Dec. 19, 1939. W. A. SCHULZE 2,183,591

PROCESS FOR TREATMENT OF HYDROCARBONS

Filed Oct. 20, 1936 2 Sheets-Sheet 1

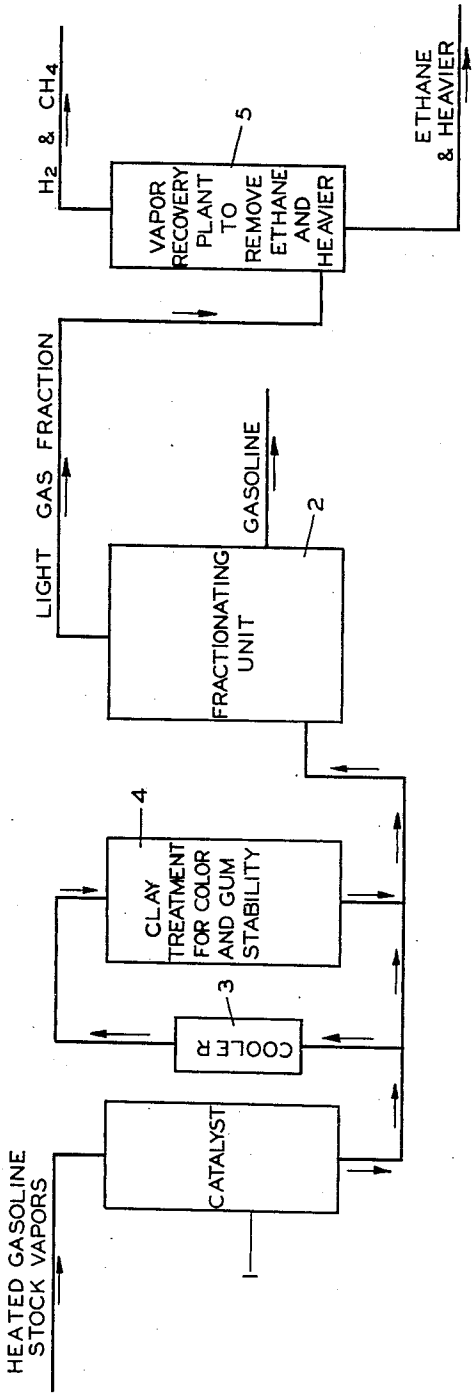

FIG. 1

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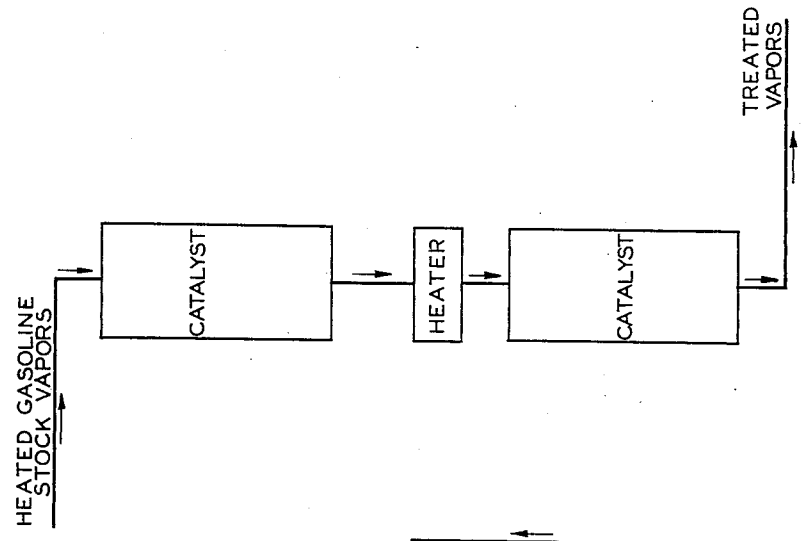

FIG. 4

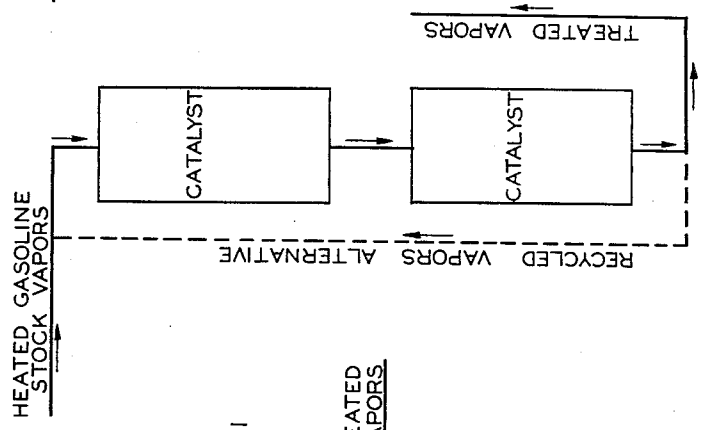

FIG. 3

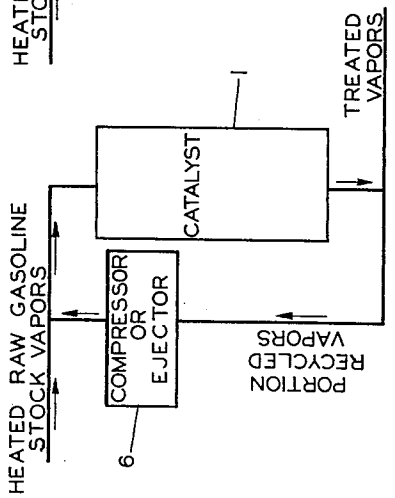

FIG. 2

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Patented Dec. 19, 1939

2,183,591

UNITED STATES PATENT OFFICE

2,183,591

PROCESS FOR TREATMENT OF HYDROCARBONS

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Application October 20, 1936, Serial No. 106,697

5 Claims. (Cl. 196—52)

This invention relates to the treatment of hydrocarbons and relates more particularly to improved catalytic methods of treating petroleum oils, such as straight run and cracked gasolines, pressure distillates, naphthas, polymerized gasolines and natural gasolines, to produce an improved type of motor fuel.

In a more specific sense one of the objects of this invention is a process of treating such motor fuel components, referred to hereinafter as gasoline stocks, in the vapor form over certain catalytic materials to increase their octane ratings and improve their antiknock qualities, to remove the organic sulfur compounds which are so deleterious to the octane number and lead susceptibility, and to produce other desirable refining effects.

In copending applications 104,303, 104,306 and 106,698, applicant has disclosed methods of increasing the life of catalysts of the adsorbent type by employing specific high flow rates, increasing the catalyst life and favorably influencing the treatment by the addition to the vapors of a substantial inert gas, and improvement of gasoline by treatment over bauxite catalyst and certain specific temperatures and flow rates, respectively. The present application differs from the aforementioned applications in the specific catalyst employed.

It is well known that motor fuel specifications call for much higher octane ratings now than formerly, and gasoline stocks are being subjected to extensive refining and reforming operations in order to meet these more rigid specifications. Since the advent of "Q" gasoline several years ago, large quantities of lead tetraethyl, also, have been added to gasolines to raise them to 70 octane number, the rating of the average housebrand gasoline at the present time. All of these practices are quite expensive.

More recently certain results showing the deleterious effects of impurities of the sulfur type on the octane number and lead response of motor fuels were published in an article by Schulze and Buell (Oil and Gas Journal, Vol. 34, No. 21, page 22 (1935). Organic sulfur compounds of different types exist in varying percentages in all gasoline stocks and are present in unusually large amounts in those from West Texas and certain other regions. The form of combination of the sulfur also varies, e. g., mercaptans, alkyl, sulfides, thiophenes and thiophanes. Some of these compounds are much more deleterious than others to the octane number and lead response of the motor fuels; hence the magnitude of the reduction in sulfur content may or may not be a criterion of the improvement in antiknock characteristics.

In a copending application, Serial No. 104,306, filed October 6, 1936, I have shown that still greater improvement in antiknock characteristics can be obtained by treating the gasoline stock vapors over catalytic materials of the bauxite type at temperatures of 900 to 1200° F. In addition to the decomposition and removal of the organic sulfur impurities which are so deleterious to the octane number and lead response of the gasoline stock, a second series of reactions which involve still other deleterious impurities and/or low octane number compounds are made to take place under these conditions. Therefore, the treated product has an octane number considerably higher than that produced merely by the removal of organic sulfur. While the exact changes which occur during this treatment of gasoline stocks over a catalyst of the peculiar nature of bauxite have not been proven conclusively, it is reasonably certain that the remarkable improvement in quality of the gasoline stock results from several concurrent reactions, namely (1) decomposition of deleterious organic sulfur compounds to hydrogen sulfide which may be removed, (2) decomposition and subsequent removal of impurities other than the sulfur type, (3) dehydrogenation of hydrocarbon constituents, and (4) changes in molecular structure of certain of the hydrocarbons. The extent of the improvement from each of these sources varies, of course, with the gasoline stock being treated.

I have now discovered certain improvements in the use of catalytic materials for effecting these changes which result in such remarkable improvement in quality of the gasoline stock with only a small decrease in volume of product boiling within the same range as the untreated stock. The improved catalytic materials described herein are effective at considerably lower temperature levels than bauxite alone and thus permit of a process operating at these lower temperatures.

A further object of this invention is the production of larger quantities of hydrogen during the treatment of gasoline stocks over these improved catalytic materials, the increased quantity of hydrogen being due to more extensive dehydrogenation and rearrangement of the hydrocarbon constituents. The improvement in the antiknock characteristics of the gasoline stock is likewise increased.

In its broader aspects, the invention lies in

the use of the peculiar combination, or intimate mixture, of a highly adsorbent material such as bauxite with a metallic oxide which exerts a strong dehydrogenation activity on hydrocarbons, which combination or mixture is utilized as a contact catalyst for simultaneously decomposing the objectionable organic sulfur compounds and the like and dehydrogenating certain of the hydrocarbon constituents and changing the molecular structure of certain others.

In one specific embodiment of this invention, dehydrated bauxite is impregnated with a solution of a soluble chromium salt such as the nitrate. The chromium salt in rather concentrated solution is merely sprayed as a mist onto the dehydrated bauxite which completely adsorbs the solution and immediately appears dry. The chromium nitrate is subsequently reduced to the oxide form by passing hydrogen or other reducing gas over the impregnated bauxite at elevated temperature.

Heretofore certain refining materials have been made by combining certain metal salts with finely divided or colloidal clay by dissolving the salt in a liquid solvent and adding the solution to the clay to form a gel, but in such instances the liquid and clay were first stirred into a paste, or cream, and the solvent removed later. Obviously my process of manufacturing catalytic material is far different, and due to its simplicity has many economic advantages. Furthermore, I believe no mention has ever been made to this specific catalytic material comprising bauxite and a chromium salt or oxide.

I have discovered that bauxite impregnated with chromium oxide is an extremely effective catalytic material for dehydrogenation of hydrocarbons and simultaneous conversion of organic sulfur compounds to hydrogen sulfide. It is recognized that chromium oxide has dehydrogenating properties but such catalysts are generally very susceptible to poisoning, especially by sulfur compounds and the like. It is known, too, that bauxite has excellent desulfurizing activity and organic sulfur compounds such as mercaptans, alkyl sulfides and the like are decomposed to hydrogen sulfide. It is possible, therefore, to treat the sulfur bearing hydrocarbon vapors in an initial step with bauxite whereby the sulfur compounds are decomposed to hydrogen sulfide, then romove the hydrogen sulfide, and subsequently contact the desulfurized vapors over chromium oxide gel whereby some dehydrogenation of the hydrocarbons takes place. I have found, however, that these combined results can substantially be obtained in one catalytic step through the use of bauxite impregnated with chromium oxide.

I believe the excellent results obtained with the bauxite-chromium oxide catalyst are due to the fact that the chromium oxide in this mixture is not readily poisoned by the sulfur compounds in the hydrocarbon vapors. I have found that when treating sulfur-bearing hydrocarbon vapors over chromium oxide alone that considerable hydrogen sulfide is taken up either by adsorption or by conversion of the oxide to the sulfide. Similarly when treating such vapors over bauxite or aluminum oxide very little hydrogen sulfide is retained by the catalyst. I have concluded, therefore, that adsorption and desorption of hydrogen sulfide from bauxite are both very rapid whereas desorption of hydrogen sulfide from chromium oxide gel is very slow. It is likely that the so-called poisoning of chromium oxide for dehydrogenation is due to this slow desorption of accumulated hydrogen sulfide. The bauxite impregnated with chromium oxide constitutes a catalytic mass which desorbs hydrogen sulfide at a very high rate; hence this catalytic material is not susceptible to ordinary poisoning with sulfur compounds and is highly effective for the purposes claimed.

Instead of the bauxite-chromium nitrate preparation, a very satisfactory catalytic material may be made by impregnating bauxite with a concentrated solution of ammonium dichromate. The material may then be heated to the temperature where the amonium dichromate decomposes slowly to chromium oxide. Other soluble chromium salts readily convertible to the oxide form may, of course, be employed.

Diaspore and other naturally occurring bauxite-like materials may be used instead of the bauxite in the preparation of these improved catalytic materials. I have found moreover that certain commercial aluminas, although much more expensive than bauxite, when used for this purpose frequently make much less effective catalytic materials than the naturally occurring bauxites. I attribute this difference to the physical and chemical structure of these materials. It is fairly definitely established that gibbsite is $Al_2O_3.3H_2O$ and diaspore is $Al_2O_3.H_2O$, but the composition of bauxite is still doubtful.

In utilizing catalysts of the present type in the treatment of hydrocarbon vapors, they may be employed alone or in admixture with relatively inert siliceous spacing materials.

Catalytic materials containing various percentages of chromium oxide may, of course, be prepared according to my invention. A very satisfactory material consists of 95 parts by weight bauxite and 5 parts chromium oxide. Smaller or larger percentages of chromium oxide may obviously be used but extremely economic catalysts can be prepared through the use of less than 5 per cent chromium oxide.

It has been found that with use these catalysts gradually lose their activity due to the accumulation of carbonaceous residues, but they may be reactivated indefinitely by burning out in situ with steam and air, or an oxidizing gas, or by burning in a furnace.

It is a feature of the present invention that when employing catalysts of the type disclosed that relatively low temperatures are sufficient to produce a marked reduction in sulfur content and in improvement in antiknock characteristics of the gasoline stocks. For example, temperatures of from 800° F. to 1100° F. are sufficient, although higher temperatures may, of course, be employed, if desired. High pressures are not needed in the operation of this process, extremely good results being obtained in the range of atmospheric to 100 pounds. Higher or lower pressures may be employed if economic conditions warrant them. In practice, however, it is usually desirable to use pressures somewhat above atmospheric so that the vapors may be conducted directly to a fractionator or to treating tanks for final processing. The preferred flow rate is of the order of 1 to 10 liquid volumes of gasoline stock per hour per volume of catalyst. At the higher temperature levels shorter contact times are sufficient; therefore, flow rates as high as 100 liquid volumes per hour per volume of catalyst may be employed.

Numerous examples might be given of the effects obtained by using the particular catalytic

materials comprised within the scope of the invention in the treatment of gasoline stocks, but the following are sufficiently indicative to show the improved results which were obtained.

Example 1

Depentanized natural gasoline from mid-continent stock was passed in the vapor form over catalytic material consisting of 95 parts by weight bauxite impregnated with 5 parts chromium oxide at a temperature of 875° F. and a flow rate of about two liquid volumes of gasoline per hour per volume of catalyst. After removal of the decomposed impurities, the following improvement in quality of the gasoline was noted:

	A.S.T.M. octane number	Specific gravity	Unsaturation, mol per cent
Untreated gasoline	59.9	.7026	0.3
Treated gasoline	65.2	.7064	9.0

During this treatment 250 cubic feet (S. T. P.) of hydrogen and 20 cubic feet of methane were formed per barrel of gasoline charged.

Example 2

A high-sulfur refinery straight run gasoline from Panhandle crude was passed in the vapor form over catalytic material consisting of 95 parts by weight bauxite impregnated with 5 parts by weight chromium oxide at a temperature of 1000–1010° F. and a flow rate of about two liquid volumes of gasoline per hour per volume of catalyst. After the removal of the decomposed impurities the following remarkable improvement was noted.

	Before treatment	After treatment
A. S. T. M. octane number (0 cc. TEL)	46.8	60.0
With 1.0 cc. TEL/gallon	55.7	69.8
With 2.0 cc. TEL/gallon	60.9	74.8
With 3.0 cc. TEL/gallon	65.1	75.5
Sulfur content, per cent	0.075	0.010
Specific gravity	0.7351	0.7436
Reid vapor pressure	7.80	9.20
Unsaturation, mol per cent	0.2	9.3
Engler distillation:		
10% evaporated, °F.	156	160
50% evaporated, °F.	255	247
90% evaporated, °F.	371	368

Low temperature fractional analyses of the gasoline before and after treatment showed only a minor change in composition. The three and four carbon atom compounds were increased by only 0.4 of one per cent.

The fixed gas formed during the treatment of this gasoline amounted to 370 cubic feet (S. T. P.) per barrel of gasoline charged. The analysis of the gas was as follows: Hydrogen, 66.8 per cent; carbon monoxide, 0.4 per cent; methane, 19.9 per cent; ethylene, 3.6 per cent; ethane, 4.5 per cent; propylene, 2.6 per cent; propane, 2.2 per cent. The hydrogen amounted to 247 cubic feet per barrel of gasoline and the methane to 73 cubic feet, a hydrogen methane ratio of 3.55. The gas loss calculated as weight per cent of the gasoline charged was 3.7 per cent. The total loss in volume of gasoline boiling within the same range as the untreated was about 5 per cent.

The treated gasoline was made into a 70 octane number motor fuel merely by adding 1.05 cc. tetraethyl lead (TEL) per gallon whereas the untreated gasoline with the addition of 3 cc. of tetraethyl lead per gallon was only raised to 65 octane number.

The marked improvement in antiknock characteristics which results from the treatment with my catalytic materials is not due to "cracking" in the usual sense of the word, since in the absence of the catalytic materials and under otherwise identical conditions of temperature and contact time there is no appreciable change in the characteristics of the gasoline stock. Furthermore the improvement which results from the treatment with these bauxite-like catalysts impregnated with chromium salts convertible to the oxide form under the conditions mentioned is not due to an accelerated reforming similar to that occasioned by the presence of adsorbent porous material sometimes referred to as material of the clay type. For example, when the same gasoline stock is contacted with fuller's earth under identical conditions of temperature, pressure and contact time the improvement is almost nil as compared with that obtained by my catalysts described herein.

I have found that in the treatment of gasoline stocks in the vapor form over these bauxite catalysts impregnated with chromium oxide in the temperature range of 800 to 1100° F., as shown in the examples given above, considerable dehydrogenation of the hydrocarbons occurs. There is only a very slight amount of cracking, as evidenced by the small proportion of methane in the gas, providing, of course, the temperature and contact time are properly chosen, since it is obvious that substantially long contact times at temperatures above those needed for the dehydrogenation reactions will produce cracking. With proper choice of the temperature and contact time, both of which vary somewhat with the gasoline stock being treated, it is possible by means of this invention to substantially avoid the formation of methane and other products of cracking. Hydrogen to methane ratios as high as 30 to 1, and sometimes higher, can readily be obtained.

In the practice of my process for the treatment of gasoline stocks to obtain desulfurization, dehydrogenation and the like concurrently, best results are obtained with rather thoroughly dehydrated catalytic materials. The first step in this process usually consists, therefore, in dehydrating the bauxite-chromium oxide catalyst, preferably in situ, by raising the temperature gradually to the temperature of operation or higher while a slow stream of air or hydrocarbon gas is passed over it. Vacuum drying may be done, if desired. This step of passing air or hydrocarbon gas over the catalyst can obviously be omitted in practice, and the gasoline vapors started immediately over the catalyst. Much of the improvement normally obtained in the gasoline stock will be lost, of course, during the first few hours of operation in this manner, or at least until the working temperature has been reached and the catalyst has been substantially dehydrated.

It has been found that the hydrogen-bearing gas which is formed during the treatment of gasoline stocks according to my invention may be recycled through the system by adding such gas, or a portion of it, to the gasoline vapors prior to passage over the catalyst. Such hydrogen gas should, of course, not be allowed to pyramid too much or the reactions may be unfavorably influenced. Also, in processing gasoline stocks containing appreciable quantities of sulfur com-

pounds, the hydrogen sulfide should be removed from the gas prior to recycling.

Obviously the hydrogen gas produced as a by-product in my process has considerable economic value. A gas containing up to 95 per cent hydrogen and the balance methane can be readily obtained by applying simple extraction methods for the removal of the small amounts of hydrocarbons higher than methane. Concentrations of hydrogen higher than 95 per cent can be obtained by more elaborate extraction methods. In any event the hydrogen for hydrogenation and/or other purposes can be obtained in this treatment of gasoline stocks over bauxite-chromium oxide catalysts at extremely low cost. A very distinct advantage of my process is the formation of relatively large quantities of hydrogen from such hydrocarbons as those of the aliphatic series with methane being the only impurity in appreciable amount. Obviously this gas can be utilized for many purposes where the more common mixture of hydrogen and carbon monoxide cannot be tolerated at any cost.

If desired, the gasoline stock vapors may be given two or more successive treatments with the bauxite-chromium oxide catalyst in a series of towers, or the vapors or any fraction thereof may be recycled with the fresh vapors through the catalyst tower. Some additional heat, also, may be supplied to the vapors prior to the second and/or successive catalytic treatments.

Following the treatment of the vapors over the catalyst the decomposed impurities and light gas fraction are separated from the gasoline hydrocarbons by fractional condensation or any other conventional means, as will be well understood by those skilled in the art. If desired, the uncondensed light gas fraction may be passed through a vapor recovery plant of the absorption or other conventional type whereby the hydrocarbons other than methane may be recovered and made useful for other purposes. Also, the decomposed impurities may be removed by chemical means in a step apart from that of removal of the hydrogen and low boiling hydrocarbons from the gasoline hydrocarbons.

The gasoline stocks after treatment according to this invention sometimes require a subsequent treatment to remove small quantities of colored and gum forming constituents in order to make them suitable as motor fuel. This final purification step may be carried out in conventional manner such as clay treating in which case the vapors are generally cooled to about 400° F. prior to treatment.

Figure 1 represents schematically one type of apparatus in which my process may be used. This drawing shows the heated gasoline stock vapors entering the catalyst chamber 1. Upon leaving the catalyst chamber, the vapors may pass directly to the fractionating unit 2, or they may be passed through the cooler 3 and the clay tower 4, to improve color and gum stability, and thence to the fractionating unit 2, where the gasoline is separated from the light gas. The light gas fraction passes from the fractionating unit to a vapor recovery plant 5, for the separation of hydrogen and methane from the ethane and heavier fraction.

The foregoing specification and examples have disclosed and illustrated the invention, but since it is of generally wide application and the number of examples of results obtainable by its use might be multiplied greatly, neither is to be construed as imposing limitations upon the scope of the invention. The term gasoline stock as used herein includes natural gasolines, refinery straight run, cracked and vapor recovery gasolines, polymerized gasolines, naphthas, pressure distillates, and/or mixtures or blends of any two or more of these or of similar hydrocarbon mixtures. Light gases associated with such stocks may be treated along with the hydrocarbons boiling within the gasoline range, or, if desired, such gases may be treated alone.

Figure 2 represents apparatus for the recycling of part of the stream of hot treated vapors for a second pass through the catalyst tower. In this instance, the stream of hot treated vapors leaving the catalyst tower, 1, is split, one part going to the fractionating unit and the other through a compressor 6, (or its equivalent) wherein the pressure is raised just enough to force the recycled vapors into the stream of heated raw gasoline stock vapors prior to passage into the catalyst tower. Figure 3 illustrates an alternative method for giving gasoline stock vapors successive treatments in two catalyst towers in series with the alternative also of recycling a portion of the hot treated vapors. Figure 4 illustrates a method for supplying additional heat to the gasoline stock vapors prior to the second catalyst tower.

I claim as my invention:

1. The process of improving the antiknock characteristics and substantially increasing the unsaturation of a gasoline stock, comprising contacting said gasoline stock in the vapor form at pressures in the range of atmospheric to 100 pounds per square inch with solid adsorbent mineral ore of the bauxite type impregnated with a solution of a chromium compound subsequently converted to the oxide, the catalyst containing a major proportion of bauxite and a minor proportion of chromium oxide, at a temperature in the range of 800 to 1100° F. and a flow rate of about 1 to 10 liquid volumes of gasoline stock per hour per volume of catalyst, separating the decomposed impurities and the light gas fraction high in hydrogen from the hydrocarbons boiling within the gasoline range, and thereby obtaining a gasoline stock which based on equivalent boiling range has greatly improved antiknock characteristics and substantially increased unsaturation.

2. The process of treating a gasoline stock to increase its octane number, which comprises contacting said gasoline stock in the vapor form at pressures in the range of atmospheric to 100 pounds per square inch with a bauxite catalyst impregnated with a solution of a chromium compound subsequently converted to the oxide, the catalyst containing a major proportion of bauxite and a minor proportion of chromium oxide, at a temperature in the range of 800 to 1100° F. and a flow rate of about 1 to 10 liquid volumes of gasoline stock per hour per volume of catalyst, separating the decomposed impurities and the light gas fraction containing a substantial proportion of hydrogen from the hydrocarbons boiling within the gasoline range, and thereby obtaining a gasoline stock with a higher octane number than the untreated gasoline stock boiling within the same temperature range.

3. The process of improving the antiknock characteristics of a gasoline stock and producing a gas with a hydrogen to methane ratio greater than one, which comprises contacting the gasoline stock in the vapor form at a pressure between atmospheric and 100 pounds per square

inch with solid adsorbent mineral ore of the bauxite type impregnated with a solution of a chromium compound subsequently converted to the oxide, the catalyst containing a major proportion of bauxite and a minor proportion of chromium oxide, at a temperature in the range of 800 to 1100° F. and a flow rate of about 1 to 10 liquid volumes of gasoline stock per hour per volume of catalyst, cooling the vapors and separating by condensation the gasoline hydrocarbons from the uncondensed gas, and passing the uncondensed gas through a vapor recovery system whereby the hydrocarbons other than methane are substantially completely removed and a gas with a hydrogen to methane ratio greater than one is obtained.

4. The process of improving the antiknock characteristics of a gasoline stock and producing a gas with a hydrogen to methane ratio greater than one, which comprises contacting the gasoline stock in the vapor form at a pressure between atmospheric and 100 pounds per square inch with a bauxite catalyst impregnated with a solution of a chromium compound subsequently converted to the oxide, the catalyst containing a major proportion of bauxite and a minor proportion of chromium oxide, at a temperature in the range of 800 to 1100° F. and a flow rate of about 1 to 10 liquid volumes of gasoline stock per hour per volume of catalyst, cooling the vapors and separating by condensation the gasoline hydrocarbons from the uncondensed gas, and passing the uncondensed gas through a vapor recovery system whereby the hydrocarbons other than methane are substantially completely removed and a gas with a hydrogen to methane ratio greater than one is obtained.

5. The process of improving the antiknock characteristics of a gasoline stock, comprising contacting said gasoline stock in the vapor form at a pressure between atmospheric and 100 pounds per square inch with a bauxite catalyst impregnated with a solution of a chromium compound subsequently converted to the oxide, the catalyst containing a major proportion of bauxite and a minor proportion of chromium oxide, at a temperature in the range of 800 to 1100° F. and a flow rate of about 1 to 10 liquid volumes of gasoline stock per hour per volume of catalyst, splitting the treated vapors into two streams, recycling one of the streams without substantial cooling back into the heated raw vapors prior to the catalyst chamber, separating from the other stream of treated vapors the decomposed impurities and the light gas fraction containing a substantial proportion of hydrogen gas from the hydrocarbons boiling within the gasoline range, and thereby obtaining a gasoline stock which has greatly improved antiknock characteristics.

WALTER A. SCHULZE.