

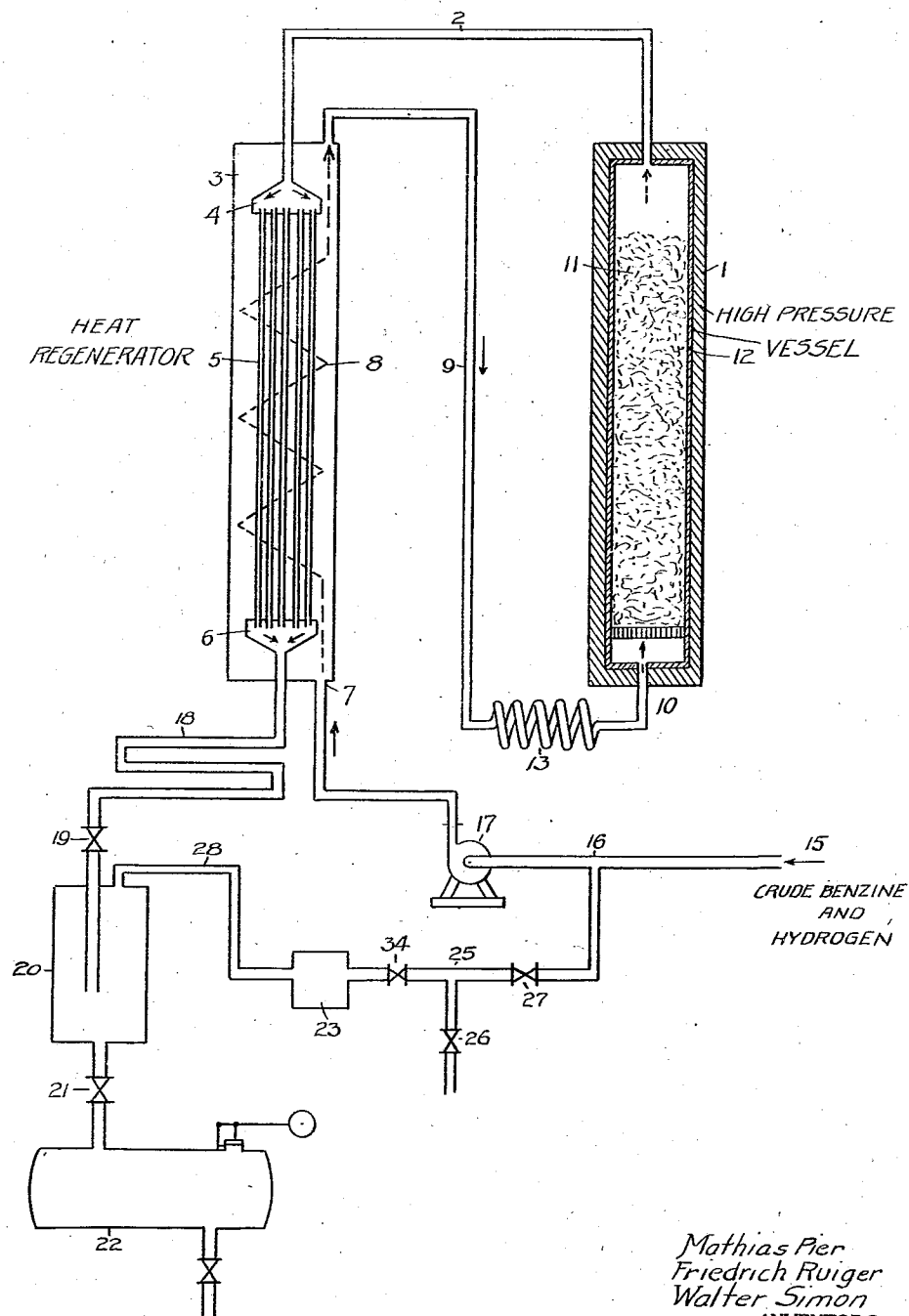
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M. PIER ET AL

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PRODUCTION OF REFINED HYDROCARBON OILS

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Mathias Pier
Friedrich Ruiger
Walter Simon
INVENTORS

BY
Hauffell Warlow
ATTORNEYS

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PRODUCTION OF REFINED HYDROCARBON OILS

Mathias Pier, Heidelberg, and Friedrich Ringer and Walter Simon, Ludwigshafen-on-the-Rhine, Germany, assignors, by mesne assignments, to Standard-I. G. Company, Linden, N. J., a corporation of Delaware

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This invention relates to the purification of crude petroleum hydrocarbon oils, and has for its object to produce refined hydrocarbon oils, in particular refined motor fuels, burning oils, lubricating oils and the like.

The crude light, middle or heavy mineral oils, such as crude benzine, crude illuminating oil, crude gas oil and the like when obtained by distillation, cracking or destructive hydrogenation without catalysts, preferably under pressure, according to the nature and origin of the initial materials, contain more or less sulfur, in particular in the form of organic compounds, and other constituents which are disadvantageous and especially so when the said materials are to be employed as motor fuels or burning oils. The known refining methods by use of chemicals, such as acids and alkalis lead to considerable waste. Refining by means of adsorption agents, such as fuller's earth and the like has also been attempted, but the results as a rule are unsatisfactory.

We have now found that motor fuels and burning oils practically free from sulfur and directly suitable for use may be obtained from crude petroleum hydrocarbon oils by which are meant for the purposes of the present invention natural or synthetic crude mineral oils or fractions thereof, such as crude benzine, crude petroleum, gas oil and the like, by subjecting these in the form of vapor or in the liquid phase together with hydrogen or gases containing or supplying the same, and at temperatures above 300° C. and under a pressure of at least 10 atmospheres, to the action of catalysts which are immune against poisoning by sulfur, and in such a manner and also for such a period of time that no appreciable formation of low-boiling and gaseous hydrocarbons occurs. The temperature and pressure employed depend on the particular materials to be treated or on the sulfur content of the same as well as on the kind of catalyst employed and on the duration of the treatment. As a rule the tendency to the formation of gaseous hydrocarbons and such of low boiling point will increase with the duration of the treatment. The duration of the treatment then must be so correlated with the temperature and pressure that substantially no decomposition of the starting material to lower boiling hydrocarbons takes place so that the end product has substantially the same boiling point and viscosity range as the starting material.

It will be a relatively simple matter for a person skilled in this art to properly coordinate the

conditions of the process to attain the above result. The gases issuing from the reaction chamber may, for instance, be analyzed to determine the content of hydrogen sulphide therein. If the process is being effected in a continuous manner, it will be necessary to increase the duration of the treatment when an analysis shows a decrease in content of the hydrogen sulphide and water in said gases. The increase in the duration of the treatment may be effected by passing the starting material more slowly through the reaction vessel so that it remains in contact with the catalyst for a longer period of time.

The starting material is also analyzed to determine its content of sulphur and oxygen whereby the degree of desulphurization can easily be determined from said gas analysis. Whether any substantial decomposition of the starting material takes place can be determined by an examination of the boiling point curve of the products issuing from the process or by ascertaining the molecular weight of these products.

Applicants of course realize that persons skilled in this particular art will be in a position to devise other suitable methods for controlling the reaction conditions. They do not, therefore, propose to be limited to the method discussed just above.

The process may be carried out at temperatures of about 300° C. or more, but preferably not above 420° C. Pressures of 20 atmospheres or more are usually employed, but it is also possible to use higher pressures, for example 100, 200 atmospheres or more. By carrying out the process under these conditions besides the unsaturated compounds present, the sulfur compounds which are also present as a rule, react with hydrogen with the formation of hydrogen sulfid.

As catalysts immune to sulfur poisoning particularly suitable for the purposes of the present invention may be mentioned catalysts comprising compounds containing sulfur in combination, for example metallic sulfids, in particular the heavy metal sulfids and more especially those of the iron group, either alone or as mixtures with one another or with other materials of a catalytic or of inert nature. The sulfur may also be introduced into the catalyst by the addition of sulfur to metals or oxids. A very suitable catalyst may be obtained by treating iron with hydrogen sulfid at an elevated temperature. Particularly suitable catalysts of this class are for example cobalt sulfid, iron sulfid, zinc sulfid, nickel sulfid, manganese sulfid and the like or mixtures thereof, for example, mixtures of cobalt sulfid

with nickel sulfid or of cobalt sulfid with manganese sulfid, or of cobalt sulfid mixed with iron sulfid, or with zinc sulfid or with aluminium sulfid, with or without an addition of inert substances. Catalysts consisting of or containing metals of the sixth group of the periodic system, such as, molybdenum, chromium, uranium or tungsten or the compounds thereof or mixtures of those substances are also particularly suitable.

As examples of this type of catalyst may be mentioned molybdic acid or ammonium molybdate, molybdic nitrid, molybdenum phosphate, tungsten sulfid, tungstic acid, tungstic nitrid, tungstic selenid, chromium hydroxid, chromium acid and uranium oxide, furthermore, mixtures containing molecular proportions of molybdic acid with magnesia or with aluminium hydroxid, or mixtures of tungstic acid with zinc oxid or of vanadium oxid with magnesia furnish good results. Excellent catalysts are likewise molybdic acid with about 10 per cent of chromium oxid or of vanadium oxid, molybdic acid with about 10 per cent of uranium oxid or of thorium oxid or of manganous oxid, furthermore, tungstic acid containing about 10 per cent of chromium oxid or of a mixture of uranium oxid, cobalt and a small amount of chromium oxid. Mixtures of chromium or tungsten with other hydrogenating catalysts such as with cobalt, nickel or iron which are not themselves immune to sulphur poisoning may also be employed. Activation of the catalysts or the addition of substances increasing their mechanical strength may also be of advantage. Carriers such as lumps of aluminium silicate may also be employed with advantage. As further catalysts may be mentioned oxidic catalysts containing oxides which are difficult to reduce, such as, zinc oxid, chromium oxid or manganese oxid or vanadium oxid or mixtures of these. These said oxidic catalysts may be employed in conjunction with other substances such as lumps of fire-clay, quartz, asbestos, pumice, coke, active charcoal, metals, in particular heavy metals, oxids, sulfids, carbids and the like and mixtures thereof with the said substances. Further may be mentioned catalysts containing vanadium oxid or thorium oxid or cobalt oxid or a mixture of compounds of uranium and zinc or of silver and tungsten. As further suitable catalysts may be mentioned catalysts containing active charcoal or active silica or halogens.

The duration of treatment ranges about between 10 and 100 seconds with reference to each particle of initial material to be treated. The said duration is dependent on the temperature and pressure and the nature of the catalyst, further also somewhat on the dimensions and the form of the reaction vessels.

Besides benzines and middle oils obtained by distillation or slow combustion, other initial materials may be employed, in particular liquid products of the nature of benzines or illuminating oils obtained by destructive hydrogenation, preferably under pressure, and without the employment of catalysts, or by cracking.

The benzines and oils obtained in accordance with the present invention are practically free from sulfur and other substances which produce resinous deposits or unpleasant odors when burning, and can advantageously be employed for operating motors as well as for burning oils.

The process is particularly suitable for refining crude lubricating oils and for the production of oils for Diesel engines. This is more particularly the case, since according to the process

of the present invention, destructive hydrogenation of fractions coming into question for use as oils for Diesel engines takes place whilst decomposition to hydrocarbons of low boiling point range is substantially avoided. The process may, for example, be carried out in such a manner that fuels having a boiling point range rendering them suitable for employment as oils for Diesel engines which burn slowly in the engine are treated in the presence of catalysts having a hydrogenating action. A suitable initial material for the production of Diesel oils may for example be obtained by dividing oils obtained by the destructive hydrogenation of coal into constituents, which are rich in hydrogen and such which are poor in hydrogen, for example with the aid of sulfur dioxide and the like and then treating the constituents poor in hydrogen according to the process of the present invention. Thus a valuable oil for Diesel engines may be obtained, for example from coal tar.

An apparatus suitable for carrying out the process according to the present invention is illustrated diagrammatically in elevation and partly in section in the accompanying drawing, though it should be understood that the invention is not limited to refining carried out in the specific form of apparatus illustrated.

A mixture of crude benzine and hydrogen is introduced into the plant at 15 and is compressed to the necessary pressure by means of the compressor 17. Preferably the pressure should be about 40 atmospheres. The mixture then passes at 7 into the heat regenerator 3 and is passed around the pipes 5 in the manner indicated by the dotted line 8. The mixture thus preheated is then passed by way of the pipe 9 to the heating coil 13 in which it attains the temperature requisite for the reaction, for example a temperature of about 350° C. Then the mixture is passed at 10 into the high pressure reaction vessel 1 provided with the lining 12 of highly alloyed chromium steel. The said reaction vessel is filled with a catalyst, immune from poisoning by sulphur, as for example a catalyst prepared from molybdic acid and magnesium oxide. The rate of flow is adjusted so that substantially no decomposition of benzine takes place, for example the rate of flow may be adjusted at 0.5 liter of vaporized benzine per hour per liter of reaction space. The refined mixture passes off from the reaction vessel by way of the pipe 2 into the heat regenerator 3. The products are passed through the header 4 into the tubes 5 and thence into the header 6. Thereupon they are passed through the condenser 18 and the pressure release valve 19 into the stripping vessel 20. The liquid products are drawn off through the valve 21 into the collecting vessel 22. The gases are passed off from the said stripping vessel to the pipe 28 and hydrogen sulphide and other impurities are removed therefrom in the purification plant 23. They are then either recycled by way of valves 24 and 27 to the branch point 16, or drawn off at 25 through valve 26.

The following examples will further illustrate how the invention may be carried into practical effect but the invention is not restricted to these examples.

Example 1

Crude benzine, obtained by destructive hydrogenation of brown coal without the employment of catalysts having an iodine value of 106 and

a sulfur content of about 1 per cent, which becomes black after standing in light for one or two days, and which can only be rendered fit for use as a motor fuel by means of a wasteful refining process, is passed at 200 atmospheres pressure and at a temperature of 375° C. over a catalyst consisting of molybdenum trioxid and zinc oxid which have been treated with magnesia. The treatment is carried out for about 50 seconds.

The product has an agreeable benzine-like odor and is stable to light. The iodine value has decreased to 15 and the sulfur content amounts to less than 0.1 per cent. The formation of wasteful gas is not appreciable.

The molybdenum in the catalyst may be replaced by tungsten, and a catalyst containing molybdenum and chromium or compounds of the same, or cobalt compounds may also be advantageously employed.

Example 2

Benzine obtained by destructive hydrogenation of Panuco crude oil without the employment of catalysts, which contains 0.5 to 1 per cent of sulfur and has an iodine value of 80 to 100, is passed for a period of about 100 seconds in a stream of hydrogen at 400° C. and at a pressure of 50 atmospheres over a catalyst consisting of a mixture of molybdic acid and molybdenum sulfid.

The benzine obtained has an iodine value of 20 to 25 and a sulfur content of 0.07 per cent.

A catalyst obtained by treating molybdenum oxid with hydrogen sulfid at elevated temperatures and containing about 25 per cent of sulfur may be employed.

Example 3

A dark colored, unrefined benzine, obtained by destructive hydrogenation of brown coal tar without the employment of catalysts, with an iodine value of 108 and a sulfur content of 0.75 per cent is passed at 400° C. and under a pressure of 200 atmospheres with hydrogen over a catalyst containing molybdenum and zinc. The time of treatment is about 30 seconds. A colorless benzine with an iodine value of 17 and a sulfur content of 0.006 per cent is obtained.

In a similar manner, middle oil obtained by destructive hydrogenation of brown coal without the employment of catalysts, having an iodine value of 100, and a sulfur content of about 1 per cent yields a colorless product containing about 0.04 per cent of sulfur, and suitable for the preparation of illuminating oil. Instead of the catalyst described cobalt oxid or cobalt sulfid may be employed.

Example 4

Benzine, obtained by distillation from Panuco crude oil, with an iodine value of 22.9 and a sulfur content of 0.6 per cent is passed together with hydrogen at 400° C. and under 150 atmospheres pressure, over a catalyst consisting of molybdic acid and zinc oxid. The operation is carried out for about 75 seconds. A colorless, agreeably smelling benzine, stable to light and containing 0.02 per cent of sulfur is obtained. The iodine value is 14.4. A sulfid catalyst may be employed instead of the oxid catalyst.

The benzine obtained from Panuco crude oil may be replaced by middle oil obtained by distillation from Panuco crude oil, and under similar conditions the sulfur content is reduced from

1.5 per cent to 0.05 per cent. Practically no formation of benzine occurs.

Example 5

An unrefined American cracked benzine with an iodine value of 120 is passed for about 20 seconds at 420° C. and at 200 atmospheres pressure over a catalyst consisting of molybdenum trioxid. The product is colorless and stable to light without further refining. The iodine value is 21.5.

Example 6

A highly unsaturated benzine, obtained from American shale oil, containing about 2 per cent of sulfur, is passed for about 30 seconds in a stream of hydrogen and at 400° C. and at 200 atmospheres pressure over a tungsten trioxid catalyst. An almost colorless product which is stable to light and has an iodine value of 25 and a sulfur content of 0.03 per cent, is obtained, which may be employed as a motor fuel.

In a similar manner benzenes and the like obtained from Esthonian shale may be refined.

Example 7

Crude lubricating oil obtained by distillation of brown-coal tar is passed together with hydrogen at 380° C. and at 200 atmospheres over a catalyst consisting of molybdic acid and molybdenum sulfid. The duration of treatment is about one minute. A good yield of a resin-free lubricating oil, with no appreciable formation of low-boiling hydrocarbons, is obtained, which may be advantageously employed as an engine oil.

The refining of the said crude lubricating oil can only be carried out with considerable waste by the known methods.

Example 8

A crude lubricating oil obtained from brown coal low-temperature carbonization tar by fractional distillation and which according to the ordinary method of working could only be refined with great difficulty and with considerable losses, is passed together with hydrogen in the liquid phase at about 400° C. and under a pressure of 200 atmospheres at such a rate over a catalyst which has been obtained from zinc oxid, magnesia and molybdic acid, that no decomposition to products of lower boiling point takes place. In this manner mainly a lubricating oil having a character of a middle engine oil with an acid number of 1.3 is obtained which is directly suitable for use without any substantial further refinery. A catalyst produced from zinc oxid and chromic acid may also be employed in place of the catalyst mentioned.

Example 9

A fraction of an American crude oil boiling above 325° C. is passed in a current of hydrogen and in the liquid phase at 420° C. and under a pressure of 200 atmospheres in the liquid phase over a rigidly arranged catalyst, which has been obtained from molybdic acid, manganous oxid and chromic acid at such a rate that the product obtained contains practically no benzine. The said product consists to the extent of more than 50 per cent of constituents rich in hydrogen boiling between 200 and 325° C. and having a specific weight 0.835 to 0.840 and is particularly suitable for employment as a fuel for Diesel engines.

The fuels so obtained are characterized by lack of knocking, and by their anti-knocking action

when mixed with other fuels which have a tendency to knock.

What we claim is:—

1. A process for refining a crude petroleum distillate containing sulphur such as a gasoline, kerosene or a lubricating oil which comprises subjecting said crude distillate to the action of a gas containing hydrogen at a temperature between 300 and 420° C. and a pressure of at least 10 atmospheres in the presence of a catalyst immune to sulphur poisoning selected from the class consisting of metallic sulphides, difficultly reducible metal oxides and metals from group 6 of the periodic system for only such a period of time that no substantial decomposition of hydrocarbons of said crude distillate into hydrocarbons of lower boiling point ensues to thereby remove the sulphur as hydrogen sulphide and produce as end products refined hydrocarbons of substantially the same boiling point and viscosity range as the starting material.

2. A process for the production of refined hydrocarbon oils suitable for direct use as motor fuels from crude gasoline containing sulphur which comprises subjecting said gasoline to the action of a gas containing hydrogen at a temperature between 300 and 420° C. and a pressure of at least 10 atmospheres in the presence of a catalyst immune to sulphur poisoning selected from the class consisting of metallic sulphides, difficultly reducible metal oxides and metals from group 6 of the periodic system for only such a period of time that no substantial decomposition of the hydrocarbons of said gasoline into hydrocarbons of lower boiling point ensues to thereby remove the sulphur as hydrogen sulphide and produce as end products refined hydrocarbons of substantially the same boiling point and viscosity range as the starting material.

3. A process for refining a crude petroleum distillate containing sulphur such as a gasoline, kerosene or a lubricating oil which comprises subjecting said crude distillate to the action of a gas containing hydrogen at a temperature between 300 and 420° C. and a pressure of at least 10 atmospheres in the presence of a catalyst immune to sulphur poisoning and comprising an element selected from the 6th group of the periodic system for only such a period of time that no substantial decomposition hydrocarbons of said crude distillate into hydrocarbons of lower boiling point ensues to thereby remove the sulphur as hydrogen sulphide and produce as end products refined hydrocarbons of substantially the same boiling point and viscosity range as the starting material.

4. A process for refining a crude petroleum distillate containing sulphur such as a gasoline, kerosene or a lubricating oil which comprises subjecting said crude distillate to the action of a gas containing hydrogen at a temperature between 300 and 420° C. and a pressure of at least 10 atmospheres in the presence of a catalyst immune to sulphur poisoning and containing molybdenum for only such a period of time that no substantial decomposition of hydrocarbons of said

crude distillate into hydrocarbons of lower boiling point ensues to thereby remove the sulphur as hydrogen sulphide and produce as end products refined hydrocarbons of substantially the same boiling point and viscosity range as the starting material.

5. A process as defined in claim 1 wherein the catalyst comprises a metal from group 6 and a difficultly reducible metal oxide.

6. A process for refining crude benzines containing sulphur obtained by the destructive hydrogenation of crude mineral oils without the use of catalysts, which comprises subjecting said crude benzines to the action of a gas containing hydrogen at a pressure of about 50 atmospheres and a temperature about 400° C. in the presence of a catalyst immune to sulphur poisoning and comprising a mixture of molybdic acid and molybdenum sulphide for only such a period of time that no substantial decomposition of said benzines into lower boiling hydrocarbons ensues to thereby remove the sulphur as hydrogen sulphide and produce as end products refined benzines of substantially the same boiling point and viscosity range as the starting material.

7. An improved process for producing higher grade lubricating oils in relatively large yields from lower grade petroleum, comprising subjecting the lower grade oil to the action of hydrogen in the presence of catalysts immune to sulphur poisoning at a temperature lying within the range of temperatures usually employed in liquid phase cracking and at a pressure in excess of 10 atmospheres, and limiting the duration of operation so that an improved lubricating oil is obtained of substantially the same viscosity range and boiling point as the starting material.

8. A process for producing refined lubricating oil from crude petroleum oil fractions containing sulphur impurities, comprising subjecting the crude oil to the action of hydrogen in the presence of a compound of a metal in the sixth group at a temperature between the proximate limits 300 and 420° C. and at a pressure in excess of 10 atmospheres for so long a time that an improved oil is obtained of substantially the same boiling point and viscosity range as the starting material.

9. A process for refining a crude petroleum distillate containing sulphur, such as a gasoline, a kerosene or a lubricating oil which comprises subjecting said distillate to the action of a gas containing hydrogen in the presence of catalysts immune to sulphur poisoning at a temperature lying within the range of temperatures usually employed in liquid phase cracking and at a pressure in excess of 10 atmospheres for only such a period of time that no substantial decomposition of the hydrocarbons of said crude distillate into hydrocarbons of lower boiling point ensues to thereby remove the sulphur as hydrogen sulphide and produce as end products refined hydrocarbons of substantially the same boiling point and viscosity range as the starting material.

MATHIAS PIER.

FRIEDRICH RINGER.

WALTER SIMON.