

July 25, 1939.

W. A. SCHULZE

2,167,602

TREATMENT OF HYDROCARBON OILS

Filed Oct. 6, 1936

2 Sheets-Sheet 1

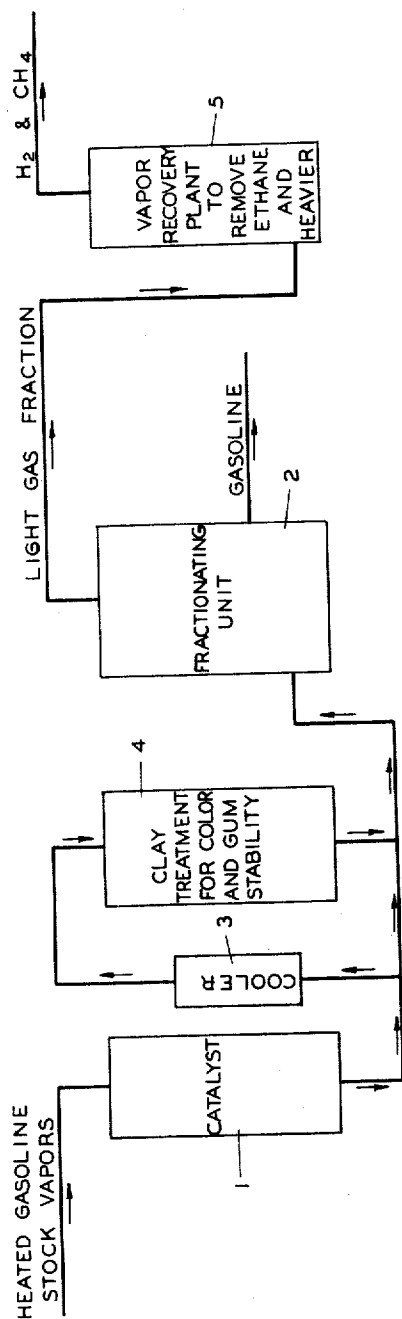


FIG. 1

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2 Sheets-Sheet 2

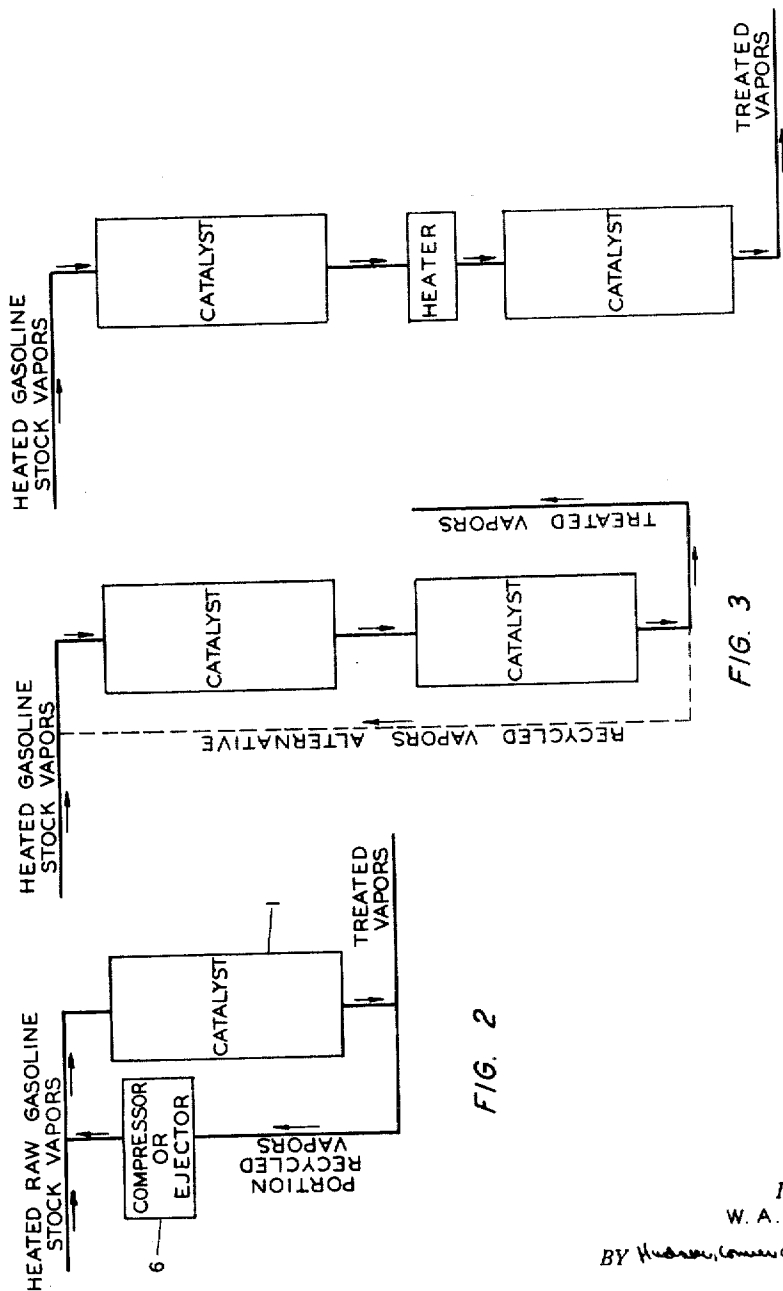


FIG. 4

FIG. 3

FIG. 2

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UNITED STATES PATENT OFFICE

2,167,602

TREATMENT OF HYDROCARBON OILS

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Delaware

Application October 6, 1936, Serial No. 104,306

2 Claims. (Cl. 196—52)

This invention relates to the treatment of hydrocarbons and relates more particularly to 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.

Applicant's co-pending application Serial No. 104,303 differs from the present invention in that it relates to a method of reducing poisoning of adsorbent desulfurization catalysts operating in a temperature range substantially lower than that specified in the present application, and Serial No. 104,304 relates to a process similar in some respects to the present process but employing a different catalyst.

In a more specific sense an object of this invention is a process for treating such motor fuel components 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.

Another object of the invention lies in the production of this enormous improvement in the characteristics of the petroleum oil with only a small decrease in volume of product boiling within the same range as the untreated oil. This is in contradistinction to the large losses which occur in such conventional operations as thermal reforming of the oils.

A further object of the invention is the production of a petroleum oil with both a higher specific gravity and a higher octane rating than the untreated oil, whereas cracking of oils in the established manner produces higher octane products but of lower specific gravity.

A still further object of the invention is the production of a by-product gas relatively rich in hydrogen, such gas being quite useful in hydrogenation processes as well as for many other purposes.

It is well known that motor fuel specifications call for much higher octane ratings today than formerly, and gasoline stocks are being subjected to extensive reforming operations in order to meet these specifications. Since the advent of "Q" gasoline several years ago, large quantities of tetraethyl lead, also, have been added to gasolines to raise them to 70 octane number, the rating of the average house-brand 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, p. 22 (1935)). Organic sulfur compounds of different types exist in varying percentages in all petroleum distillates 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. Schulze and Buell in an application, Serial No. 756,142, filed December 5, 1934, describe catalytic processes for removing these impurities from sulfur-bearing petroleum oils, thereby obtaining marked improvement in octane number and lead response of such products as natural gasolines and refinery straight run, cracked and vapor recovery gasolines.

I have discovered that still greater improvement in antiknock characteristics can be obtained when the motor fuel stocks are treated under the conditions specified below. 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 motor fuel, certain reactions which involve still other deleterious impurities and/or low octane number compounds are made to take place; therefore, the treated product has an octane number considerably higher than that produced merely by the removal of organic sulfur.

In one specific embodiment of the invention, the gasoline stock is passed in the vapor form over a catalyst such as well dehydrated bauxite at a temperature in the range of 900° F. to 1200° F. and at a flow rate of 1 to 100 liquid volumes per hour per volume of catalyst. For example, at a temperature of 1000° to 1025° F. the preferred flow rate is of the order of 2 to 10 liquid volumes per hour per volume of catalyst. At higher temperatures shorter contact times are sufficient; therefore, flow rates as high as 100 liquid volumes per hour per volume of catalyst may be employed.

I have discovered that in treating gasoline stocks in the vapor state over bauxite catalyst

that there are specific temperature ranges for the reactions involving the decomposition of those compounds responsible for the low octane rating of the gasoline. At temperatures in the range of 600° to 750° F. the organic sulfur compounds of the mercaptan and sulfide types are decomposed into hydrogen sulfide without any substantial decomposition of the hydrocarbon constituents, at temperatures in the range of 750° to 900° F. there is little or no additional improvement in octane number over that obtained in the simple desulfurization treatment, but at temperatures above 900° F. a second series of reactions takes place as evidenced by the formation of large quantities of hydrogen gas and by the marked increase in octane number of the treated oil.

The improvement which results from the treatment at temperatures above 900° F. is not due to "cracking" in the usual sense of the word, since in the absence of the bauxite catalyst and under otherwise similar conditions of temperature and contact time there is no appreciable change in the characteristics of the oil. For example, in the treatment of a pentane free-oil free natural gasoline of 59.9 octane number at a temperature of 1,025° F. and a flow rate of 1.75 liquid volumes per hour over dehydrated bauxite catalyst the octane rating was increased by 5.1 octane numbers. At a temperature of 1,055° F. and a flow rate of 2.0 liquid volumes per hour the octane rating was raised 7.9 octane numbers. With the same gasoline at a temperature of 1,045° F. and a flow rate of 1.6 liquid volumes per hour but without the catalyst, the octane rating was increased only 0.3 of an octane number. At 1,075° F. and a flow rate of 1.5 liquid volumes per hour without the catalyst, the improvement was only 0.7 of an octane number.

Furthermore, the improvement which results from the treatment with bauxite 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, the same stock of natural gasoline was passed over fuller's earth and bauxite under identical conditions of temperature, pressure and contact time. The improvement in the bauxite test was 5.3 octane numbers while in the fuller's earth the change was only 0.4 of an octane number.

In the operation of this process high pressures are not needed, extremely good results being obtained in the range of atmospheric to 100 pounds. Higher or lower pressures may, of course, be employed. In practice it is usually desirable to use pressures somewhat above atmospheric so that the vapors can be conducted directly to a fractionator or to treating tanks for final processing.

Several typical examples of the operation of this process are given as illustrative of the results which have been obtained in the treatment of various gasoline stocks, but these examples are in no sense to be interpreted as limiting the invention.

Example 1

Refinery low end-point straight run gasoline from Panhandle crude oil was contacted in the vapor form with dehydrated bauxite catalyst maintained at a temperature of 1,000° F. and a flow rate of about 1.4 volumes of liquid gasoline per hour volume of catalyst. After removal of

the decomposed impurities the following improvement was noted:

	A. S. T. M. Octane No.	Sulfur content percent	Specific gravity
Untreated gasoline.....	56.4	0.0334	.7179
Treated gasoline.....	65.2	0.0026	.7197

The response to 1 cc. tetraethyl lead per gallon was 10.6 octane numbers on the untreated and 10.8 octane numbers on the treated. When it is taken into consideration that the octane level is much higher on the treated gasoline, or that the octane numbers are converted into compression ratio, it is realized that an excellent improvement in lead response resulted.

The fixed gas formed during the treatment of this gasoline amounted to 235 cu. ft. per barrel of gasoline charged. Most of this gas was hydrogen. There was only a small amount of methane, the hydrogen to methane ratio being greater than eight. The total loss in volume of product boiling within the gasoline range was about two per cent.

Example 2

Refinery straight run gasoline from Michigan crude was passed in the vapor form over dehydrated bauxite at a temperature of 1,000 to 1,010° F. and a flow rate of 2.0 liquid volumes of gasoline per hour per volume of catalyst. After removal of the decomposed impurities the following remarkable improvement was noted.

	Before treatment	After treatment
A. S. T. M. octane number (0 cc. TEL).....	36.8	51.7
With 1.0 cc. tetraethyl lead/gallon.....	48.1	63.7
With 2.0 cc. tetraethyl lead/gallon.....	54.7	71.1
With 3.0 cc. tetraethyl lead/gallon.....	58.6	74.7
Sulfur content, per cent.....	0.050	0.004
Specific gravity.....	0.7093	0.7157
Raid vapor pressure.....	8.55	9.65
Unsaturation, mol per cent.....	0.6	7.0
Engler distillation:		
10% evaporated.....°F	141	141
50% evaporated.....°F	215	214
95% evaporated.....°F	300	299

Low temperature fractional analyses of the gasoline before and after treatment showed only a minor change in composition. The two, three and four carbon atom compounds were increased by only 0.3 of one per cent.

The fixed gas formed during the treatment of this gasoline amounted to 260 cu. ft. (S. T. P.) per barrel of gasoline charged. The analysis of the gas was as follows: Hydrogen, 82.0 per cent; carbon monoxide, 0.9 per cent; methane, 6.5 per cent; ethylene, 2.4 per cent; ethane, 3.6 per cent; propylene, 1.9 per cent; propane, 2.7 per cent. The hydrogen amounted to 213 cubic feet per barrel of gasoline and the methane to 17 cubic feet, a hydrogen to methane ratio of 12.6. The gas loss calculated as weight per cent of the gasoline charged was only 1.98 per cent. The total loss in volume of gasoline boiling within the same range as the untreated was about 3 per cent.

The treated gasoline was made into a 70 octane number motor fuel merely by adding 1.80 cc. tetraethyl lead per gallon whereas the untreated gasoline could not be raised to 70 octane number even with the addition of an excessive amount of tetraethyl lead.

Example 3

Twelve pound Reid vapor pressure natural gasoline from West Texas was passed in the vapor form over well dehydrated bauxite catalyst at a temperature of 1040° to 1050° F. After removal of the decomposed impurities the following improvement was noted.

	A. S. T. M. octane number	Sulfur content per cent	Specific gravity	Unsaturation mol per cent
Untreated gasoline.....	67.2	0.0609	.6754	11.9
Treated gasoline.....	76.5	0.0033	.6829	

During this treatment 192 cubic feet of hydrogen and 105 cubic feet of methane were formed per barrel of gasoline charged, a hydrogen to methane ratio of 1.8.

A depentanized product made from the treated gasoline with a vapor pressure of 4.3 pounds had an octane rating of 69.4. This represents an enormous gain over that of the untreated gasoline which had a rating of only 67.2 with a vapor pressure of 12.0 pounds.

Example 4

Depentanized Mid-Continent natural gasoline was passed in the vapor form over a bauxite catalyst at a temperature of 1,025° F. After removal of the decomposed impurities the following improvement was noted.

	A. S. T. M. octane number	Specific gravity	Unsaturation mol per cent
Untreated gasoline.....	59.9	.7026	0.3
Treated gasoline.....	65.0	.7064	8.8

During this treatment 249 cubic feet (S. T. P.) of hydrogen and 24 cubic feet of methane were formed per barrel of gasoline charged, a hydrogen to methane ratio of 10.

Example 5

Gasoline from pressure cracking of topped Panhandle crude was passed in the vapor form over a dehydrated bauxite catalyst at 1,000° F. After removal of the decomposed impurities the following improvement was noted.

	A. S. T. M. octane number	Sulfur content per cent	Specific gravity
Untreated gasoline.....	58.2	0.096	.7607
Treated gasoline.....	63.8	0.056	.7555

The response to 1 cc. of tetraethyl lead per gallon was 7.2 octane numbers on the untreated and 7.4 octane numbers on the treated gasoline. When it is taken into consideration that the octane level is much higher on the treated gasoline, it is realized that a good improvement in lead response was obtained along with the large gain in original octane number.

During this treatment considerable hydrogen and a little methane were formed, the hydrogen to methane ratio being relatively high. The total loss in volume of gasoline boiling within the same range as the original was about three per cent.

Example 6

Pure normal heptane free of water vapor was passed in the vapor form over thoroughly dehy-

drated bauxite catalyst at a temperature of 1,000° F. Under these conditions 170 cubic feet of hydrogen was formed per barrel of normal heptane treated. The product, as determined by bromine titration, had an unsaturation of eight mol per cent. The following improvement in antiknock characteristics was obtained.

	Before treatment	After treatment
A. S. T. M. octane number (0 cc. TEL).....	0	16.3
A. S. T. M. octane number with 1.0 cc. TEL/gallon.....	22.1	35.2
A. S. T. M. octane number with 3.0 cc. TEL/gallon.....	44.3	56.0

I have found that in the treatment of gasoline stocks in the vapor form over bauxite in the temperature range, that some 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 of 1,100° F. and above will produce cracking. With proper choice of the temperature and contact time, however, it is possible by means of this invention to substantially avoid the formation of methane and other products of cracking. In Example 2 the hydrogen to methane ratio was 12.8. At other times still higher hydrogen to methane ratios have been secured.

I have found that although dehydrogenation of certain of the hydrocarbons occurs during the treatment according to this invention, this dehydrogenation is only one of several reactions taking place. It is evident from the results such as those given under Example 2 that the improvement of 15 to 16 octane numbers could not have resulted merely by the conversion of 7 per cent of saturated aliphatic hydrocarbons to simple unsaturated hydrocarbons of the olefin type. Neither can it be accounted for on the basis of the amount of hydrogen formed. While I am not certain of the exact changes which occur during this treatment of gasoline stocks over a catalyst of the peculiar nature of bauxite, I believe the remarkable improvement in octane number results from several concurrent reactions, namely, (1) decomposition of deleterious organic sulfur compounds to hydrogen sulfide and the subsequent removal of the hydrogen sulfide, (2) decomposition and removal of impurities other than the sulfur type, (3) dehydrogenation of hydrocarbons, 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.

Various catalysts have been used heretofore in connection with desulfurization processes and others in connection with dehydrogenation processes. Certain catalysts such as fuller's earth and other clay like materials have been proposed also for accelerating reforming reactions, but as shown above fuller's earth does not give results similar to bauxite under the conditions specified herein. I believe that heretofore it has not been shown that the results enumerated above for my process could be obtained by means of either a single catalyst or a combination of catalytic steps.

In the practice of the present invention the bauxite or the bauxite like material is crushed to a suitable size, usually 10 to 30 mesh. If de-

sired it may be diluted with diluents such as naturally associated active and/or inactive substances or substances which are suitable for diluting purposes although not naturally associated with the catalytic material.

Bauxite is essentially a hydrated aluminum oxide of highly porous and peculiar internal structure. On heating to elevated temperatures much water is given off. This water of hydration is not driven off gradually with increasing temperature, such as is the case with fuller's earth and hydrosilicates in general, but very rapidly at a threshold temperature somewhere near 550° F. Therefore, since in practice of this invention the best results are obtained with thoroughly dehydrated bauxite, the first step usually consists in dehydrating the bauxite, preferably in situ, by raising the temperature gradually to the temperature of operation while a slow stream of air or hydrocarbon gas is passed over it. This step of passing air or hydrocarbon gas over the bauxite can obviously be omitted, if desired, and the gasoline vapors started over the bauxite immediately. The improvement in the gasoline during the first few hours of operation will be lost, of course, by operating in this manner.

It has been found that the bauxite gradually loses its catalytic activity with use but it may be reactivated indefinitely in the manner described in U. S. Patent 2,016,271 to Buell and Schulze.

Instead of bauxite catalyst, diasporé and other bauxite like materials may be used in my process. Likewise alumina prepared in various manners may be employed.

It has been found that the hydrogen-bearing gas which is formed during the treatment of gasoline stocks according to my invention may be re-cycled 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 reaction may be unfavorably influenced. Also in processing gasolines containing appreciable quantities of sulfur compounds, the hydrogen sulfide should be removed from the gas prior to recycling.

Obviously the hydrogen gas produced as by 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 amount of hydrocarbons higher than methane. Concentrations of hydrogen higher than 95 per cent can be obtained by more elaborate extraction methods. In any event hydrogen for hydrogenation and/or other purposes can be obtained in this treatment of gasoline stocks over bauxite at an extremely low cost. A very distinct advantage of my process is the formation of relatively large quantities of hydrogen 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 catalytic material such as bauxite in a series of catalyst 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. 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 stock after treatment in the described manner usually requires a subsequent treatment to remove small amounts of colored and gum-forming constituents in order to make the stock suitable as motor fuel. This final purification step can 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.

In the accompanying drawings Figures 1-4 inclusive are diagrammatic illustrations of apparatus for carrying out the invention.

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.

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.

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. Light gases associated with such stocks may, if desired, be treated along with the hydrocarbons boiling within the gasoline range.

I claim as my invention:

1. The method of improving the anti-knock characteristics of a gasoline stock and producing a gas with a hydrogen to methane ratio greater than one, which comprises containing the gasoline stock in the vapor form at a pressure between atmospheric and 100 pounds per square inch with a bauxite catalyst at a temperature in the range of 900 to 1050° 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.
2. 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 at a temperature in the range of 900 to 1050° 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.

CERTIFICATE OF CORRECTION.

Patent No. 2,167,602.

July 25, 1939.

WALTER A. SCHULZE.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, first column, line 5, claim 1, for the word "containing" read contacting; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 10th day of October, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

I claim as my invention:

1. The method of improving the anti-knock characteristics of a gasoline stock and producing a gas with a hydrogen to methane ratio greater than one, which comprises containing the gasoline stock in the vapor form at a pressure between atmospheric and 100 pounds per square inch with a bauxite catalyst at a temperature in the range of 900 to 1050° 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.
2. 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 at a temperature in the range of 900 to 1050° 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.

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(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.