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**STABILIZATION OF A HIGHLY OLEFINIC GASOLINE**

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This invention relates to the treatment of hydrocarbon oils and is more particularly concerned with the treatment of a raw cracked gasoline fraction. The invention is concerned primarily with the treatment of raw cracked gasoline fractions to produce a finished gasoline of commercially acceptable storage stability and octane number.

At the present time, specifications for commercially acceptable motor gasoline require that it pass an "existent gum" test, in accordance with ASTM method D381, in which the gasoline must show less than 5 mg. of gum per 100 ml. In addition, it is highly desirable that commercial motor gasoline meet the storage stability requirements set forth in ASTM methods D910-48T or D525-49. Finally, the demands of modern high compression engines make necessary the production of motor gasoline possessing a high octane rating, usually determined as "clear research octane number" in accordance with ASTM method D908-48T. Arithmetic averages in January 1952, for motor gasoline sold in 45 U. S. cities indicate research octane ratings of 83.2 and 90.0 for "regular" and "premium" gasolines, respectively, with such gasolines containing an average of 1.35 and 1.75 cc./gal., respectively, of tetraethyl lead.

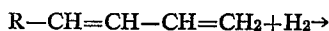
In modern petroleum refining practice, it is highly advantageous to convert part or all of the higher boiling fractions of the crude oil to materials boiling in the gasoline range. This is effected by processes which involve the "cracking" of the higher boiling hydrocarbons into hydrocarbons boiling in the gasoline range. However, in many cases, the gasoline fraction which is produced by cracking (hereinafter referred to as "raw" gasoline) requires further processing to provide a commercially acceptable product having an existent gum content, storage stability and octane number within the above specified limits. When such raw gasoline does not meet requirements for gum content or storage stability, it is usually found that the gasoline contains over 1% by volume of diolefins and often over 5% by volume of such constituents. Furthermore, it is generally known that such constituents, e. g., acyclic and cyclic diolefins, are mainly responsible for high gum content and/or poor storage stability (Sachanen; Conversion of Petroleum, 2nd edition, 1948, Rheinhold Publishing Corp., page 498), although certain nitrogen and oxygen compounds are similarly unstable.

Various processes have been proposed for treating such raw gasoline fractions to bring them within the desired specification limits, and some of these processes have been commercially used with varying effectiveness. However, cracked raw gasolines are generally of moderate to high octane number, containing 10 to 50% by volume of aromatic hydrocarbons and at least 20% by volume of olefins, and known methods for removing gum-forming constituents and improving the storage stability bring about the destruction or conversion of some of these unsaturated compounds. In treatment with sulfuric acid at 0 to 200° F., or over clay at 400 to 700° F., for example, copolymerization of aromatics, monoolefins and diolefins

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is effected, resulting in a finished gasoline of markedly lower clear research octane number, with the yield of finished gasoline approximating 80% by volume for a raw gasoline containing 5 to 10% by volume of diolefins.

Thus it is preferable to hydrogenate raw gasolines containing diolefins, so that diolefins are converted to monoolefins, i. e.:



The mono-olefin products are of approximately the same clear research octane number as the diolefins, and are of approximately the same boiling point range, so that if such hydrogenation is effected, losses of octane number and of yield due to polymerization are substantially avoided. However, when hydrogenation at relatively high pressures and relatively low temperatures is employed, the olefins present in the cracked gasoline are completely hydrogenated to paraffins, i. e.



It is well known that such paraffins have clear research octane numbers which are as much as 40 octane numbers lower than the corresponding olefins from which they were formed. Thus, such treatment of a raw cracked gasoline fraction produces a finished gasoline which is generally of appreciably lower clear research octane number than the raw gasoline, and which is in all cases of lower clear research octane number than would have been obtained if the olefins had not been hydrogenated. Where the cracking operation produces a raw gasoline which satisfies octane number requirements without the addition of tetraethyl lead, e. g., above 83 clear research octane number, such utilization of conventional hydrogenation treatment to remove gum-forming constituents results in a finished gasoline which is of considerably reduced clear octane number and which consequently requires significant quantities of anti-knock additives to achieve octane requirements. Thus, the principal problem which these cracked raw gasoline fractions of high octane number and of unsatisfactory existent gum content and storage stability present is that of lowering existent gum and increasing storage stability to commercially acceptable limits, while maintaining a high yield of finished gasoline and avoiding any substantial impairment of the clear research octane number. This is a problem which has not been solved in a satisfactory and efficient manner by prior processes for treating raw gasoline.

A principal object of the present invention is to provide a process for treating raw gasoline fractions containing at least 20% by volume of olefins and of unsatisfactory existent gum content and storage stability, which process will eliminate a substantial portion of the undesired gum-forming constituents, while maintaining the major portion of said olefins.

It is a further important object to provide a process for treating said raw gasoline fractions, which will eliminate a substantial portion of the gum-forming constituents and impart a satisfactory storage stability, while increasing or at least maintaining the clear research octane ratings of said raw gasolines.

It is another object of the invention to provide a process of the character indicated in which high yields of finished gasoline are obtained.

It is another object to provide an improved cracked raw gasoline treating process which avoids the shortcomings of treating processes heretofore proposed.

It is a feature of the invention that cracked raw gasoline is treated in the presence of a material having catalytic activity at elevated temperatures and at a predetermined

hydrogen partial pressure such that the bodies which render the gasoline unstable are converted to more stable forms, without significantly decreasing the clear research octane number of the raw cracked gasoline, even when the octane number exceeds 80. In many cases, the process of this invention increases the octane number. Thus, the application of the process to raw gasoline of clear research octane number exceeding 80 makes it possible to meet commercial octane requirements without the addition of anti-knock agents. Furthermore, in accordance with the invention, finished gasoline yields of more than 90% by volume are obtained even when the raw gasoline contains a large percentage of diolefins, e. g., 5% by volume or more.

In accordance with the invention, a cracked raw gasoline fraction of unsatisfactory storage stability, i. e., failing to meet the commercial existent gum and storage stability requirements in accordance with ASTM methods D381 and D910-48T or D525-49, and containing at least 20% by volume of olefins, is introduced, together with hydrogen, into a treating zone maintained at a temperature of 750 to 875° F., preferably at a temperature of about 775 to 850° F., in contact with particulate material of the character hereinbelow described. The total pressure in the treating zone and the introduction of hydrogen and raw gasoline are controlled in known manner to provide a hydrogen partial pressure of 50 to 325 p. s. i. (pounds per square inch), preferably 100 to 250 p. s. i. The total pressure of the system may vary over a relatively wide range, but it is generally preferred to use a total pressure not exceeding about 1000 p. s. i. g. (pounds per square inch gage).

The particulate contact material employed in the treating zone is a siliceous catalyst of the type which has been employed for cracking hydrocarbons.

Typical suitable siliceous catalysts are acid-treated clays, heat-treated montmorillonite, and natural and synthetic silicates containing some hydrogen atoms which are relatively mobile.

It is today generally accepted that a certain "acidic" nature is essential for the effectiveness of catalysts for cracking of high molecular hydrocarbons to lower molecular fragments, for isomerization of paraffins and olefins of relatively low octane number to corresponding compounds of higher octane number and for other reactions desired in the refining of petroleum hydrocarbons. This same acidic nature is apparently also essential to the siliceous catalysts used in the process of this invention.

A class of catalysts with the proper acidic nature which can be used in accordance with the present invention is that of solid particles containing silica, and such amounts of difficultly reducible metal oxides that the molecular ratio of silica to the other oxides exceeds appreciably the value of 1. As all these combinations of silica with other oxides, such as for instance, alumina, zirconia, titania, chromium oxide, magnesium oxide and others, contain small amounts of water, it is quite likely that the solid phase comprises a kind of complex acid in which some hydrogen atoms are in a rather mobile state especially at the surface of the solid particles. This view and experimental support for it have been presented by R. C. Hansford in a paper entitled, "A Mechanism of Catalytic Cracking," *Ind. and Eng. Chem.*, 39, 849 (1947). The specific catalyst mentioned in this paper was composed of approximately 12% alumina and 88% by weight silica (on dry basis). In another paper entitled, "Montmorillonite Cracking Catalyst," *Ind. and Eng. Chem.*, 41, 1485 (1949) Alexander Grenall has demonstrated the presence of hydrogen ion in Filtrol clay catalysts.

Silica gels which have been impregnated, even with as little as 1% alumina, have been shown to be efficient catalysts for cracking by Pitzer in "Advancing Fronts in Chemistry," vol. 1, page 33, 1945, Rheinhold Publishing Corp. Another catalyst has been described by O'Kelly et al. in *Ind. and Eng. Chem.*, 39, 154 (1947), as being

prepared by the co-precipitation of the hydrous oxides of silicon and aluminum in a weight ratio of 9:1 of silica to alumina. A tri-component catalyst consisting of silica alumina and zirconia has been described by Thomas et al in *J. Am. Chem. Soc.*, 66, 1694 (1944).

Suitable catalysts can be prepared by using natural clays as a starting material. Many clays contain silica and alumina in a ratio which corresponds to the postulate that the number of moles of silica exceed appreciably the number of moles of alumina or other oxides. However, some of these clays contain, instead of mobile hydrogen atoms combined with excess silica, other atoms, such as alkali and alkaline earth atoms. Such clays can be "activated" by removing part or all of the alkali and alkaline earth atoms and replacing them with hydrogen atoms by treatment with acid. Other clays, which already in their original composition have a potential acidic nature by having the proper ratio of silica to alumina or other oxides, can be activated by heat treatment (cf. Alexander Grenall I. c.).

All of the aforementioned natural and synthetic materials are effective siliceous catalysts for the purposes of this invention. To recapitulate, the siliceous catalyst is a combination of a major weight proportion of silica and a minor weight proportion of one or more difficultly reducible metal oxides, preferably aluminum oxide; this combination may be effected synthetically or it may be derived from natural materials like clays through activation by heat and/or acid treatment. It is observed that the siliceous catalysts of this invention are materials which can generally be classed as natural or synthetic silicates, aluminum silicates being prominent in this classification.

While substantially pure hydrogen is advantageously used in the process, a gas mixture containing hydrogen and inert gases, such as nitrogen or methane, may be employed with efficacy. In the latter case it is preferable to use a gas mixture having at least about 30% by volume of hydrogen in order to avoid the necessity of passing excessively large amounts of gas through the reaction zone to provide the desired hydrogen partial pressure of 50 to 325 p. s. i. and in order to avoid the necessity of raising the total pressure of the system to a high value.

The term "gasoline fraction" as herein used has its conventional meaning, viz., a hydrocarbon fraction boiling within the temperature range of 90 to 400° F., although it will be apparent that the treating process of this invention is applicable to hydrocarbon fractions in which material boiling within the gasoline range comprises the predominant portion of the fraction.

Cracked raw gasoline fractions from various sources are advantageously treated in accordance with the process of the invention but the improved process is of particular value, as already mentioned, in reducing the content of gum-forming constituents and increasing the storage stability of cracked raw gasoline fractions of relatively high octane number, e. g., clear research octane numbers of at least about 80, and more particularly between 80 and 90, containing substantial quantities of monoolefins, such as gasoline fractions produced by the process described and claimed in the copending applications of Percival C. Keith, Serial No. 139,758, filed January 20, 1950, now U. S. Patent 2,606,862. As previously mentioned, the present process is effective to remove even large proportions of gum-forming constituents without any appreciable adverse effect upon the high octane number of the raw gasoline. In some cases the octane number is essentially unaffected, i. e., it is not changed by more than one or two units, whereas in other cases it is even increased by a substantial extent.

In the process described in the above-mentioned Keith application, a crude hydrocarbon oil, particularly a heavy residual product, is cracked at a temperature of 800 to 1050° F. and at a total pressure of 200 to 800 p. s. i. g. in the presence of a particulate contact material and the regeneration product gases produced by treating spent

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contact material contaminated with carbonaceous material at a temperature of about 1600 to 2500° F. with steam and oxygen of at least 90% by volume purity. The hydrocarbon effluent from that process is fractionated to yield a cracked raw gasoline which may suitably be treated by the process of this invention.

The invention is, however, not limited to cracked raw gasoline fractions produced in any particular manner but is applicable to any cracked raw gasoline having at least 20% by volume of olefins, and thus a clear research octane number greater than that of a virgin naphtha, e. g., above about 40. The present process is of particular effectiveness, however, on those cracked raw gasoline fractions having an exceptionally high olefin content, e. g., of the order of 30% by volume or higher, and high clear research octane numbers of the order of 80 to 90.

A typical raw gasoline produced by the process of the above-mentioned Keith application has a relatively high octane number, e. g., a clear research octane number of about 90, and contains a high proportion of olefins. Such a raw gasoline generally has, however, a substantial amount of diolefins which tend to render the gasoline unstable as by depositing gums on standing. Cracked raw gasoline fractions to which the present process is of particular application, such as gasoline produced in accordance with the above-mentioned Keith procedure, will generally have the following approximate composition (percent by volume):

0-20% paraffins and naphthenes  
25-40% aromatics  
30-60% olefins  
2-10% diolefins

Without tying the invention to any particular theory of operation, the process appears to involve the following types of reactions which take place more or less simultaneously. Diolefins are substantially converted to mono-olefins. At the same time, aromatic hydrocarbons are not affected and only mild hydrogenation of mono-olefins takes place so that the excellent anti-knock properties of the raw gasoline are not impaired. In addition, dehydrogenation of naphthenes is facilitated by the conditions employed, resulting in the formation of additional quantities of aromatic compounds of excellent anti-knock characteristics. Cracking reactions also occur and these reactions maintain the octane number of the gasoline at a high level without excessive degradation of the gasoline to less valuable gaseous products. The catalysts employed, containing relatively mobile hydrogen atoms, likewise promote isomerization reactions which also assure a relatively high octane number in the finished gasoline.

The raw gasoline treating process is suitably carried out in conventional gasoline treating apparatus wherein, in accordance with the invention, the raw gasoline is introduced into a reaction zone in contact with the catalyst. The apparatus shown in the above-mentioned Keith application may be employed, but preferably the process is carried out in a fluidized bed such as is used commercially in the catalytic cracking of hydrocarbon oils, the hydrogen or hydrogen-containing gas being advantageously employed as the fluidizing medium. The contact material is continuously or intermittently withdrawn from the treating zone and regenerated in any convenient manner, as by treating it at elevated temperature with oxygen or air and, if desired, other gaseous materials such as steam.

The particular apparatus used for the process and the particular method of regenerating the catalyst form no part of the present invention and any convenient apparatus and method of catalyst regeneration may be employed. In regenerating the catalyst care must be taken, however, in accordance with commercial regeneration techniques, to avoid the use of temperatures which destroy or adversely affect the catalyst. In the regeneration of the catalyst of the present process, temperatures in excess of 1200° F. are generally to be avoided.

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In order to facilitate the maintenance of the desired temperature in the reaction zone, the raw cracked gasoline to be treated is advantageously preheated to a temperature of 400° to 800° F., preferably about 500° to 700° F., before being fed into the reaction zone. At such temperatures the gasoline is at least partially vaporized. The hydrogen or hydrogen-containing gas may also be preheated to about the same temperature as the gasoline.

Treatment of the cracked raw gasoline in the reaction zone under the specified conditions is carried out to an extent sufficient to reduce the content of gum-forming constituents in the raw gasoline and to improve its stability to the desired degree. Advantageously, the desired reaction is insured by employing a raw gasoline feed rate in the range of 0.5 to 5, preferably 0.5 to 1.5, volumes of liquid per hour per volume of catalyst, while employing a hydrogen flow rate of 500 to 2500 standard cubic feet (calculated as pure hydrogen) per barrel of raw gasoline fed.

The effluent from the treating zone will contain vapors of the hydrocarbons within the gasoline range admixed with a small amount of higher boiling hydrocarbons and more volatile compounds. The effluent is fractionally distilled to separate the desired gasoline fraction from the other constituents. The finished gasoline fraction thus produced is of high stability and high octane number and meets the specifications for commercial motor gasoline notwithstanding the presence of a substantial quantity of diolefins originally in the cracked raw gasoline.

For a further understanding of the invention, reference is made to the following specific example which is intended as illustrative of the process without, however, being intended as limitative thereof.

The cracked raw gasoline which is treated was obtained from a heavy hydrocarbon oil which was subjected to cracking in accordance with the aforesaid Keith process at a temperature of about 900° F. in the presence of the regeneration gases resulting from the decomposition of the carbonaceous residue on the particulate carrier with steam and oxygen of 95% by volume purity at a temperature of about 1700° F. The effluent from the cracking operation was condensed and fractionally distilled to separate the raw gasoline fraction which has a 400° F. end point and has the following characteristics:

45	Octane number, CFRR clear (ASTM-D908-48T)---	87
	Bromine number, cg./gm. (ASTM-D875-46)-----	74
	Olefin content, vol. percent.-----	51
	Copper dish gum, mg./100 ml. (ASTM-D910-48T)---	400
	Stability, minutes (ASTM-D525-49)-----	115

In accordance with the present invention, this raw gasoline is heated, as by passing through the coils of a tube still, to a temperature of about 700° F. The gasoline is then discharged into a reaction zone containing fluidized particles of a commercial synthetic silica-alumina catalyst prepared by co-precipitation of the hydrous oxides in the ratio of about 9:1 by weight of silica to alumina. The gaseous treating atmosphere is provided and fluidization of the catalyst is effected simultaneously by introducing a stream of hydrogen into the bottom of the reaction zone. A portion of the fluidized catalyst is continuously removed from the reaction zone and passed to a regenerator, and a corresponding amount of regenerated catalyst, with or without pretreatment with hydrogen, is continuously returned to the reaction zone. In the reaction zone, the temperature is maintained at 825° F. and the total pressure is maintained at 225 pounds per square inch gage. The heated raw gasoline is introduced at a rate to provide a space velocity of 1.0 volume of liquid gasoline per hour per volume of catalyst in the reaction zone and the hydrogen is introduced at a rate to provide a hydrogen partial pressure of 215 pounds per square inch.

The gasiform effluent is continuously removed from the top of the reaction zone, condensed and then subjected to fractional distillation to separate from the gasoline more volatile hydrocarbons and gases, and particles which may

have been carried over with the effluent and a small proportion of higher boiling hydrocarbons formed in the reaction zone. By the foregoing treatment the above-identified raw gasoline fraction is converted into a finished gasoline fraction having the following characteristics:

Octane number, CFRR clear (ASTM-D908-48T)---- 87  
 Bromine number, cg./gm. (ASTM-D875-46)----- 70  
 Olefin content, vol. percent----- 48  
 Copper dish gum, mg./100 ml. (ASTM-D910-48T)----- less than 10  
 Stability, minutes (ASTM-D525-49)---- more than 1200  
 Existent gum, mg./100 ml. (ASTM-D381-49)----- less than 5

The yield of gasoline is 90% by volume of charge, and the total yield of liquid products is 96% by volume of charge.

It will be seen from the foregoing example that, in accordance with the process therein described, a cracked gasoline having a high content of gum-forming constituents, as indicated by the 400 mgs. obtained in the copper dish gum test and the 115 minutes breakdown in the stability test, is converted to a finished gasoline containing a substantial quantity of olefins, and having a stability and gum-forming characteristics meeting commercial requirements. In the foregoing example, these significant improvements in the gasoline have been effected without change in octane number. The yield of this high quality finished gasoline is excellent.

The olefin content of the raw gasoline and the finished gasoline is determined conventionally by the ASTM bromine number procedure (ASTM-D875-46). Other analyses are obtained by use of conventional ASTM procedures, as indicated.

In view of the various modifications of the invention which will occur to those skilled in the art upon consideration of the foregoing disclosure without departing from the spirit or scope thereof, only such limitations should be imposed as are indicated by the appended claims.

What is claimed is:

1. A method of eliminating gum-forming constituents from a highly olefinic hydrocarbon fraction, which comprises bringing hydrogen and a hydrocarbon fraction containing gum-forming constituents and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 20% by volume of said hydrocarbon fraction and imparting to said hydrocarbon fraction a high octane number into contact with a siliceous catalyst consisting essentially of a major weight proportion of silica and a minor weight proportion of at least one difficultly reducible metal oxide in a reaction zone maintained at a temperature in the range of 750 to 875° F., the contact of said hydrogen and said hydrocarbon fraction resulting in a net consumption of hydrogen, passing said hydrocarbon fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said siliceous catalyst, maintaining the partial pressure of hydrogen in said reaction zone in the range of 50 to 325 p. s. i., and recovering from the resulting reaction effluent a highly olefinic hydrocarbon fraction with a substantially decreased content of gum-forming constituents and containing a major portion of said olefins and having a high octane number.

2. A method of eliminating gum-forming constituents from a highly olefinic hydrocarbon fraction, which comprises bringing hydrogen and a hydrocarbon fraction containing gum-forming constituents and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 30% by volume of said hydrocarbon fraction and imparting to said hydrocarbon fraction a high octane number into contact with a siliceous catalyst consisting essentially of a major weight proportion of silica and a minor weight proportion of at least one difficultly reducible metal oxide in a reaction zone maintained at a temperature in the range

of 775 to 850° F., the contact of said hydrogen and said hydrocarbon fraction resulting in a net consumption of hydrogen, passing said hydrocarbon fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said siliceous catalyst, maintaining the partial pressure of hydrogen in said reaction zone in the range of 50 to 325 p. s. i., and recovering from the resulting reaction effluent a highly olefinic hydrocarbon fraction with a substantially decreased content of gum-forming constituents and containing a major portion of said olefins and having a high octane number.

3. A method of eliminating gum-forming constituents from a highly olefinic gasoline fraction, which comprises bringing hydrogen and a gasoline fraction containing more than 2% by volume of diolefins and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 30% by volume of said gasoline fraction which has a clear research octane number of at least about 80 into contact with a siliceous catalyst consisting essentially of a major weight proportion of silica and a minor weight proportion of at least one difficultly reducible metal oxide in a reaction zone maintained at a temperature in the range of 775 to 850° F., the contact of said hydrogen and said gasoline fraction resulting in a net consumption of hydrogen, passing said gasoline fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said siliceous catalyst, maintaining the partial pressure of hydrogen in said reaction zone in the range of 50 to 325 p. s. i., and recovering from the resulting reaction effluent a highly olefinic gasoline fraction with a substantially decreased content of said diolefins and containing a major portion of said olefins and having a clear research octane number of at least about 80.

4. A method according to claim 3 wherein the siliceous catalyst contains silica and alumina in the approximate weight ratio of 9:1 and the hydrogen partial pressure is in the range of 100 to 250 p. s. i.

5. A method of eliminating gum-forming constituents from a highly olefinic gasoline fraction, which comprises bringing hydrogen and a gasoline fraction containing gum-forming constituents and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 20% by volume of said gasoline fraction and imparting to said gasoline fraction a high octane number into contact with a siliceous catalyst consisting essentially of a major weight proportion of silica and a minor weight proportion of at least one difficultly reducible metal oxide in a reaction zone maintained at a temperature in the range of 750 to 875° F., the contact of said hydrogen and said gasoline fraction resulting in a net consumption of hydrogen, passing said gasoline fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said siliceous catalyst, maintaining the partial pressure of hydrogen in said reaction zone in the range of 100 to 250 p. s. i., and recovering from the resulting reaction effluent a highly olefinic gasoline fraction with a substantially decreased content of gum-forming constituents and containing a major portion of said olefins and having a high octane number.

6. A method of eliminating gum-forming constituents from a highly olefinic gasoline fraction, which comprises bringing hydrogen and a gasoline fraction containing gum-forming constituents and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 20% by volume of said gasoline fraction which has a clear research octane number of at least about 80 into contact with a siliceous catalyst consisting essentially of a major weight proportion of silica and a minor weight proportion of at least one difficultly reducible metal oxide in a reaction zone maintained at a temperature in the range of 775 to 850° F.,

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the contact of said hydrogen and said gasoline fraction resulting in a net consumption of hydrogen, passing said gasoline fraction through the reaction zone at a space velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said siliceous catalyst, maintaining the partial pressure of hydrogen in said reaction zone in the range of 50 to 325 p. s. i., and recovering from the resulting reaction effluent a highly olefinic gasoline fraction with a substantially decreased content of gum-forming constituents and containing a major portion of said olefins and having a clear research octane number of at least about 80.

7. A method according to claim 6 wherein the gasoline fraction passes through the reaction zone at a space velocity of 0.5 to 1.5 liquid volumes per hour per volume of said siliceous catalyst.

8. A method of eliminating gum-forming constituents from a highly olefinic raw gasoline, which comprises bringing hydrogen and a raw gasoline containing a troublesome quantity of diolefins and a volume of olefins greater than the volume of paraffins and naphthenes therein, said volume of olefins being more than 20% by volume of said raw gasoline, which has a clear research octane number of at least about 80, into contact with a siliceous catalyst consisting essentially of a major weight proportion of silica and a minor weight proportion of at least one difficultly reducible metal oxide in a reaction zone maintained at a temperature in the range of 750 to 875° F., the contact of said hydrogen and said raw gasoline resulting in a net consumption of hydrogen, passing said raw gasoline through the reaction zone at a space

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velocity in the range of about 0.5 to 5 liquid volumes per hour per volume of said siliceous catalyst, maintaining the partial pressure of hydrogen in said reaction zone in the range of 100 to 250 p. s. i., and recovering from the resulting reaction effluent a highly olefinic finished gasoline substantially free of said diolefins and containing at least 20% by volume of said olefins and having a clear research octane number over 80.

9. A method according to claim 8 wherein the raw gasoline passes through the reaction zone at a space velocity of 0.5 to 1.5 liquid volumes per hour per volume of said siliceous catalyst.

10. A method according to claim 8 wherein the siliceous catalyst is an aluminum silicate.

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