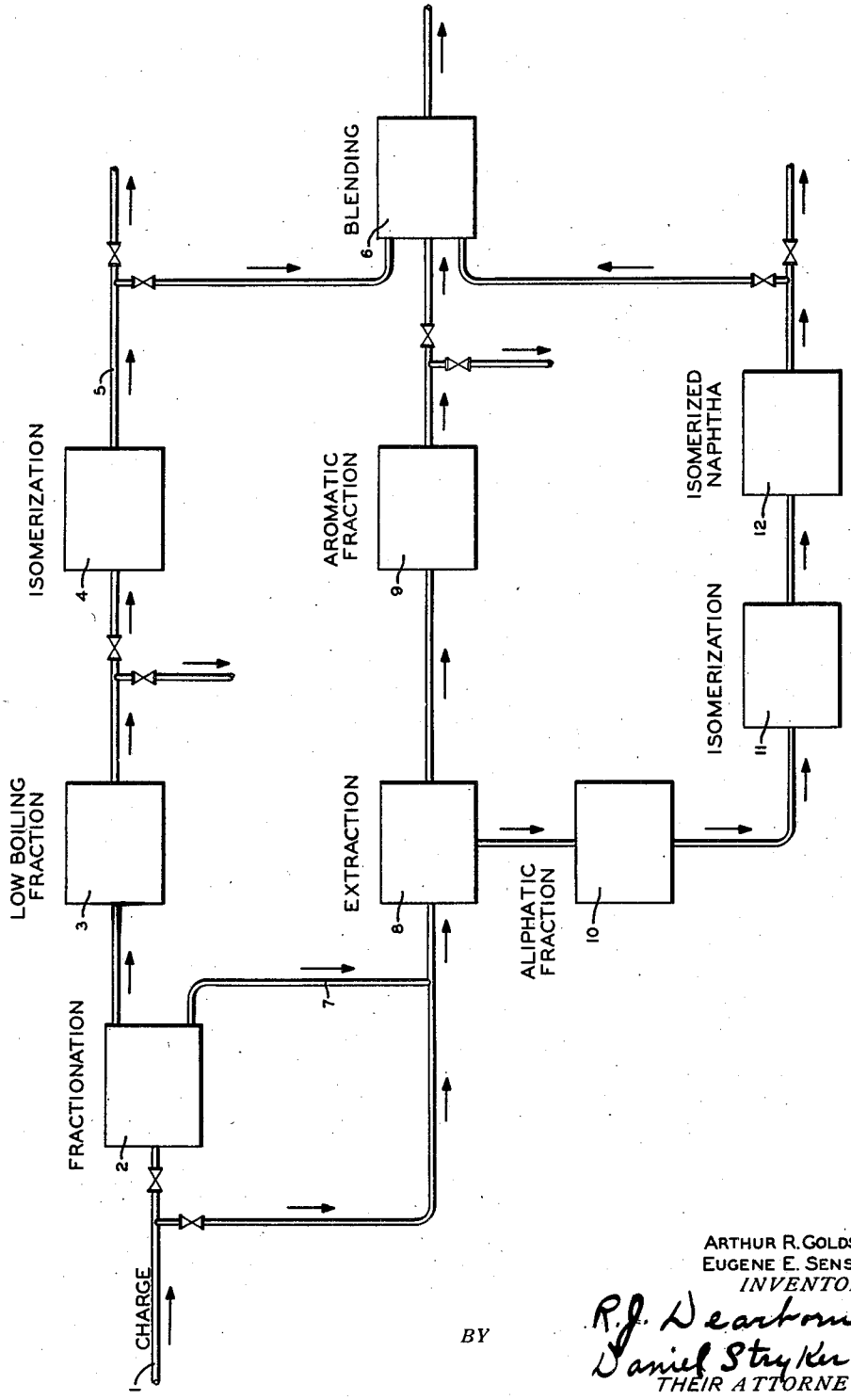
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MANUFACTURE OF ANTIKNOCK MOTOR FUELS

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ARTHUR R. GOLDSBY
EUGENE E. SENSEL
INVENTORS

BY R. J. Dearborn
Daniel Stryker
THEIR ATTORNEYS

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MANUFACTURE OF ANTIKNOCK MOTOR FUELS

Arthur R. Goldsby and Eugene E. Sensel, Beacon, N. Y., assignors, by mesne assignments, to The Texas Company, New York, N. Y., a corporation of Delaware

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This invention relates to the manufacture of antiknock motor fuels and has to do particularly with the treatment of petroleum naphthas to improve the antiknock property.

It is known that naphthas or gasolines, consisting mainly of straight chain paraffin hydrocarbons of relatively low antiknock value, may be substantially improved in antiknock value by treatment with an isomerization catalyst, whereby the straight chain paraffin hydrocarbons are converted into branch chain or isoparaffin hydrocarbons of high antiknock value.

It has been found that certain naphthas, particularly those of high boiling range, or wide boiling range naphthas containing higher boiling fractions, on isomerization with catalysts, such as metallic halides, may give relatively poor results due to low octane improvement and high catalyst loss or consumption. This has been found particularly true of those naphthas containing substantial amounts of aromatic and/or unsaturated hydrocarbons. The aromatic and unsaturated hydrocarbons generally have a high octane in their original form and as a result improve the octane of the naphtha. Moreover, such aromatic and unsaturated hydrocarbons have in general the highest reactivity with the catalyst to form complexes or sludge and are consequently removed or lost in the reaction. The net advantage, therefore, of the isomerization of such naphthas to convert normal paraffins to isoparaffins may be largely offset by the loss of the unsaturated and aromatic content.

In accordance with the present invention, naphthas, normally containing constituents which cause deterioration of the catalyst, are treated under extracting conditions with a solvent selective for the removal of the constituents which cause deterioration of the catalyst. The refined naphtha, after separation of the solvent and extract, can be treated with the isomerization catalyst whereby the antiknock property of the treated naphtha may be substantially improved, with increased effectiveness and yield per unit weight of catalyst. The aromatic and unsaturated hydrocarbons which are removed in the extract can be recovered for use in blending with the isomerized product or other motor fuel base stock.

Naphthas which may be treated are of wide variety. It is intended to treat any naphthas or gasolines, or fractions thereof, which contain a substantial proportion of low octane paraffn hydrocarbons, as well as constituents which cause objectionable deterioration of the catalyst. Naphthas specifically intended are straight run naphthas, containing aromatics and/or unsaturated compounds; cracked naphthas; mixtures of straight run and cracked naphthas; and naphthas resulting from catalytic cyclization of olefins.

The naphthas or gasolines to be treated with the isomerization catalyst may be separated into two or more fractions and one or more of the fractions treated and the products blended. Thus a naphtha may be separated into low boiling and high boiling fractions and each fraction treated separately, or only one fraction, such as the high boiling fraction, treated. The fractions may then be recombined.

For example, a straight run naphtha may desirably be separated into two fractions. One may be a low boiling fraction having an end point below the boiling point of the lowest boiling aromatic constituents in the stock in question, such as below about 200° F. The other may be a higher boiling fraction containing substantially all the aromatic content of that stock. The low boiling fraction is isomerized or may be left untreated, depending upon the octane thereof and the octane of the final product desired. The higher boiling fraction is solvent refined and the resulting raffinate thereafter isomerized. The resulting fractions may then be blended with each other or with other base stocks.

Moreover, any cut may be made from a naphtha, the cut or fraction treated to remove the unsaturated or aromatic constituents, and the treated fraction isomerized. Such a fraction, for example, may be one of boiling range of about 100° to 200° F. A low boiling fraction of this type ordinarily does not contain a large amount of aromatics, but even a small amount is harmful to the isomerization reaction. A cracked naphtha fraction, however, of such boiling range contains unsaturated or olefinic hydrocarbons which are advantageously removed.

Furthermore, a fraction of safety fuel boiling range, for example, a product with a flash above 100° F., and a boiling range of about 300° to 500° F. may be treated, if desired. The preliminary removal of aromatics and unsaturates enables the treated product to be successfully isomerized to improve the antiknock characteristics.

In case the proportion of aromatics or unsaturates in the oil is low, as in the case of some straight run paraffinic naphthas, it may be desirable to treat the naphtha with acid or aluminum chloride to remove the small amount of

aromatics or unsaturates and then isomerize the treated product, rather than to isomerize the naphtha directly, or to solvent refine and then isomerize.

The preliminary solvent refining or extraction step may be carried out by conventional processes and with any solvent suitable for this purpose. The solvent extraction of light oils is quite well known in the art, and it is intended that any of these methods may be used. Specific solvents which may be mentioned are sulfur dioxide or mixtures of sulfur dioxide with methyl alcohol, benzyl alcohol or diacetone alcohol. The sulfur dioxide extraction is ordinarily carried out in the liquid phase at temperatures of about 10° to −60° F. In carrying out the extraction process, the solvent is contacted with the oil under temperature and pressure conditions to cause an extraction of certain constituents such as unsaturates and olefins, thereby forming an extract and raffinate layer, and then separating the two layers. Any solvent retained in the two layers may be removed, for example, by distillation or washing with water. The raffinate layer will contain straight chain or paraffin hydrocarbons of low antiknock value suitable for treatment by isomerization. The extract layer after separation of the solvent will usually contain high antiknock hydrocarbons which may be used for motor fuel, for example, by reblending with the isomerized raffinate.

The preliminary treatment with reagents, such as aluminum halides or sulfuric acid, produces chiefly polymerization products of the unsaturates, or complexes or sludge with the unsaturates or aromatics, which may be separated from the treated oil as sludges. The treatment may be conducted at low temperatures within the range specified for solvent refining or at somewhat higher temperatures. Such treatment may be economical with naphtha containing relatively small amounts of unsaturates or aromatics or both. The treating agent is usually contacted with the oil in the conventional manner of acid treating.

The isomerization of straight chain paraffin hydrocabons to isoparaffins is known in the art. Catalysts, which have been proposed for that purpose, include anhydrous metallic halides, particularly the chlorides, bromides, etc., of aluminum, zirconium, iron, zinc, tin, barium, columbium, tantalum and boron, together with small amounts of hydrogen halides, such as hydrogen chloride, as promoters. We prefer to use aluminum chloride and hydrogen chloride. The reaction may be carried out in the liquid or vapor phase by contacting the oil with the catalyst, alone or supported on a suitable carrier, such as clay, pumice, brick, coke, activated alumina or carbon. It is preferable to carry out the reaction under temperature and pressure conditions such as to maintain the liquid phase. The deterioration of the catalyst may be retarded by carrying out the process in the presence of substantial amounts of low boiling isoparaffins, such as isobutane or isopentane. The temperatures are preferably in the range of about 180° F. to 270° F. although temperatures up to 360° F. or higher may be used.

The amount of the catalyst may vary from about 1 to 20% or more by weight, preferably about 5 to 15% based on the weight of the hydrocarbon charged, and the promoter may vary between about 0.1 and 5% or more, preferably about 1%. The latter figures are based on batch operations. In continuous or cyclic operations, for example wherein the oil is contacted with the catalyst in a packed tower, the proportion of catalyst to oil undergoing treatment at any given interval of time may be considerably larger than in the case of batch operations, but the ultimate yield of total hydrocarbon treated per unit of catalyst may be considerably larger in the continuous type of operation.

As an example of the operation of the invention, a straight run gasoline of 100° to 390° F. boiling range from Gulf Coast crude, and having an antiknock value of about 53, is treated with sulfur dioxide in the ratio of about two parts of solvent to one part of naphtha at a temperature of about −30° F. The extract and raffinate layers are separated and the solvent removed. About 25% of extract, having an antiknock value of about 90, and 75% raffinate, having an antiknock value of about 40, are obtained. The raffinate is treated with about 15% aluminum chloride and 0.8% hydrogen chloride. The yield of treated naphtha is about 95% and the antiknock value thereof is about 65. When the extracted hydrocarbons are readded to the treated naphtha, a blend having an octane number of about 71 may be obtained. The same naphtha, without the preliminary extraction step, could not be successfully treated with the isomerization catalyst, due to the formation of a black liquid complex.

In order to describe the invention in more detail reference will now be made to the accompanying drawing.

As indicated in this drawing a naphtha charge conducted from a source not shown through a pipe 1 is subjected to fractionation in a fractionation unit 2. The fractionation is such as to produce a fraction boiling in the range of around 100–200° F. This fraction is withdrawn and conducted to a receiver 3.

From the receiver 3 the low boiling material may be passed to an isomerization unit 4 wherein it is subjected to isomerization. The isomerized hydrocarbons are drawn off through a pipe 5 and, all or in part, conducted to a tank 6.

The higher boiling fraction formed in the fractionation unit 2 is drawn off through a pipe 7 to an extraction unit 8. In this extraction unit the naphtha hydrocarbons are treated so as to extract from them unsaturated and aromatic hydrocarbons. This extraction may be effected by treatment with acid or aluminum chloride or by treatment with a selective solvent such as sulfur dioxide.

The unsaturated and aromatic hydrocarbons so extracted from the naphtha are separated from the extracting medium and passed to a tank 9 from which they may be passed, all or in part, to the previously mentioned tank 6.

The naphtha hydrocarbons from which the unsaturated and aromatic constituents have been removed are passed to a tank 10 and from there conducted to an isomerization unit 11 wherein they are subjected to contact with an isomerization catalyst. The resulting isomerized naphtha is passed to a tank 12 from which it may be passed, all or in part, to the previously mentioned tank 6 for blending with the other fractions previously referred to.

As indicated in the drawing a modified procedure involves passing the naphtha charge directly to the extraction unit 8. In such case the step of segregating a low boiling fraction for separate treatment is omitted.

The process of the present invention, wherein the oil is treated to remove aromatics and unsaturates, prior to isomerization, produces a yield of about 80 to 95% of product showing an octane improvement of about 15 to 40 points. Similar isomerization treatments, without the preliminary solvent extraction treatment, produce yields of about 50 to 80% with very little improvement obtained. In fact, some times a loss in octane may occur, due to removal of unsaturates and aromatics. Moreover, the catalyst deterioration is usually substantially less in treating gasolines which have been subjected to the preliminary solvent extraction step.

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.

We claim:

1. A process involving catalytic isomerization, for improving the antiknock properties of naphtha of relatively low antiknock value and normally containing constituents of the class of unsaturates and aromatics which cause deterioration of the catalyst, which comprises separating the naphtha into a low boiling fraction having an end point below the boiling range of at least the major portion of the aromatics in the stock and a high boiling fraction, solvent refining the high boiling fraction to remove constituents which cause deterioration of an aluminum chloride isomerization catalyst, subjecting the treated high boiling fraction under isomerizing conditions with said isomerization catalyst and blending the isomerized high boiling fraction with the low boiling fraction.

2. A process according to claim 1 in which the original naphtha is a straight run product and the low boiling fraction is isomerized prior to blending with the high boiling fraction.

3. A process according to claim 1 in which the original naphtha is a cracked product and the low boiling fraction is treated to remove unsaturated products therefrom and then isomerized prior to blending with the high boiling fraction.

4. A process, involving catalytic isomerization, for improving the antiknock properties of naphtha of relatively low antiknock value and normally containing constituents of the class of unsaturates and aromatics which are capable of causing deterioration of the catalyst, which comprises separating the naphtha into a low boiling fraction having an end point below the boiling range of at least the major portion of the aromatics in the stock and a high boiling fraction, separating from the high boiling fraction constituents which are capable of causing deterioration of an active metallic halide isomerization catalyst, subjecting the high boiling fraction from which said constituents have been separated to contact with an active metallic halide isomerization catalyst under conditions such that there is substantial isomerization of naphtha hydrocarbons, and blending at least in part isomerized high boiling fraction with the low boiling fraction.

5. A process for improving the antiknock properties of naphtha of relatively low antiknock value and containing unsaturated constituents, aromatic hydrocarbons and non-aromatic hydrocarbons including paraffins, involving treatment with an isomerization catalyst, which comprises separating the naphtha into a low boiling fraction having an end point below the booling range of at least the major portion of the aromatics in the stock and a high boiling fraction, separating from the high boiling fraction a fraction rich in aromatic hydrocarbons and comprising constituents highly reactive toward the catalyst and capable of causing substantial catalyst deterioration, subjecting the high boiling naphtha hydrocarbons from which said aromatic-rich fraction has been removed to contact with an isomerization catalyst under conditions such that isomerization of non-aromatic constituents constitutes the principal reaction and said reaction is effected with substantial decrease in catalyst deterioration, and blending resulting isomerized hydrocarbons with at least a portion of the low boiling fraction.

6. A process for improving the antiknock properties of naphtha of relatively low antiknock value and containing unsaturated constituents, aromatic hydrocarbons and non-aromatic hydrocarbons including paraffins, involving treatment with an isomerization catalyst, which comprises fractionating the naphtha into a low boiling fraction having an end point below the boiling range of at least the major portion of the aromatics in the stock and a high boiling fraction, separating from said high boiling fraction a fraction rich in aromatic hydrocarbons and comprising constituents highly reactive toward the catalyst and capable of causing substantial catalyst deterioration, subjecting the low boiling fraction and said high boiling naphtha hydrocarbons from which the aromatic-rich fraction has been removed to contact with an isomerization catalyst under conditions such that isomerization of non-aromatic constituents constitutes the principal reaction and said isomerization is effected with substantial decrease in catalyst deterioration, and blending resulting isomerized hydrocarbons with aromatic hydrocarbons separated from said high boiling fraction.

7. A process, involving catalytic isomerization, for improving the antiknock properties of naphtha of relatively low antiknock value and normally containing constituents of the class of unsaturates and aromatics which cause deterioration of the catalyst, which comprises separating the naphtha into a low boiling fraction having an end point below the boiling range of at least the major portion of the aromatics in the stock and a high boiling fraction, chemically treating the high boiling fraction to remove constituents which cause deterioration of an aluminum chloride isomerization catalyst, subjecting the treated high boiling fraction under isomerizing conditions with said isomerization catalyst and blending resulting isomerized hydrocarbons with at least a portion of the low boiling fraction.

8. The process according to claim 4 in which the original naphtha is obtained by catalytic conversion of hydrocarbons and the low boiling fraction is treated to remove unsaturated products therefrom and then isomerized prior to blending with the high boiling fraction.

9. The process according to claim 4 in which the original naphtha is obtained by cracking hydrocarbons and the low boiling fraction is treated to remove unsaturated products therefrom and then isomerized prior to blending with the high boiling fraction.

10. The process according to claim 5 in which isomerized hydrocarbons, the low boiling fraction and aromatic hydrocarbons separated from the high boiling fraction are blended.

11. A process, involving catalytic isomerization, for improving the antiknock properties of naphtha of relatively low antiknock value and normally containing constituents of the class of unsaturates and aromatics which are capable of causing deterioration of the catalyst, which comprises separating the naphtha into a low boiling fraction having an end point below the boiling range of at least the major portion of the aromatics in the stock and a high boiling fraction, separating from the high boiling fraction constituents which are capable of causing deterioration of an active metallic halide isomerization catalyst, subjecting the low boiling fraction and said high boiling fraction from which said constituents have been separated to contact with an active metallic halide isomerization catalyst under conditions such that there is substantial isomerization of naphtha hydrocarbons and forming a blend comprising isomerized hydrocarbons from both said fractions.

ARTHUR R. GOLDSBY.
EUGENE E. SENSEL.