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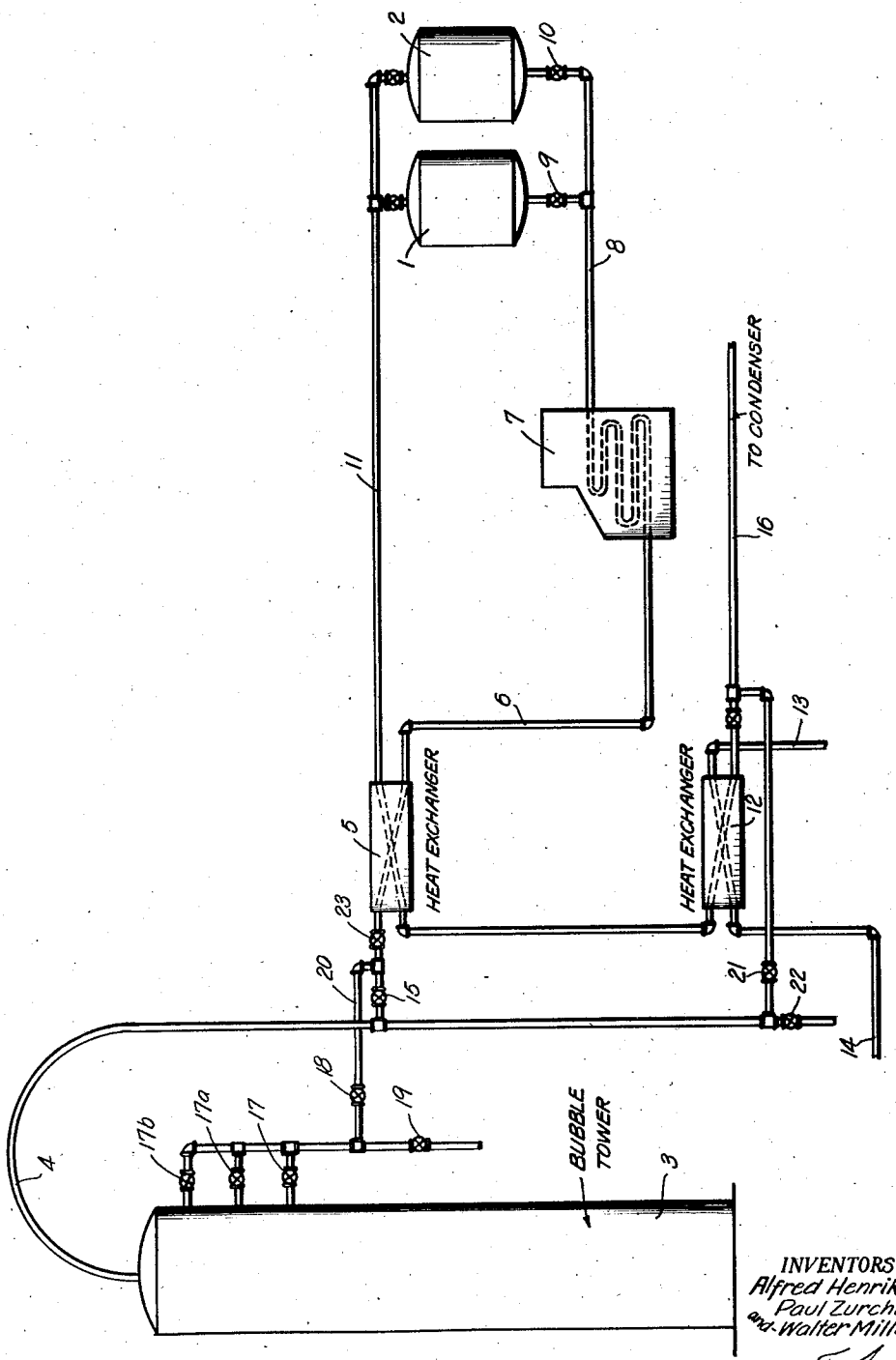

INVENTORS
Alfred Henriksen
Paul Zurcher
and Walter Miller

By Thos. E. Scofield
ATTORNEY

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WALTER MILLER, ALFRED HENRIKSEN, AND PAUL ZURCHER, OF PONCA CITY, OKLAHOMA, ASSIGNORS TO CONTINENTAL OIL COMPANY, OF PONCA CITY, OKLAHOMA, A CORPORATION OF DELAWARE

METHOD FOR CONVERTING HYDROCARBON MATERIALS

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This invention relates to improvements in converting hydrocarbon materials and refers more particularly to a process for converting hydrocarbons to produce an improved type of motor fuel. The novelty of the invention lies primarily in heating oil in the vapor phase considerably above its normal temperature of vaporization and, while in this highly heated condition, passing the vapors through a catalytic material such as fuller's earth, to produce from the vapor subsequently condensed an improved type of motor fuel having high antiknock qualities.

The process is applicable to hydrocarbons recovered from normal atmospheric distillation of crude petroleum oils or vapors discharged from any type of preferred distillation or cracking process. The catalytic material, such as clay, including a number of the well known varieties of the character of fuller's earth as hereinafter set out, is maintained at a temperature above the normal vapor temperature at the existing pressure of the hydrocarbons under treatment. After cooling, the vapors passing through the system are condensed to liquid distillates and may be later treated by known hydrocarbon treating processes including redistillation, if required.

The materials with which the superheated vapors are intimately contacted and designated as clay, are understood to include such substances as fuller's earth, montmorillonite, bauxite, Willonite, Pyrophyllite, Kaolinite, diatomaceous earth, and kindred substances either in their natural state, synthetically prepared, chemically treated as with acid, or metallized with copper, iron, or other metals included under the hydrogen sulphide or ammonium sulphide group tests.

Generally speaking, the higher boiling point fractions of an oil from which motor fuel is to be extracted contain hydrocarbons with higher knocking tendencies than the lower boiling fractions. If the various 10 per cent fractions of a motor fuel as obtained by distillation are tested in a machine for determining the knocking qualities of the fractions, and rated according to the cubic centimeters of lead tetraethyl required to meet predetermined standard fuel requirements, a range of differences in the knocking qualities will be somewhat according to the following list, which is a typical example:

10% cuts	Cu. cm. tetraethyl lead to meet standard fuel requirements
First cut	1.1
Second cut	1.7
Third cut	2.4
Fourth cut	3.1
Fifth cut	3.5
Sixth cut	3.8
Seventh cut	4.6
Eighth cut	5.6

From this example, it will be noted that the first four cuts, when combined, would give a relatively good antiknocking fuel and would not require further treatment. The present invention contemplates, when characteristics permit, removing and treating separate fractions of the motor fuel and then recombining the treated fractions with the untreated fractions by a blending operation to obtain the proper specifications with reference to anti-knock qualities. Also the treated material may be used with separate oils as a blending material.

With some crude petroleum oils, it is advisable to pass the total crude oil through the process and remove the motor fuel from the total treated crude. In a like manner, in connection with certain types of cracking processes, it is desirable to treat the entire discharge from the cracking process in order to procure the desired results in the final product. The higher boiling point fractions of the total treated crude, or the higher boiling fractions from a cracking operation not included in the motor fuel to be treated by the present process, may be mixed with the fresh raw stock to be vaporized and thus retreated indefinitely until it has accumulated to the extent that it becomes unprofitable to reheat it for distillation purposes.

The following description, which is a preferred type of operation, is offered merely for the purpose of disclosing the different

stages, to include the various temperatures and conditions which exist, and is not to be considered as limitation thereto, as it is appreciated that the method is capable of innumerable modifications which are included within the general scope of the invention.

The single figure is a schematic diagram of the process. There has been eliminated from the drawing a showing of the distillation apparatus such as a crude still in the form of a shell or pipe still, or a cracking apparatus located ahead of the bubble tower shown in the drawing. Such distillation apparatus is well known in the art and has been omitted in the interest of simplicity. In the drawing, chambers 1 and 2 are charged with the selected clay or the like which has been found to be the most effective with the oil undergoing treatment. The material is ground to a sufficient degree of fineness to assure intimate contact between the vapors and the treating substance. The particle size is maintained sufficiently large to prevent packing of the material in the chambers, and to afford free access of the vapors therethrough.

Vapors from the fractionating tower 3 are directed through a vapor line 4 and a heat exchanger 5. In this heat exchanger, the vapors are passed in countercurrent flow with the vapors discharged from the chambers 1 and 2 as hereinafter explained.

From the heat exchanger 5, the vapors pass out through the line 6 to the superheater 7. The superheater may be of any suitable type, including a small pipe still positioned in the furnace, a superheating coil in an insulated casing, or other well known available and convenient means. This superheater may acquire its heat by the burning of any suitable type of fuel.

From the superheating device, the vapors are directed through an insulated line 8, which is connected through lines 9 and 10 with either of the chambers 1 and 2. In the lines 9 and 10 are interposed suitable valves for cutting out either one of the chambers as the material therein becomes contaminated. Similar valves are interposed in the discharge lines from the chambers.

The vapors may be passed through the chambers entering either near the bottom or the top, so that the passage can be either upwardly through the material, or downwardly, as desired. Two chambers are provided in order to obtain continuous operation, the clay in one chamber being regenerated while the other one is in use. The regeneration is effected by blowing superheated steam or air through the chamber while the same is cut out of the system by manipulation of the valves as explained. The regenerating apparatus is not shown and forms no part of the present invention, as it is a practice known in the handling of materials of this type in connection with the purification of hydrocarbon vapor.

The chambers 1 and 2 may be heated as desired by independent burners or by passing over them the hot flue gases from the furnace of superheater 7. The heating facilities for the chambers has been omitted from the drawing in the interest of simplicity.

The treated vapors leaving the chambers 1 and 2 pass through the vapor line 11 and are cooled in the heat exchanger 5, and subsequently cooled in the second heat exchanger 12. A cooling medium such as cold crude oil, is supplied to the heat exchanger 12 through the line 13 and is withdrawn from the heat exchanger through the line 14, after which it may be passed to a still or other apparatus for further processing.

It is contemplated that any medium besides oil may be used in the heat exchanger apparatus shown in the drawing. A valve 15 is positioned in the line which connects the vapor line 4 to the heat exchanger 5 and, when this valve is closed, the process is bypassed and the vapors discharged directly into the line 16, which is connected to suitable condensing apparatus not shown.

The lines 17, 17*a* and 17*b* are connected into the side of the tower 3, to furnish withdrawal lines from the tower at different heights in order to remove different fractions of the oil for treatment. These lines are equipped with suitable control valves. A cut or fraction of the vapor which does not require treatment may be taken off from the line 4 and passed direct to the condensers and storage through the line 16 or pipe 22. Simultaneously, a separate cut may be removed through any or all of the lines 17, 17*a* or 17*b*, and processed by this invention, by closing the valve 19 and opening the valve 18, allowing the hydrocarbon fractions to pass through the line 20 to heat exchanger 5, thence to the superheater and treating chamber. Also both the vapors passing through line 4 and liquid withdrawn from the tower through pipes 17, 17*a* and 17*b* may be combined and simultaneously treated. The liquid is vaporized and properly superheated at 7, as previously described. The untreated vapors removed through the line 4 and the treated fractions removed through the lines 17, 17*a* and 17*b*, or either of them, may be combined in the line 16 and passed to condensers, or the two cuts may be collected separately by closing the valves 15 and 18 and passing the overhead materials through the vapor pipe 4 to the condensers through the line 22.

As suggested, the process may be bypassed by closing the valves 15 and 18, or by closing valve 23 and passing the material to either of the condensers through pipe 16 or 22.

The invention contemplates refractionation of the hydrocarbons treated by the proc-

ess when required. Examples are given to clarify the process but are not to be interpreted as limitations to the invention.

Example 1.—The total straight run gasoline of 428° F. maximum boiling point contained in a crude petroleum required 5 cubic centimeters of tetraethyl lead to equal a standard antiknocking fuel. This product was treated by this invention at 600° F. to 900° F. The product from the process was completely refined to 30 color on the Saybolt colorimeter.

	1	2	3	4	5	6	7
Temperature of treating	Untreated	600° F.	700° F.	800° F.	900° F.	800° F.	900° F.
Maximum boiling point of treated product	428° F.	410° F.	407° F.	412° F.	412° F.	422° F.	422° F.
Color	30	30	30	30	30	30	30
Pb(et)4 required to equal standard fuel	5	1.5	1.4	1.2	1.2	1.6	1.6

Example 2.—A low sulfur crude oil was tested by this process which contained approximately 70% of a 434° F. maximum boiling point gasoline requiring 7 cubic centimeters of tetraethyl lead to equal a standard antiknock fuel. The total crude was charged to the still and the overhead vapors and clay drums heated and held at 970° F. for one test and 1050° F. for another test. A yield of 72.9% gasoline of 420° F. maximum boiling point was obtained on the 970° F. test which required only 2 cubic centimeters of tetraethyl lead to equal standard reference fuel. The test at 1050° F. gave a similar yield of gasoline requiring only 0.5 cubic centimeter of tetraethyl lead to equal the standard reference fuel. The heavy bottoms remaining in the still after the 1050° F. test were blended with fresh crude and treated at 1050° F. yielding a gasoline requiring only 0.3 cubic centimeter of tetraethyl lead to equal the standard reference fuel. Again the 31% of heavy bottoms from this last test were blended with fresh crude and treated at 1050° F. yielding a gasoline better than the standard reference fuel. That is 0.5 cubic centimeter of tetraethyl lead was added to the standard reference antiknock fuel to equal the gasoline produced.

Example 3.—The same crude as used in Example 2 was stripped of 10% of its gasoline and the remaining 90% charged to the process, the vapors and clay being held at 1000° F. for the treatment. The treated gasoline and untreated gasoline were blended, giving a combined gasoline requiring only 1.4 cubic centimeters of tetraethyl lead to equal the standard reference fuel. On another test 30% of the gasoline content of the crude was removed and the remaining 70% treated by the process at 1000° F. The crude stripped of 30% of its gasoline yielded by treatment 44.9% of 405° F. maximum boiling point gasoline requiring only 2.6 cubic centimeters of tetraethyl lead to equal the standard reference fuel.

In the practice of the invention, it has been found that the particular characteristics of the hydrocarbons being treated and the characteristics of the clay or similar material being used influences the temperature at which the treatment is most effective. Working with the same hydrocarbon oil and the same conditions, it was found that the Utah fuller's earth must be heated to approximately 100° F. higher temperature than a Texas fuller's earth, to obtain the same results. Texas fuller's earth may be used at temperatures approximately 1200° F., while Utah fuller's earth, to obtain like results, requires a 1300° F. temperature. Other clays or products of a similar nature which were used, varied within a range of from 1000° to 1300° F.

The pressure under which this process should be conducted depends entirely on the characteristics of the hydrocarbons treated, the clay used for treatment, and the temperature of treatment. The process may be conducted under sub-atmospheric pressures, atmospheric pressures, or superatmospheric pressure. The best results have been found to be obtained under pressures below 100 pounds per square inch. Elevated pressures used in this process are primarily for lowering the temperatures of treatment, reducing gas loss and for condensation above atmospheric pressure, and not for the cracking or decomposition effect.

It has been found that, at a pressure of 50 to 75 pounds, the temperature of treating hydrocarbons by the process may be substantially reduced and the same results obtained. By the use of pressures below 100 pounds per square inch, it is possible to always conduct the process between 750° F. and 1200° F.

We claim as our invention:

1. A method of increasing the antiknock qualities of motor fuels comprising the steps of vaporizing the fuel in a primary heating zone without substantially pyrolytic decomposition and superheating the vapors above their normal vapor temperatures in a subsequent heating zone and, while substantially at such temperatures and without substan-

tial condensation, passing the vapors through a mineral material of the clay type.

2. A method of increasing the antiknock qualities of motor fuels comprising the steps of vaporizing the fuel in a primary heating zone without substantial pyrolytic decomposition and superheating the vapors above 600° F. in a subsequent heating zone and, while substantially at such temperature and without substantial condensation, passing the vapors through a mineral material of the clay type.

3. A method of increasing the antiknock qualities of motor fuels comprising the steps of vaporizing the fuel in a primary heating zone without substantial pyrolytic decomposition and superheating the vapors to temperatures ranging from 600° F. to 1500° F. in a subsequent heating zone and, while substantially at such temperatures and without substantial condensation, passing the vapors through a mineral material of the clay type.

4. The method of increasing the anti-knock qualities of motor fuel comprising the steps of vaporizing petroleum oil, fractionating said vapors, withdrawing fractions suitable for use as motor fuel from the fractionating stage, superheating said fractions above their normal vapor temperatures, passing said superheated fractions while substantially at such temperatures and without substantial condensation through mineral matter of the clay type whereby motor fuel having antiknock qualities is produced, and condensing said vapors.

In testimony whereof we affix our signatures.

WALTER MILLER.
ALFRED HENRIKSEN.
PAUL ZURCHER.