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TREATMENT OF HYDROCARBON OILS

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This invention concerns a process for manufacturing stable motor fuels of high antiknock value from olefin-containing hydrocarbon distillates. More particularly, the process relates to a method of reforming highly unsaturated hydrocarbon mixtures of substantially motor fuel boiling range in order to improve the properties thereof in respect to susceptibility to added anti-detonating agents, as well as improved storage stability and decreased sulfur content.

Although the process may apply to the production of motor fuels for use in any type of internal combustion engine, it finds special application in the manufacture of fuels for use in airplane motors. This is true because of the highly stable character of the finished product, as well as its great susceptibility to increases in antiknock value by the addition of tetraethyl lead.

Numerous processes have been developed for the production of increased yields of motor fuel from crude petroleum and other hydrocarbon sources. Among these is the non-catalytic thermal cracking process whereby heavy oils are converted to substantial yields of gasoline having relatively high antiknock value. Straight-run gasoline and naphthas which may have poor antiknock properties are non-catalytically reformed to produce gasoline of improved octane number. This process also yields substantial quantities of gases containing polymerizable olefins, and various polymerization processes may be used in conjunction therewith to augment the yields of valuable motor fuel produced.

Another process of more recent development is the catalytic cracking process wherein hydrocarbon fractions containing substantially no gasoline are converted to high yields of premium grade motor fuel.

The octane numbers obtainable by commercial non-catalytic cracking and reforming processes are relatively limited, since improved antiknock properties beyond a certain point can be gained only at the expense of yield of gasoline, so that eventually a point is reached wherein it is no longer economical to increase the octane rating in this manner. Catalytic cracking and polymerization processes may be used to produce motor fuel of higher octane rating than is economically feasible according to the non-catalytic methods of operation.

However, the products of cracking processes have a common characteristic in that all of them contain considerable percentages of olefinic hydrocarbons. Cracked and reformed gasolines have not been considered suitable for use in the aviation industry, because of the olefinic hydro-

carbons present. Moreover, cracked gasolines because of their olefinic hydrocarbons are usually less susceptible to improvements in octane rating by the addition of substances such as tetraethyl lead, than the saturated straight-run gasolines of similar boiling range and antiknock value.

Various methods have been practiced for increasing the stability of cracked gasolines, including treatment with sulfuric acid, metal salts, clays, and/or inhibitors, in order to prevent gum formation and the development of undesirable color during storage. However, chemical treatment, such as with sulfuric acid, metal salts, and the like, results in removal of part or all of the olefinic constituents of the gasoline with consequent loss in antiknock properties of the finished gasoline. Inhibitors prevent the formation of gum, but have no effect on the olefin content of the gasoline.

It is with improvements in methods of increasing the saturation of cracked gasolines containing unsaturated hydrocarbons, by catalytically reforming them in order to increase storage stability, decrease sulfur content, and improve susceptibility to the addition of tetraethyl lead, that the present invention is concerned.

In one specific embodiment the present invention comprises contacting catalytically or non-catalytically cracked hydrocarbon distillates of substantially motor fuel boiling range with a composite of precipitated silica, having added thereto a minor portion of precipitated alumina, zirconia, or alumina-zirconia, said mass being substantially free of alkali-metal ions, at a temperature within the range of approximately 650–900° F., and a pressure of approximately atmospheric to 1000 pounds per square inch, and recovering the reaction products.

The catalysts which are useful in the present process may include cracking catalysts of various types but preferably synthetic precipitated composites consisting essentially of a major portion of precipitated silica hydrogel having added thereto relatively minor portions of precipitated refractory oxide hydrogels to form masses consisting of silica-alumina, silica-zirconia, silica-alumina-zirconia, etc. said composites being substantially free of alkali metal compounds.

In the following specification the term "silica-alumina, silica-zirconia, and silica-alumina-zirconia" masses are used in a broad sense. Inasmuch as the chemical knowledge of the solid state has not been developed perfectly, it is not possible to give the structure of all solid substances. All that can be said definitely concerning these masses is that they contain silicon, oxygen, alu-

minum, and/or zirconium in combination. Generally speaking, however, all these components indicate more or less low catalytic activity individually but in the aggregate display high activity. This activity is not an additive function, it being relatively constant for a wide range of proportions of the components, whether in molecular or fractions of molecular proportions. No one component can be determined as the one for which the remaining components may be considered as the promoters according to conventional terminology, nor can any components be determined as the support and the others the catalyst proper.

According to the description of the preparation of the preferred catalysts given below, precipitated hydrated alumina and/or hydrated zirconia are composited with hydrated silica gel, otherwise known as silica hydrogel, and then the composite is washed, dried, and calcined, producing a catalytic mass. However, the different catalysts which may be so produced therefrom do not necessarily give equivalent results.

A large number of catalysts developed to assist in thermal cracking of hydrocarbon oils tend to accelerate the formation of gas rather than gasoline. Among these are the reduced metal catalysts, such as nickel or iron. A further characteristic of this type of catalyst is that poisoning by sulfur occurs and the catalyst surfaces are rendered inert by coatings of carbonaceous material.

The preferred catalysts of this invention are characterized by selectivity and by accelerating gasoline-forming reactions, rather than gas and carbon-forming reactions, by their refractory character which enables them to retain their catalytic activity through many repeated periods of use and reactivation under severe conditions of temperature by not being poisoned by sulfur, and by the ease and simplicity of manufacture and their exact reproducibility.

The finished catalytic masses contain alumina and/or zirconia in amounts varying over a considerable range, for example, from 1-30 weight per cent and are preferably of the order of approximately 5-30 weight per cent of the compound calculated as Al_2O_3 or ZrO_2 .

The present catalytic masses may be prepared according to a number of alternative methods which will be discussed in a general way in the following description. Briefly, the method involves the precipitation of hydrogels of silica and the added compound, either simultaneously by coprecipitation methods, or by separate precipitation of the hydrogels, followed by mixing in such a manner as to produce a more or less uniform mixture, or by the successive precipitation of silica hydrogel and the added alumina and/or zirconia hydrogel constituent.

A convenient method of preparation is to precipitate a silica hydrogel by the addition of an acid (or an electrolyte) to a solution of water-soluble silicate. The precipitation of the silica gels should be carried out under controlled conditions in order to produce material which, when composited with alumina and/or zirconia as hereinafter described, results in a catalytic mass of a high degree of activity. In general, when precipitating silica gel from solutions of sodium silicate, it is desirable to add sufficient acid to cause complete gel formation. If the excess of acid used exceeds approximately 20%, the precipitated hydrogel becomes extremely difficult to filter, and its more desirable properties partly lost.

After precipitation the silica gel is preferably washed free of soluble salts. This may be done by washing the hydrogel with dilute solutions of a mineral acid, such as hydrochloric acid, or with water containing small amounts of ammonium chloride or aluminum chloride. An alternative method of conducting the washing will be described later.

According to a preferred method of preparation aluminum hydroxide and/or zirconium hydroxide gels are deposited on the silica hydrogel by addition of a suitable salt such as aluminum and/or zirconium chloride to the silica hydrogel suspension, followed by the addition of ammonium hydroxide to effect the precipitation of the hydrogel. All precipitation steps are carried out with rapid stirring and the addition at a regular rate of precipitants in order to produce a uniform mass. The hydrogel is then separated and may be dried at a temperature of approximately 300° F., and ground to a suitable size.

According to another method of preparation aluminum or zirconium salts may be added to the precipitated silica hydrogel or the freshly precipitated hydroxides may be added to the hydrogel and the mixture boiled together to produce a mixture of hydrated silica and hydrated alumina and/or zirconia. This may then be washed with water or water-containing added materials, such as hydrochloric acid, ammonium chloride, aluminum chloride, etc. The gel is then filtered and dried at approximately 300° F.

According to another method of preparation suitable salts of aluminum and/or zirconium may be taken into solution and added to a solution of a soluble silicate, such as sodium silicate, whereby hydrogels of silica and alumina and/or zirconia are coprecipitated. If insufficient metal salt is added to the mixture to effect complete precipitation of the silica gel, this may be carried out by simultaneous or separate addition of a suitable mineral acid, such as hydrochloric acid. The gel is then separated, washed as previously described, and dried.

After formation of the hydrogel composites the washed and dried material may be comminuted to pass approximately a 30 mesh screen, and formed into pellets, spheres or briquettes by compression methods. The aggregates thus formed are usually heated for a period of time at approximately the highest temperature to be attained during use of the catalytic mass, suitable temperatures being of the order of 1000-1500° F. over a period of one-half to ten hours.

An alternative method of washing the composites prepared according to any of the above described methods is to wash said composites superficially while in the gelatinous form, followed by drying at a temperature of approximately 300° F., and then conducting a final series of washings on the granulated mass thus formed. After washing, the catalyst is formed into shapes as previously described.

A further method of preparing catalyst particles comprises extruding the hydrogel into suitable shapes and sizes while the composite is in the gelatinous form prior to drying. In this case the extruded particles are dried and finally calcined prior to use.

The removal of the alkali-metal ions, from the catalyst composites during preparation is of particular importance, since the presence of these ions apparently causes certain undesirable side reactions to occur and also causes a substantial decrease in catalytic selectivity and activity.

This may possibly be caused by reactions resulting in a decrease, at elevated temperatures, in the active surface and porosity of the catalysts to an extent where the predominant reaction is no longer catalytic in character. It may also be possible that other reactions of an unknown character such as the catalyzing of undesirable reactions by alkali-metal components may account for the observed detrimental effects. Whatever the explanation, we have observed that the removal of alkali-metal compounds is of primary importance and our preferred catalysts are all of this nature.

The catalytic masses described may be used in any suitable type of reactor, such as, for example, bundles of tubes disposed in a heated zone or in reaction chambers, or may be used in the form of powders suspended in a stream of liquid or vaporized hydrocarbons.

The temperature at which the reforming operation is carried out is usually maintained within the limits of approximately 650-900° F., and preferably of the order of 700-800° F. The pressure may vary from atmospheric or slightly superatmospheric to approximately 500 pounds per square inch or higher, and may even reach 1000 pounds per square inch in some instances but is preferably of the order of 100-200 pounds per square inch. The time of contact is dependent largely on the operating conditions used. Liquid space velocities of approximately 0.5 to 5, and usually of the order of 0.5 to 2, are normally used. The liquid space velocity is defined as the volume of oil charged per volume of catalyst present per hour.

The reaction, as is the case with many operations involving the use of catalysts, undergoes considerable change in rate and character depending on the length of time of processing. Thus, for a given set of operating conditions, the degree of conversion obtained while the catalyst is fresh or freshly regenerated is relatively high, and as the processing proceeds the catalytic surfaces become less active, and the degree of conversion is considerably diminished, possibly due to deposition of carbonaceous deposits thereon. It becomes necessary to reactivate the catalyst mass at intervals. In order to provide a continuous operation it is usually the practice to provide two or more sets of catalytic reactors, whereby one set may be used for the catalytic conversion, while others are undergoing reactivation.

The plant is usually operated in a cycle wherein processing is carried out for a fixed interval and reactivation is carried out for another interval of time, which may be the same or different from that used in the process step. The catalyst is usually reactivated by passing an oxygen-containing gas over it at a temperature in excess of 900° F., whereby the carbonaceous deposits thereon are removed by combustion.

When an olefin-containing distillate, such as a non-catalytically cracked or reformed gasoline, is treated according to the present invention a marked reduction in the olefin content occurs. The extent of olefin reduction will vary with the length of time over which the catalyst mass is used, due to decreases in the activity of the catalytic surfaces. The olefin hydrocarbons are not removed in the usual sense of the term, as is evidenced by the fact that volume losses of gasoline as gas and carbon are relatively small. Instead the olefin hydrocarbons appear to be converted into other types of hydrocarbons.

The exact nature of the reactions involved is

not known with absolute certainty. It seems, however, that these reactions involve the consecutive or simultaneous steps of cyclization of a part of the olefins, dehydrogenation of the cyclic compounds to form aromatics, and hydrogenation of the remaining olefins with the hydrogen thus produced to yield paraffin hydrocarbons.

It is possible that the straight-chain olefins of six and more carbon atoms are cyclized to form naphthenic or hydroaromatic compounds and that these are, in turn, dehydrogenated to form aromatic hydrocarbons and hydrogen. Any hydroaromatics which may be present in the original mixture may also be dehydrogenated. The hydrogen liberated is momentarily in the nascent or highly reactive state whereby it is capable of combining with unsaturated hydrocarbons that may also be present. Thus, for example, highly branched-chain olefins present in the original distillate should react with the highly active hydrogen and thereby be saturated. The net result of the reaction is to produce a distillate comprising essentially a mixture of paraffinic and aromatic hydrocarbons with possibly a relatively small amount of unreacted olefins present.

There may also occur some isomerization whereby the structure of the aliphatic hydrocarbons may undergo rearrangement. The data presented in the following examples show that the type of reactions described in the foregoing paragraph are apparently those occurring during the catalytic reforming of olefin-containing distillates according to this invention. The amount of olefins remaining in the distillate following the reforming step is largely dependent on the activity of the catalyst and the length of processing period chosen. As will be seen from the following examples the activity of the catalyst decreases in time and the degree of conversion drops off. This, however, can be regulated by suitable choice of operating conditions and by recycling of a part of the reformed gasoline either to the same step or to an additional step which may be operated at the same or substantially different conditions. Moreover, a major part of the reforming may be accomplished in one step and the remaining relatively small portion of olefin hydrocarbons which have not been converted may be saturated in a hydrogenation step, or may be removed by various well-known methods, such as solvent extraction or acid treatment. As a rule such additional treatment of the gasoline is unnecessary and the degree of saturation can be controlled economically.

The gasolines treated according to the present process are improved in regard to storage stability and color stability, have low copper dish gum contents, and in addition the sulfur content of the treated gasoline is lower than that of the original charge. The storage stability and gum content of the treated gasoline are related in part to the olefin content thereof, although a relatively stable gasoline can be produced which contains considerable portions of olefins. The amount of desulfurization obtained does not appear to be strictly related to the degree of saturation of the treated gasoline. Thus, the catalyst may be used to desulfurize over a longer period of time than it can be used to produce a substantially saturated gasoline.

The term "stable gasoline" or "stable motor fuels" is intended to mean gasolines which are stable in regard to color and which do not readily undergo oxidation reactions resulting in

the formation of gums and peroxides. Stable gasolines thus have low copper dish gum contents and relatively longer induction periods as measured by the oxygen bomb test than unstable gasolines.

The following examples are given to illustrate the practicability of the invention, but should not be construed as limiting it to the exact materials and conditions indicated therein.

Example I

The stock treated was a catalytically cracked gasoline obtained by cracking a Mid-Continent gas oil with the catalyst described hereinafter at a temperature of 950° F., and substantially at atmospheric pressure. It contained approximately 74% olefins, 16% aromatics, 4% naphthenes, and 6% paraffins.

Catalyst pellets were placed in a reactor consisting of a series of manifolded catalyst tubes in a heated zone. The catalytically cracked gasoline was contacted with the catalyst at an operating temperature of 750° F., and a pressure of 100 pounds per square inch. A liquid space velocity of one was maintained throughout. The liquid recovered amounted to 91% of the gasoline charged. After 30 minutes of operation the gasoline contained no olefins, 46% aromatics, and 54% paraffin hydrocarbons. After one hour of operation the product contained 10% olefins, 42% aromatics, no naphthenes, and 48% paraffin hydrocarbons. By additional treatment the olefinic constituents were converted substantially completely into aromatics and paraffins, so that the resultant gasoline contained these types of hydrocarbons only. The bromine number of the original gasoline was 105. After the one-half hour cycle the bromine number of the gasoline was one, indicating the products to be substantially completely free of olefin hydrocarbons. After one hour of operation the bromine number was 15. The octane number of the original gasoline was 79.5, which increased to 87.5 with 6 cc. of tetraethyl lead per gallon. The octane number of the treated gasoline was 79 which increased to 96 with 6 cc. of tetraethyl lead per gallon.

The catalyst used was produced as follows: A solution of commercial sodium silicate analyzing approximately 9% by weight of sodium oxide and 28.5% of silicon dioxide was diluted with 10 volumes of water. Hydrochloric acid was slowly added and with constant agitation of the mixture until it was barely alkaline to phenolphthalein. The mixture was allowed to stand until a gel formed which was broken up and an additional amount of hydrochloric acid was added until the mixture was just acid to Congo red. Ammonium hydroxide was added until the mixture was neutral to litmus. It was then charged to a centrifuge type of filter and thoroughly washed with water until the filtrate was substantially sodium-free when tested with magnesium uranyl acetate reagent. It was then washed with a dilute solution of aluminum chloride equivalent to one part $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ to 16.5 parts by weight of the original sodium silicate. The filter cake was again water washed. It was removed from the filter and made into a slurry in water and a solution of aluminum chloride added. The amount of aluminum chloride was equivalent to 15% of Al_2O_3 based on the final dried catalytic mass. A solution of zirconium chloride in amount equivalent to 5% ZrO_2 based on the final dried catalytic mass was also added. Ammonium hydroxide was

added with stirring until the mixture was just acid to litmus, after which it was again filtered and washed until free of sodium, as indicated by the qualitative test. The filter cake was removed and dried to approximately 20% water content and was then ground to pass a 30 mesh screen. The powder was compressed into pellets and calcined.

Example II

The charge for reforming was an on-catalytic thermally cracked gasoline (400° F. end point) produced from a Mid-Continent topped crude oil. It had an octane number of 72, and a bromine number of 85, and contained 60% olefins, 14% aromatics, 6% naphthenes, and 20% paraffins. It was reformed according to the present process by passing it over a silica-alumina-zirconia catalyst prepared in the manner described in the foregoing specification, at a temperature of 700° F., a pressure of 150 pounds per square inch, and a liquid space velocity of one. The finished gasoline had a bromine number of two, and an octane number of 72 which was raised to 91 by the addition of 6 cc. of tetraethyl lead per gallon. It amounted to 90.5% of the charge. An analysis of the product showed that it consisted of a trace of olefins, 45% aromatics, 54% paraffins, and 1% naphthenes. The sulfur content was reduced from 0.17% in the original gasoline to 0.08% after treatment. The color was 30+ Saybolt and the oxygen bomb induction period in excess of 12 hours.

It appears evident from the above-described analyses that the reactions taking place in this process comprise cyclization of olefins to naphthenes; followed by dehydrogenation of the naphthenes produced by the cyclization reactions, as well as those originally present in the gasoline, to form aromatics; and a simultaneous hydrogenation of a remaining portion of the olefins with the hydrogen liberated. Possibly some isomerization of olefin or paraffin hydrocarbons occurs. It is probable that the olefins which are cyclized are straight-chain or slightly branched-chain hydrocarbons, while those which are hydrogenated to form paraffins are of a more highly branched-chain type. This is indicated by the fact that substantially no change in octane rating occurs as a result of the treatment, as well as the fact that the treated gasoline has a very high susceptibility to antiknock improvement by the addition of tetraethyl lead.

I claim as my invention:

1. A process for manufacturing stable motor fuels of high antiknock value from olefin-containing gasoline distillates which comprises contacting said olefin-containing distillate at a cracking temperature and a liquid space velocity of approximately 0.5 to 5 with a composite consisting essentially of a major portion of precipitated silica having added thereto a minor portion of a compound selected from the group consisting of precipitated alumina, precipitated zirconia, and precipitated alumina-zirconia, said composite being substantially free of alkali-metal compounds.

2. A process for manufacturing stable motor fuels of a substantially saturated character, high octane number, and susceptibility to tetraethyl lead, from gasoline boiling range distillates containing olefin hydrocarbons, which comprises contacting said gasoline boiling range distillate with a catalytic composite selected from the group consisting of silica-alumina, silica-zirconia, and silica-alumina-zirconia, at a temperature within

the range of approximately 650-900° F., a liquid space velocity of approximately 0.5 to 5 and a pressure of substantially atmospheric to 1000 pounds per square inch, and recovering a substantially saturated product.

3. A process for manufacturing stable gasoline from a thermally cracked distillate of gasoline boiling range which comprises contacting said thermally cracked distillate with a catalytic composite selected from the group consisting of silica-alumina, silica-zirconia, and silica-alumina-zirconia, at a temperature within the range of approximately 650-900° F., a liquid space velocity of approximately 0.5 to 5 and a pressure of substantially atmospheric to 1000 pounds per square inch, and recovering a substantially olefin-free gasoline.

4. A method of manufacturing stable gasoline from a catalytically cracked gasoline containing olefin hydrocarbons which comprises contacting said catalytically cracked gasoline with a catalytic composite selected from the group consisting of silica-alumina, silica-zirconia, and silica-alumina-zirconia, at a temperature within the range of approximately 650-900° F., a liquid space velocity of approximately 0.5 to 5 and a pressure of substantially atmospheric to 1000 pounds per square inch, and recovering a substantially saturated gasoline.

5. A process for manufacturing stable gasoline of high antiknock value from a thermally reformed gasoline which comprises contacting said thermally reformed gasoline with a catalytic composite selected from the group consisting of silica-alumina, silica-zirconia, and silica-alumina-zirconia, at a temperature within the limits of approximately 650-900° F., a liquid space velocity of approximately 0.5 to 5 and a pressure of substantially atmospheric to 1000 pounds per square inch, and recovering a substantially olefin-free gasoline.

6. A process for catalytically reforming cracked gasolines to improve their stability and susceptibility to tetraethyl lead which comprises contacting said cracked gasolines with a catalytic mass consisting essentially of a composite of precipitated silica having added thereto a relatively minor portion of a compound selected from the group consisting of precipitated alumina, precipitated zirconia, and precipitated alumina-zirconia, said composite being substantially free of alkali-metal compounds, under conditions adequate to produce a substantially olefin-free gasoline, and recovering said gasoline.

7. A process for reforming hydrocarbon mixtures of substantially gasoline boiling range containing olefinic, aromatic, naphthenic, and paraffinic hydrocarbons, into a distillate of similar boiling range, said distillate consisting essentially of a mixture of aromatic and paraffinic hydrocarbons, which comprises contacting said mixture of hydrocarbons with a catalytic mass consisting essentially of a composite of precipitated silica having added thereto a minor portion of a compound selected from the group consisting of precipitated alumina, precipitated zirconia, and precipitated alumina-zirconia, said composite being substantially free of alkali-metal compounds, under conditions adequate to effect substantial conversion thereof, and recovering the reaction products.

8. A method for increasing the stability of olefinic gasoline which comprises contacting the gasoline with a catalytic composite substantially free of alkali metal compounds and comprising

a calcined mixture of precipitated silica hydrogel and precipitated alumina hydrogel under conditions adequate to reduce the olefin content of the gasoline by conversion of olefins to more saturated hydrocarbons.

9. A method for increasing the stability of olefinic gasoline which comprises contacting the gasoline with a catalytic composite substantially free of alkali metal compounds and comprising a calcined mixture of precipitated silica hydrogel and precipitated zirconia hydrogel under conditions adequate to reduce the olefin content of the gasoline by conversion of olefins to more saturated hydrocarbons.

10. A method for increasing the stability of olefinic gasoline which comprises contacting the gasoline with a catalytic composite substantially free of alkali metal compounds and comprising a calcined mixture of precipitated hydrogels of silica, alumina and zirconia under conditions adequate to reduce the olefin content of the gasoline by conversion of olefin to more saturated hydrocarbons.

11. A process for treating olefinic gasoline which comprises subjecting the gasoline to olefin conversion conditions in the presence of a calcined substantially alkali-metal free composite comprising precipitated silica hydrogel and precipitated alumina hydrogel.

12. A process for treating olefinic gasoline which comprises subjecting the gasoline to olefin conversion conditions in the presence of a calcined substantially alkali-metal free composite comprising precipitated silica hydrogel and precipitated zirconia hydrogel.

13. The process as defined in claim 11 further characterized in that said gasoline is a cracked distillate.

14. The process as defined in claim 12 further characterized in that said gasoline is a cracked distillate.

15. A process for increasing the stability of olefinic distillates containing gasoline fractions which comprises contacting the olefinic distillate with a catalytic composite substantially free of alkali metal compounds and comprising a calcined mixture of precipitated silica hydrogel and precipitated alumina hydrogel at a temperature in the approximate range of 650-900° F. and at a charging rate corresponding to a liquid hourly space velocity of about 0.5 to 5, whereby to convert gasoline boiling olefins present in the distillate into more saturated hydrocarbons.

16. A process for increasing the stability of olefinic distillates containing gasoline fractions which comprises contacting the olefinic distillate with a catalytic composite substantially free of alkali metal compounds and comprising a calcined mixture of precipitated silica hydrogel and precipitated zirconia hydrogel at a temperature in the approximate range of 650-900° F. and at a charging rate corresponding to a liquid hourly space velocity of about 0.5 to 5, whereby to convert gasoline boiling olefins present in the distillate into more saturated hydrocarbons.

17. A process for increasing the stability of olefinic distillates containing gasoline fractions which comprises contacting the olefinic distillate with a catalytic composite substantially free of alkali metal compounds and comprising a calcined mixture of precipitated silica hydrogel and precipitated alumina hydrogel at a temperature in the approximate range of 650-900° F. and at a charging rate corresponding to a liquid hourly space velocity of about 0.5 to 2, whereby to con-

vert gasoline boiling olefins present in the distillate into more saturated hydrocarbons.

18. A process for increasing the stability of olefinic distillates containing gasoline fractions which comprises contacting the olefinic distillate with a catalytic composite substantially free of alkali metal compounds and comprising a calcined mixture of precipitated silica hydrogel and precipitated zirconia hydrogel at a temperature

in the approximate range of 650-900° F. and at a charging rate corresponding to a liquid hourly space velocity of about 0.5 to 2, whereby to convert gasoline boiling olefins present in the distillate into more saturated hydrocarbons.

19. The process as defined in claim 15 further characterized in that said mixture contains precipitated zirconia.

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