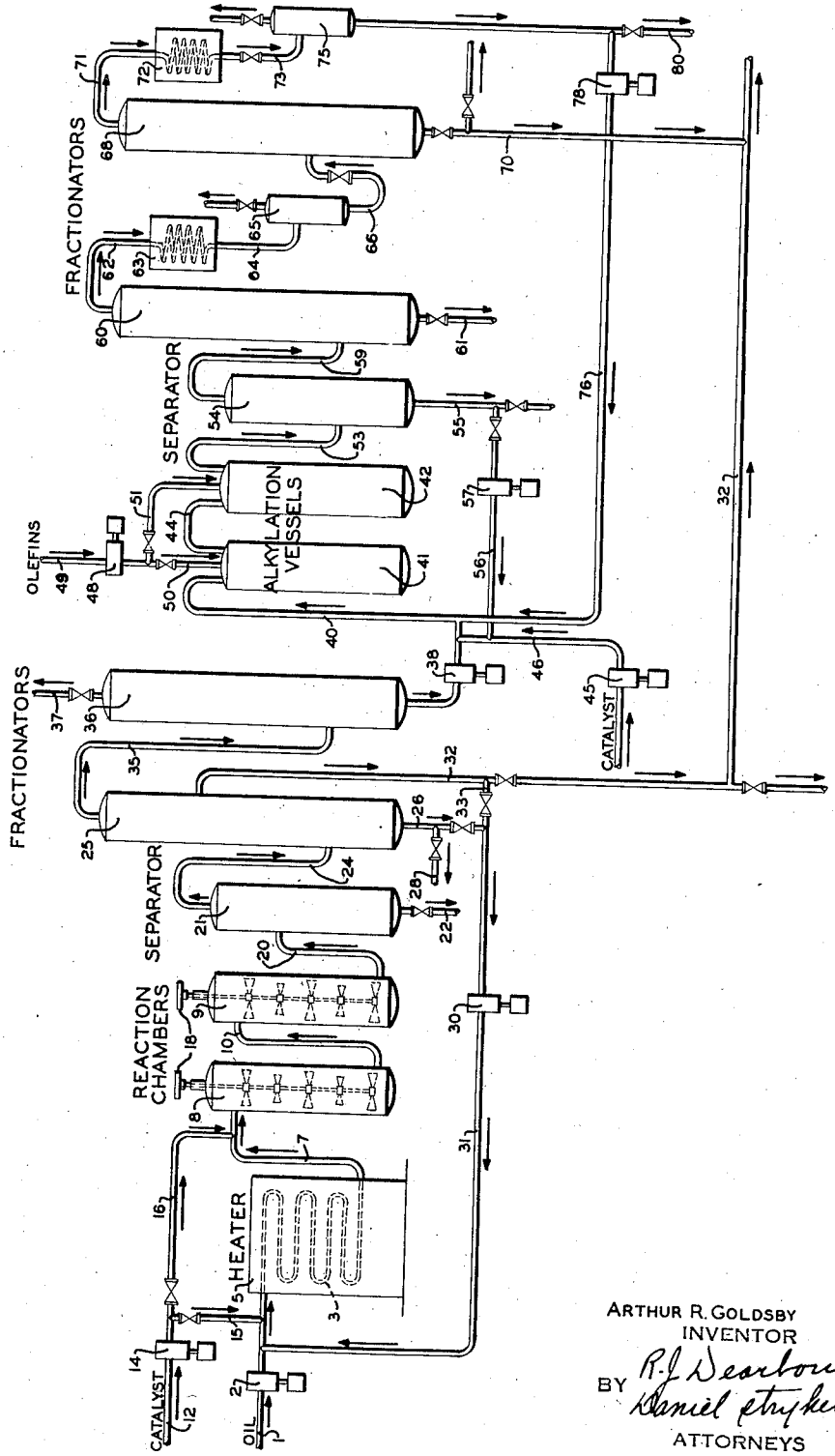
April 20, 1943. A. R. GOLDSBY 2,317,142

MANUFACTURE OF MOTOR FUEL

Filed April 27, 1939



ARTHUR R. GOLDSBY
INVENTOR
BY R. J. Dearborn
Daniel Stryker
ATTORNEYS

Patented Apr. 20, 1943 2,317,142

UNITED STATES PATENT OFFICE

2,317,142

MANUFACTURE OF MOTOR FUEL

Arthur R. Goldsby, Beacon, N. Y., assignor, by mesne assignments, to The Texas Company, New York, N. Y., a corporation of Delaware

Application April 27, 1939, Serial No. 270,338

8 Claims. (Cl. 196—10)

This invention relates to the conversion of hydrocarbon oils and gases, and has to do particularly with the production of high antiknock hydrocarbons suitable for the manufacture of motor fuel, such as aviation gasoline.

In accordance with the invention, hydrocarbon charging stock of higher molecular weight than butane is subjected to conversion at temperatures lower than normal cracking temperatures in the presence of a catalyst, whereby a substantial amount of normally gaseous hydrocarbons is formed, containing a large proportion of isobutane. The isobutane, or fraction containing the isobutane, in the presence of normally gaseous olefins, is treated with an alkylation catalyst, whereby the isobutane is alkylated by the olefins to form high antiknock hydrocarbons, such as branched chain, normally liquid hydrocarbons within the gasoline boiling point range.

It has been found that hydrocarbon oils, preferably paraffinic hydrocarbons of the lower boiling point series, may be cracked and isomerized under proper conditions and in the presence of a suitable catalyst, to produce a large yield of branched chain or isoparaffin hydrocarbons. The normally liquid hydrocarbons may simultaneously be substantially increased in antiknock property and the reaction is peculiar in the production of a substantial quantity of normally gaseous hydrocarbons predominating in isobutane. In this way, it is possible to produce from normally liquid hydrocarbons, normally gaseous hydrocarbons, containing 50% or more of isobutane and substantially free from olefins.

In the alkylation of the isoparaffins produced by the catalytic conversion operation, isobutane, for example, is treated in the presence of olefinic hydrocarbons, preferably normally gaseous olefins with an alkylation catalyst to effect alkylation of the isobutane with the olefins to form higher molecular weight, normally liquid hydrocarbons of high antiknock value, including iso-octanes. In the alkylation operation it is desirable to use a charging stock containing a high proportion of isobutane which may not be always readily available from natural sources. The present invention insures an adequate supply of isobutane and provides a unitary process for the production and alkylation of isobutane to produce high antiknock gasoline hydrocarbons.

The charging stock to the catalytic conversion operation may be any hydrocarbon oil which yields on treatment with a catalyst of substantially the cataytic properties of aluminum chloride and hydrogen chloride, a substantial yield of high antiknock gasoline and isobutane. It has been found that a paraffinic oil is suitable and preferably a low boiling naphtha fraction, such as one boiling within the range of about 97–220° F. A paraffinic or straight-run naphtha from a paraffin base crude gives good results.

The conversion operation is carried out at temperatures below those normally used in cracking and differs from a cracking operation in that no large amount of unsaturated normally gaseous products is obtained. The reaction apparently consists largely of isomerization with some splitting of the higher boiling oils into lower boiling liquid and normally gaseous isoparaffins. The temperatures used may be about 75° to 400° F. and preferably between about 150° and 300° F., although considerable latitude is intended. Good results have been obtained at about 200° to 250° F. Pressure of 75 to 150 pounds per square inch may be used although atmospheric temperatures are often satisfactory. The process may be carried out under milder conditions than normal cracking operations and, as contrasted to cracking, wherein heavier higher boiling molecules are converted into lower boiling products including aromatics, olefins and paraffins, the present operation produces low boiling products of substantially saturated and largely of branched chain type. The catalyst used may be an anhydrous metallic halide, such as an anhydrous aluminum chloride or bromide, and preferably a mixture of a metallic halide and a hydrogen halide promoter, such as hydrogen chloride or hydrogen bromide. The time of reaction depends on the temperature. At low temperature, the time is relatively long and may range from about 2 to 50 hours, for example between about 2 to 20 hours. At higher temperatures the time may be much shorter, such as 1 minute to 1 hour. The amount of catalyst in batch operation may range from 2 to 50% and preferably about 5 to 10% by weight, based on the hydrocarbon charged. In continuous operations the amount of catalyst will vary and may be considerably less. The hydrogen halide may be about 5 to 10% of the metallic halide and usually is around 2% or less.

In the alkylation step it is preferable to use normally gaseous hydrocarbons between 2 and 5 carbon atoms, such as C_3 or C_4 hydrocarbons or a mixture thereof. A portion of these is derived from the paraffin hydrocarbons formed in the above described conversion operation, for example, isobutane or a hydrocarbon fraction containing a large amount or predominating in isobutane, such as a mixture of isobutane and nor-

mal butanes or a mixture of isobutane, normal butanes and propane. The above paraffin charging stock is mixed with olefinic hydrocarbons which may be olefins of substantially the same number of carbon atoms derived from the cracking of hydrocarbon oils or gases, such as cracking still gases or refinery gases, or olefins resulting from the cracking or dehydrogenation of normally gaseous paraffin hydrocarbons. A C_4 hydrocarbon fraction, or a mixture of C_4 and C_3 hydrocarbons, comprising cracked products, is preferable, and it is desirable that the ratio of isoparaffins to olefins in the mixed feed be fairly high, for example at least about 1:1 and preferably between about 3:1 and 5:1. The excess isoparaffins, such as isobutane are recycled. The mixture of isoparaffins and olefins is intimately contacted at temperatures of about 0° F. to 100° F. and preferably about 60° to 90° F., with strong sulfuric acid, for example sulfuric acid of about 90 to 100% strength, and preferably about 94 to 98%. The reaction is carried out under sufficient pressure to maintain a liquid phase, for example, from about atmospheric to fifty pounds. The products comprise largely normally liquid branched chain, or isoparaffin hydrocarbons of high antiknock value suitable for the manufacture of gasoline.

In practicing the invention it is advantageous to blend the gasoline from the alkylation operation with the gasoline from the naphtha conversion step. The stabilized alkylation gasoline has a relatively high antiknock value but also high 10% and 50% boiling points, whereas the isomerized naphtha may be of somewhat lower octane number but a low 50% boiling point and especially low on points below 50%. The resulting blend will have a fairly high octane number and about the desired 50% boiling point. It is possible in this way to obtain a product which will meet the required specifications of an aviation gasoline.

The invention will be more fully understood by the following description read in connection with the accompanying drawing which shows diagrammatically, in elevation, one form of apparatus for carrying out the process of the invention.

Referring to the drawing, a hydrocarbon oil is charged through the line 1 by the pump 2 to a heating coil 3, located in a furnace 5. In the coil 3 the oil is raised to the desired temperature, and then transferred through the line 7 to reaction chambers 8 and 9, connected in series by the line 10. While two reactors are shown, any number may be used, or other means such as a coil may be used. A catalyst, in any suitable form, preferably in a liquid form, such as a suspension in an inert liquid, is introduced through the line 12 by the pump 14, and passed through the valve controlled line 15, which is in communication with the line 1, leading to the heating coil 3. The heating coil 3 may be by-passed, if desired, and the catalyst passed directly to the line 7 through the valve controlled line 16. In the reaction chambers 8 and 9 the oil and catalyst are intimately contacted by means of stirring mechanisms 18 for sufficient time to accomplish the desired reaction. The reaction products are transferred from the lower portion of the reaction chamber 9 through the line 20 to a separator 21 wherein the catalyst and sludge separate from the oil and are then withdrawn from the bottom of the separator through the valve controlled line 22. This sludge material may be subsequently treated, for example by hydrolysis, to separate the metal compounds from the unsaturated oil which may be used for the manufacture of resins.

The oil substantially free from the catalyst is drawn from the upper portion of the separator 21 through the line 24 and introduced into a fractionator 25. In the fractionator 25 it is intended to make a separation between the normally liquid and normally gaseous hydrocarbons. The normally liquid hydrocarbons may be withdrawn from the bottom of the fractionator through the line 26 and discharged from the system through the valve controlled line 28 or recycled to the system by pump 30 through the line 31 which communicates with the line 1, leading to the heating coil 3. The product drawn off through line 28 may require further fractionation to obtain a product suitable for use as gasoline. Such fractionation may be obtained by separate distillation or rerunning, or by suitable fractionation in the tower 25. For this purpose, a side stream of the required boiling range may be taken from the fractionator through the line 32 and discharged from the system or recycled all or in part through the branch line 33 and line 31 to the system. Instead of taking a side stream from the tower 25, it is contemplated that another fractionator may be used for fractionating out a gasoline cut of any desired boiling range. The normally gaseous hydrocarbons are withdrawn from the top of the fractionator 25 through the line 35 and introduced into a secondary fractionator 36 in which the gases are fractionated to separate and release through line 37 those of a more permanent nature, such as methane and hydrogen, and all or a portion of the C_2 and C_3 hydrocarbons, if desired.

The higher boiling normally gaseous hydrocarbons, comprising C_4 hydrocarbons, are withdrawn from the bottom of the fractionator 36 by the pump 38 and forced through the line 40 to the alkylation vessels 41 and 42 connected in series by line 44. The alkylation catalyst, such as sulfuric acid, is introduced by the pump 45 through the line 46 which communicates with the line 40. The olefin charging stock is introduced by the pump 48 through the line 49 which communicates by the branch lines 50 and 51 with the vessels 41 and 42 respectively, whereby the olefin charge may be introduced into either vessel 41 and 42 or both. The alkylation vessels 41 and 42 are provided with contacting means, such as stirrers, whereby intimate contact is provided between the mixture of hydrocarbons and the catalyst. The reaction products pass from the last alkylation vessel through the line 53 to a separator 54 wherein the acid separates and may be withdrawn from the lower portion thereof through the line 55 and discharged from the system or recycled through the line 56 by the pump 57. The hydrocarbons, substantially free from acid, are removed from the upper portion of the separator 54 through the line 59 and discharged into a fractionator 60 wherein a separation is made between the gasoline hydrocarbons and the higher boiling products, or bottoms, which are withdrawn from the bottom of the fractionator through the valve controlled line 61. The gasoline hydrocarbons are taken overhead through the vapor line 62, condenser 63 and run-down line 64 to a receiver 65. The gasoline in receiver 65 may be passed through valve controlled line 66 to a stabilizer 68 to stabilize the gasoline. In the stabilizer the light materials are separated

as vapors and may be removed overhead. A stabilized gasoline having higher 10% and 50% boiling points than required to meet commercial aviation gasoline specifications as hereinbefore set forth is withdrawn from the lower portion of tower **68** as bottoms through line **70**, and is preferably combined with the isomerized naphtha in line **32**.

The overhead products comprising isobutane are passed through the vapor line **71**, condenser **72**, and rundown line **73** to a receiver **75**. When charging C_4 hydrocarbons to the alkylation unit, the product collected in receiver **75** may be chiefly isobutane with or without some n-butane. In case hydrocarbons lighter than C_4 hydrocarbons, such as C_3 hydrocarbons, are removed from the top of stabilizer, these hydrocarbons may be separated from the isobutane and used as reflux or discharged from the system. It is contemplated, for example, that the C_3 hydrocarbons, in the latter case, may be collected in the receiver **75** and the isobutane removed as a side stream from the stabilizer **68**. The latter method of operation is not shown in the drawing. The isobutane is preferably recycled to the alkylation vessels through the line **76** in which is located pump **78**. Any portion of the isobutane may be discharged from the system through branch line **80**.

Example I

A straight run naphtha from paraffin base crude, having a boiling point range of about 185° to 220° F. and an octane number of about 50, was mixed with about 10% of anhydrous aluminum bromide and reacted at a temperature of about 200° F. for about 16 hours. About 10% by volume of sludge was formed which was separated from the reaction products. About 85% by volume of liquid products was obtained, boiling substantially within the boiling point range of the original oil. About 20 volumes of normally gaseous hydrocarbons were liberated, showing the following percentage composition by volume:

	Per cent
Methane	5.7
Propane	39.1
Normal butane	4.5
Isobutane	50.5

The gaseous hydrocarbons were fractionated to obtain a C_4 fraction comprising about 90% isobutane. This fraction was mixed with a cracked C_4 hydrocarbon fraction in such proportion that the ratio of isobutane to olefins was about 3:1. The mixture was intimately contacted with 94% sulfuric acid in the proportion of about 0.8% by weight based on the olefins and the mixture allowed to react for about one hour at about 75° F. The acid was separated from the reaction products and the hydrocarbons fractionated to obtain a gasoline fraction. The yield of gasoline was about 170% based on the olefins consumed and showed an antiknock value of about 90.

Example II

A straight run naphtha was intimately contacted with 18.9% aluminum bromide and 0.9% hydrogen bromide for 6 hours at 199° to 207° F. There was obtained 87.6% of gasoline, 5.4% of gas of which about 80% was isobutane, and 7% hydrocarbons in combination with the catalyst. The tests on the naphtha before and after treatment were as follows:

Distillation (A. S. T. M.)	Charge	Product
Initial boiling point	97	85
5		99
10	119	106
20	127	117
30	135	128
40	141	136
50	148	144
60	155	154
70	163	165
80	171	182
90	184	230
95	199	
E. P	212	404
Percent rec	97.5	94.5
Percent res		1.0
Percent loss		4.5
Octane number	67.6	80.6

The following examples are listed which show the results obtained in the catalytic isomerization of a broad boiling range straightrun naphtha or higher boiling fraction of straightrun naphtha. By comparison with Example II above, it will be noted that greatly superior results from the standpoints of octane and volatility or boiling point distribution of the isomerizate were obtained in the case of the low-boiling fraction of said Example II; and that the isomerizate of said Example II constitutes a satisfactory blending stock for alkylation gasoline stabilized to lower 10% and 50% boiling points than required to meet commercial aviation gasoline specifications, to improve the front end volatility of the latter and maintain high octane of the blended product as required to meet said commercial aviation gasoline specifications.

Example III

An acid treated straight run naphtha was intimately contacted for 2.5 hours at 230° to 241° F. and under a pressure of 110 to 131 pounds with 10% aluminum chloride and 0.8% hydrogen chloride. About 91% gasoline, 3% gas and 6% of hydrocarbons in the form of a complex with the catalyst were obtained. The gas contained about 83% of isobutane. The tests in the charge and product were as follows:

	Charge	Product
Initial boiling point	130	100
5	168	130
10	180	144
20	198	171
30	211	194
40	222	212
50	232	226
60	240	239
70	250	252
80	260	269
90	274	306
95	284	436
E. P	309	472
Percent rec	99	97.0
Percent res	1	0.8
Percent loss		2.2
Octane number	54	63
Plus 1 cc. tetraethyl lead	65	74
Plus 2 cc. tetraethyl lead	73	80

Example IV

Another example of the naphtha used in Example III was treated with 20% aluminum chloride and 0.8% hydrogen chloride, for 3.3 hours at 238° to 245° F. under a pressure of 125 to 135 pounds. About 76% of gasoline, 13.5% gas containing about 80% isobutane, and 10.5% of hydrocarbons in the form of a complex with the

catalyst, were obtained. The gasoline product showed the following tests:

	Product
Initial boiling point	96
5	127
10	140
20	162
30	181
40	200
50	219
60	236
70	251
80	270
90	320
95	455
E. P.	486
Percent rec.	97.0
Percent res.	0.9
Percent loss	2.1
Octane number	66.5
Plus 1 cc. tetraethyl lead	77
Plus 2 cc. tetraethyl lead	82

Example V

A straight run acid treated naphtha was treated with 10% aluminum chloride and 0.8% hydrogen chloride for 4.2 hours at 260° to 264° F. under a pressure of 80 to 100 pounds. Approximately 89% gasoline, 2% gas consisting of about 77% isobutane and 9% hydrocarbons in the form of a complex with the catalyst was obtained. The charge and product tested as follows:

	Charge	Product
Initial boiling point	284	102
5		150
10	300	192
20	304	266
30	308	283
40	311	301
50	315	310
60	318	316
70	322	324
80	329	334
90	340	364
95	352	500
E. P.	394	500
Percent rec.		95.5
Percent res.		0.9
Percent loss		3.6
Octane number	26.5	45.5
Plus 1 cc. tetraethyl lead	43	57
Plus 2 cc. tetraethyl lead	52.5	65

The isobutane in the gases evolved in the above examples is alcylated with C_4 or C_3 and C_4 olefins to produce a gasoline having an octane number of about 90. This product is blended with the isomerized naphtha such as produced in Example II to obtain a blend having an octane number substantially higher than the isomerized naphtha, the exact amount depending on the amount of alkylate added.

While sulfuric acid has been specified as the catalyst used in the alkylation step, it is contemplated that other alkylation catalysts may be used, such as anhydrous metallic halides, including aluminum chloride or bromide, and hydrofluoric acid.

This application is a continuation in part of my application Serial Number 210,701, filed May 28, 1938.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for the manufacture of high anti-knock aviation fuel which comprises subjecting a relatively low anti-knock paraffinic hydrocarbon charging stock of higher molecular weight than butane but boiling below about 212° F. to the action of an anhydrous metallic halide and a hydrogen halide at temperatures above 75° F. but below 400° F. to effect isomerization of the hydrocarbons without the formation of any substantial amount of unsaturated hydrocarbons, whereby substantially saturated normally liquid hydrocarbons within the gasoline boiling range of increased branched chain structure are produced together with normally gaseous substantially saturated paraffinic hydrocarbons consisting mainly of isobutane, the said charging stock of relatively low boiling range producing under the said isomerizing conditions a resultant liquid product of greatly improved antiknock value but having lower 10% and 50% boiling points than desired for commercial aviation gasoline, separating the resulting isomerized normally liquid hydrocarbons from the normally gaseous fraction, alkylating isobutane of the normally gaseous fraction with low-boiling olefins in the presence of an alkylating catalyst under alkylating conditions to produce substantially saturated hydrocarbons within the gasoline boiling range of high anti-knock value mixed with light normally gaseous hydrocarbons, stabilizing the mixture to remove the light material as vapors and produce a stabilized alkylation gasoline having higher 10% and 50% boiling points than desired for commercial aviation gasoline, and blending resulting isomerized liquid hydrocarbons with resulting alkylate for the production of a commercial aviation gasoline of high antiknock value and desired boiling range.

2. A process in accordance with claim 1, in which the alkylating catalyst is concentrated sulfuric acid of alkylation strength.

3. A process in accordance with claim 1, in which the temperature of the isomerization is maintained at about 200° to 250° F.

4. A process in accordance with claim 1, in which the anhydrous metallic halide is anhydrous aluminum chloride and the hydrogen halide is HCl.

5. A process in accordance with claim 1, in which the paraffinic hydrocarbon charging stock is a low-boiling fraction of straightrun naphtha.

6. In the manufacture of aviation gasoline of high anti-knock rating, wherein isobutane is alkylated with a low-boiling olefin in the presence of an alkylation catalyst under alkylating conditions to produce hydrocarbon reaction products, the improvement which comprises fractionating and stabilizing the hydrocarbon reaction products to separate hydrocarbons boiling above the aviation gasoline boiling range and also to separate normally gaseous hydrocarbons to thereby produce a resulting stabilized alkylation gasoline having 10% and 50% boiling points above those required to meet commercial aviation gasoline specifications, and then blending with the said stabilized alkylation gasoline a low-boiling fraction consisting essentially of normally liquid saturated hydrocarbons of largely isoparaffinic character and of high anti-knock value, which is the product of catalytic isomerization of a paraffinic hydrocarbon charging stock of higher molecular weight than butane but boiling below about 220° F., said low-boiling fraction having substantially lower 10% and 50% boiling points than required to meet said commercial aviation gasoline specifications, whereby an aviation gasoline of high anti-knock value is obtained which meets said commercial aviation gasoline volatility specifications.

7. Process as defined in claim 6, wherein the said low-boiling fraction is the product of catalytic isomerization with an aluminum halide and a hydrogen halide at temperatures of about 75–400° F. of a straightrun paraffinic naphtha fraction boiling within the range of 97–220° F.

8. In the manufacture of aviation gasoline of high anti-knock rating, wherein isobutane is alkylated with C_4 olefins of a C_4 hydrocarbon fraction in the presence of an alkylation catalyst under alkylating conditions, and resulting hydrocarbon phase is separated from catalyst phase, the improvement which comprises fractionating and stabilizing the hydrocarbon phase to separate hydrocarbons boiling above the aviation gasoline boiling range and also to separate normally gaseous hydrocarbons to thereby produce a resulting stabilized alkylation gasoline having 10% and 50% boiling points above those required to meet commercial aviation gasoline specifications, and then blending with the said stabilized alkylation gasoline a low-boiling isomerizate consisting essentially of normally liquid saturated hydrocarbons of largely isoparaffinic character and of high anti-knock value resulting from catalytic isomerization of a paraffinic charging stock of higher molecular weight than butane but boiling below about 220° F., said isomerizate having a 10% boiling point at least as low as 106° F. and a 50% boiling point at least as low as 144° F., to thereby produce a resulting gasoline of high anti-knock value meeting said commercial aviation gasoline volatility specifications.

ARTHUR R. GOLDSBY.