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## 3,116,233 LOW-TEMPERATURE SELECTIVE HYDROGENATION OF DIENES

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This invention relates to a process for the selective hydrogenation of diene-containing hydrocarbon oils.

Products from the severe cracking of hydrocarbon oils ordinarily contain sulfur compounds and considerable quantities of gum-forming dienes. Dienes in gasoline have a pronounced tendency to polymerize, particularly under the influence of air and light, to form gummy materials which deposit upon feed lines, carburetors, valves and the like when the fuel containing them is used in internal combustion engines and thus interferes with the proper operation thereof. Removal of the dienes by ordinary chemical and clay treating processes usually results in large losses of valuable antiknock fuel ingredients. Removal of the gum-forming dienes by polymerization even under optimum conditions tends to result in volumetric losses up to about 20%. Therefore, a preferred method of securing stabilization of a cracked product is one wherein the diolefins are selectively hydrogenated without substantial loss of fuel ingredients.

It is known to hydrogenate selectively a diene-containing gasoline in the presence of hydrogen at an elevated temperature over a catalyst comprising nickel supported on alumina. A catalyst comprising nickel deposited on a carrier having lower cracking and polymerization activity than gamma-alumina has also been proposed. The proposed carriers include the oxides and carbonates of calcium, magnesium, strontium, and barium, silicon carbide, quartz, diatomaceous earth, carbon, and pumice. However, these catalysts are unsatisfactory from the standpoint of activity, mechanical strength, difficulty in preparation, and the like. For example, barium oxide is practically useless as a carrier since it partially melts during catalyst preparation which thereby adversely affects the pore structure.

An object of this invention is to provide an improved method of treating unstable light hydrocarbon oils which are difficult to refine by ordinary chemical and clay treating processes without incurring large losses of valuable ingredients. A further object of this invention is to provide an improved method for improving the stability of a diene-containing gasoline by an improved selective hydrogenation treatment. More particularly, the object of this invention is to provide a process for improving the stability of diene-containing gasoline by a low temperature catalytic selective hydrogenation treatment.

It has now been found that the dienes and other highly reactive unsaturated compounds such as occur in light hydrocarbon oils obtained by cracking can be hydrogenated in a particularly selective manner to form alkenes by using a cobalt or nickel catalyst supported on an alkali earth metal sulfate as carrier. Other favorable properties of the product are not adversely affected by this selective hydrogenation but are even improved in certain cases. By light cracked hydrocarbon oils it is meant hydrocarbon oils having a final boiling point (A.S.T.M.) of not more than 375° C. which are obtained from cracking processes. Unstable very reactive unsaturated compounds occur in relatively large quantities in gasolines and kerosines obtained by thermal cracking, particularly at high temperatures and short contact time.

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The present process is particularly suitable for the treatment of gasoline or fractions thereof obtained by thermally cracking in the presence of steam a hydrocarbon oil with a final boiling point of not more than approximately 250° C. These gasolines are extremely unstable owing to the presence of a relatively high content of highly unsaturated hydrocarbons. However, these gasolines have a very high octane rating owing to the high percentage of aromatic compounds and alkenes which are in themselves stable motor gasoline components.

The highly unstable steam-cracked gasolines are produced by thermally cracking at a high temperature in the presence of steam, a hydrocarbon oil and preferably a hydrocarbon oil relatively rich in aliphatic hydrocarbons. Cracking in the presence of steam is usually effected at temperatures between approximately 550° C. and 900° C., preferably between 750° C. and 800° C., and generally under a pressure below approximately 5 atm. abs. The quantity of steam employed is usually 0.1–10 parts by weight, preferably about 1 part by weight per part by weight of starting material. Cracking in the presence of steam is mainly applied for the preparation of lower alkenes, in particular ethene and propene, which are used as starting materials in the chemical industry. During the cracking treatment, which is generally carried out in a pipe still, usually more than 50% by weight of the starting hydrocarbon oil is converted into compounds having four or fewer carbon atoms in the molecule. The by-product formed during the cracking in the presence of steam is the gasoline which is refined by the process of the present invention and which usually contains more than 30% by weight and often more than 60% by weight of aromatic compounds and has a considerable content of alkenes with a relatively high octane number. In addition, a relatively large amount of highly reactive compounds, mainly dienes, inter alia, those of the cyclopentadiene type, are present. It is also of advantage that in most cases these gasolines are practically free of sulfur, i.e. they have a content of sulfur compounds (calculated as elemental sulfur) which is considerably lower than 0.1% by weight. These gasolines usually contain little or no naphthenic hydrocarbons.

The process of the present invention enables the unstable compounds present in such gasolines to be converted into more saturated compounds by means of selective hydrogenation, whereas the valuable alkenes are hardly, if at all, affected. The process of the invention is also suitable for use with other diene-containing gasolines such as those produced from high temperature short contact catalytic or thermal cracking of gas oil fractions. The diene content of such gasolines, while appreciable, is usually less than that of steam-cracked fractions. Moreover, the process of the invention is suitable for lower boiling hydrocarbons such as a C<sub>3</sub> fraction containing diolefins such as methylacetylene and propadiene. Such low boiling fractions may be treated per se or combined with diolefin-containing gasolines in the process of the invention.

The course of the present hydrogenation is greatly affected by the nature of the carrier on which the nickel or cobalt catalyst is supported. It was found that the use of alkaline earth metal sulfates as carrier gave surprisingly suitable catalysts with which particularly selective hydrogenations could be carried out. The alkaline earth metal sulfates can be employed as such or in the form of mixtures with other carrier materials. Only those alkaline earth metal sulfates which are insoluble or substantially insoluble in water are suitable for use as a carrier since the catalyst is usually prepared by impregnating the carrier with an aqueous nickel or cobalt salt solution. In such a case a water-soluble alkaline earth metal sulfate,

for example magnesium sulfate, is manifestly unsuitable since the structure, which is very important for the action of the catalyst, will be affected during the impregnation treatment by the partial dissolution of the alkaline earth metal sulfate. Moreover, such water-soluble carriers, even should the nickel component be deposited by means other than aqueous solutions, would be unsuitable for use with water-containing feeds or would require expensive means to dehydrate the feed.

The nickel or cobalt component of the catalyst is deposited on the carrier in an amount (calculated as metal) from about 1% to about 25% by weight, and preferably from 3% to 10% by weight, based on the total catalyst.

The selective hydrogenation is carried out at average catalyst temperatures of not more than about 160° C. and preferably at average temperatures in the range of from 70° C. to 130° C.

To ensure satisfactory hydrogenation a quantity of hydrogen is employed which is at least equal to the theoretical amount required for the complete conversion of the reactive compounds present in the gasoline into more stable compounds, such as the conversion of dienes into the corresponding alkene. In order to maintain the activity of the catalyst over longer periods, however, it is preferred to use 2-5 times the theoretical amount of hydrogen.

The gas employed may be hydrogen or a hydrogen-containing gas mixture, for example a mixture of hydrogen and light hydrocarbons. When using an excess of hydrogen it is of advantage to recycle the hydrogen used, preferably after the previous removal of undesired components such as hydrogen sulfide formed during the hydrogenation. The gases employed should preferably contain more than 60% by volume of hydrogen. Very suitable are, for example, the hydrogen-containing gases obtained in the catalytic reforming of gasoline fractions.

The liquid hourly space velocity is usually 0.05-5 kg. and preferably 1-3 kg. of hydrocarbon per hour per liter of catalyst. The gas/hydrocarbon oil ratio is usually between 50 and 300 liters (standard temperature and pressure) of gas per kg. of hydrocarbon oil.

Although according to the present process the catalysts can be used in a fluidized or suspended state, a fixed bed of catalyst is preferably used. Since, as a result of the low hydrogenation temperatures, it is possible for the hydrocarbon oils to be present during the hydrogenation at least partly, i.e. as to more than 50% by weight and preferably as to more than 75% by weight, in the liquid phase without the need for excessively high pressures, the "trickle" technique is particularly suitable for this purpose. According to this technique which is described in Hoog, U.S. 2,608,521 (issued August 26, 1952), the starting hydrocarbon oil which is present partly in the liquid phase and partly in the vapor phase, is allowed to flow downward in the presence of hydrogen or of a hydrogen-containing gas over a catalyst in the form of a fixed bed, the unvaporized part of the starting material flowing over the catalyst particles in the form of a thin layer.

In the process of the invention wherein temperature is not more than 160° C., hydrogenation in the liquid phase usually proceeds at pressures between 10 and 60 atm. abs., preferably between 20 and 40 atm. abs. Because of the exothermic nature of the hydrogenating reactions there may be a certain increase in temperature in the catalyst bed. Therefore, it is of particular advantage to operate in the liquid phase, since because of the higher specific heat of the liquid there will generally be smaller rises in temperature than when operating in the gaseous phase.

The following example is illustrative of the practice of the invention and should not be considered a limitation thereof.

#### EXAMPLE

The starting material used was a gasoline obtained as a byproduct in the preparation of ethene and propene by cracking in the presence of steam a straight-run hydro-

carbon oil having a final boiling point of 230° C. This gasoline was free of naphthenic hydrocarbons and contained 11% by weight of dienes, 10% by weight of alkenes, about 36% by weight of aromatic hydrocarbons and about 43% by weight saturated hydrocarbons. The sulfur content was less than 0.01% by weight. Because of the high diene content, the gasoline was very unstable as shown by an induction period of only about 9 minutes without the addition of an inhibitor.

Other properties of the gasoline were: boiling range 41° C.-180° C. (A.S.T.M.); McIlhiney bromine number 52 g./100 g.; and an Ellis and Jones maleic anhydride number of 112 mg./g. When all the unsaturated compounds were completely saturated the hydrogen consumption was 90 liters (S.T.P.) per kilogram of oil.

The gasoline, substantially in a liquid state and in the presence of 200 liters (S.T.P.) of hydrogen per kilogram of gasoline, was passed over the catalyst (3 x 3 mm. pellets) at an average catalyst temperature of 100° C., a pressure of 40 atm. abs. and a liquid hourly space velocity of 2 kg. of gasoline per hour per liter of catalyst.

Under these conditions three experiments were conducted in which the catalysts used were:

Catalyst A—nickel supported on barium sulfate (nickel content 4.8% w.)

Catalyst B—nickel supported on barium carbonate (nickel content 4.8% w.)

Catalyst C—nickel supported on barium carbonate (nickel content 10.0% w.)

The catalysts were prepared as follows. The carrier material was impregnated by mixing it in powder form with a nickel nitrate solution to form a paste. To this end the barium sulfate was mixed with a nickel nitrate solution containing 7.5% by weight of nickel (calculated as metal) and the barium carbonate powder was mixed with nickel nitrate solutions containing 5% by weight and 10% by weight of nickel respectively. After separating the excess water, the resultant material was dried at 120° C. and then compressed with stearic acid as lubricant to form 3 x 3 mm. pellets. The stearic acid was burned off in the presence of oxygen and the catalyst was then calcined at 500° C. Finally a reduction treatment was carried out by passing over the catalyst hydrogen at a rate of 400 liters (S.T.P.) per hour per liter of catalyst for 3 hours at 400° C. and under a pressure of 40 atm. abs. Catalyst D was prepared by mixing barium sulfate powder with a cobalt nitrate solution containing 48% by weight cobalt (calculated as metal) to form a paste. This catalyst was dried, pelleted and tested with the same feed and under the same conditions as the nickel catalysts.

The data are given in the following Table I.

Table I  
HYDROGENATION OF UNSTABLE GASOLINE

	Feed	Product Obtained With Catalyst			
		A	B	C	D
Specific gravity	0.75	0.75	0.76	0.76	0.76
Bromine number, g./100 g.	52	19	52	48	49
Maleic acid anhydride number	112	8.9	94	107	36
Hydrogen consumption (liters (S.T.P.) per kg. of gasoline)	90	50	1	6	7
Weight ratio of conjugated alkenes:					
alkenes	99	2	62	110	15
F-1-1½ octane number	99.5	98.0	99.2	99.0	99.0
F-2-1½ octane number	84.4	87.5	84.8	84.5	85.2

The octane numbers after the addition of 1½ cc. of tetraethyl lead per U.S. gallon are determined according to the A.S.T.M. method D908-58 and the A.S.T.M. method 357-58.

The superior hydrogenation activity of the nickel catalyst supported on barium sulfate is shown by the figures

for the hydrogen consumption and the decrease in the maleic acid anhydride number, which is a measure of the alkadiene content and the stability of the resultant product. The selectivity is indicated by the figure showing the ratio of the quantity of conjugated alkadienes to that of the alkenes. The lower this figure, the relatively larger is the quantity of alkadienes hydrogenated and the amount of unconverted alkenes which are important for the octane number of the gasoline.

It should be noted also that the sensitivity of the gasoline is greatly improved by the selective hydrogenation over nickel supported on barium sulfate, whereas it is little affected by the other catalysts. The term "sensitivity" is a measure of the sensitivity of the gasoline to changes in the operating conditions of the engine and is determined as the difference between the F-1 and F-2 octane rating. A low sensitivity is desired in gasolines for the modern high-compression ratio engines, and particularly a low sensitivity gasoline with a high F-1 rating. The barium sulfate supported catalyst was particularly effective in this respect in that the F-2 rating was raised from 84.7 to 87.5.

We claim as our invention:

1. A process for the selective hydrogenation of diene-containing gasolines which comprises contacting said gasoline with hydrogen at a temperature of about 70° to about 130° C. in the presence of a catalyst comprising a water-insoluble alkaline earth metal sulfate on which is deposited a metal selected from the group consisting of nickel and cobalt.

2. A process for the selective hydrogenation of diene-containing gasolines which comprises contacting said gasoline with a gas containing at least 60% by volume hydrogen at a temperature of from about 70° to about 130° C. in the presence of a catalyst comprising from 1% to about 25% by weight of nickel deposited on a water-insoluble alkaline earth metal sulfate.

3. The process according to claim 2 wherein the gasoline has a sulfur content, calculated as elemental sulfur, of less than 0.1% by weight.

4. A process for the selective hydrogenation of diene-containing gasolines which comprises contacting said gasoline with a gas containing at least 60% by volume hydrogen in the presence of a catalyst comprising from 1% to about 25% by weight nickel deposited on a water-insoluble alkaline earth metal sulfate, said selective hydrogenation being carried out at a temperature of from about 70° to about 130° C., a pressure of between 10 and 60 atmospheres absolute, a liquid hourly space velocity of 0.5-5 kilograms of gasoline per hour per liter of catalyst, and a gas to gasoline ratio of 50-300 liters (measured at standard temperature and pressure) of gas per kilogram of gasoline.

5. A process for the selective hydrogenation of diene-containing gasolines which comprises contacting said gasoline with a gas containing at least 60% by volume hydrogen in the presence of a catalyst comprising from 3% to 10% by weight nickel deposited on barium sulfate, said selective hydrogenation being carried out at a temperature of from about 70° to about 130° C., a pressure between 20 and 40 atmospheres absolute, a liquid hourly space velocity of 1.0-3.0 kilograms of gasoline per hour per liter of catalyst, a hydrogen to gasoline ratio of 50-300 liters (measured at standard temperature and pressure) of hydrogen per kilogram of gasoline.

6. A process for the selective hydrogenation of diene-containing gasolines which comprises contacting said gasoline with a gas containing at least 60% by volume hydrogen at a temperature of from about 70° to about 130° C. in the presence of a catalyst comprising from 1% to about 25% by weight of cobalt deposited on a water-insoluble alkaline earth metal sulfate.

7. A process for the selective hydrogenation of diene-containing gasolines which comprises contacting said gasoline with a gas containing at least 60% by volume hydrogen in the presence of a catalyst comprising from 1% to about 25% by weight cobalt deposited on a water-insoluble alkaline earth metal sulfate, said selective hydrogenation being carried out at a temperature of from about 70° to about 130° C., a pressure of between 10 and 60 atmospheres absolute, a liquid hourly space velocity of 0.5-5 kilograms of gasoline per hour per liter of catalyst, and a gas to gasoline ratio of 50-300 liters (measured at standard temperature and pressure) of gas per kilogram of gasoline.

8. A process for the selective hydrogenation of diene-containing gasolines which comprises contacting said gasoline with a gas containing at least 60% by volume hydrogen in the presence of a catalyst comprising from 3% to 10% by weight cobalt deposited on barium sulfate, said selective hydrogenation being carried out at a temperature of from about 70° to about 130° C., a pressure between 20 and 40 atmospheres absolute, a liquid hourly space velocity of 1.0-3.0 kilograms of gasoline per hour per liter of catalyst, a hydrogen to gasoline ratio of 50-300 liters (measured at standard temperature and pressure) of hydrogen per kilogram of gasoline.

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