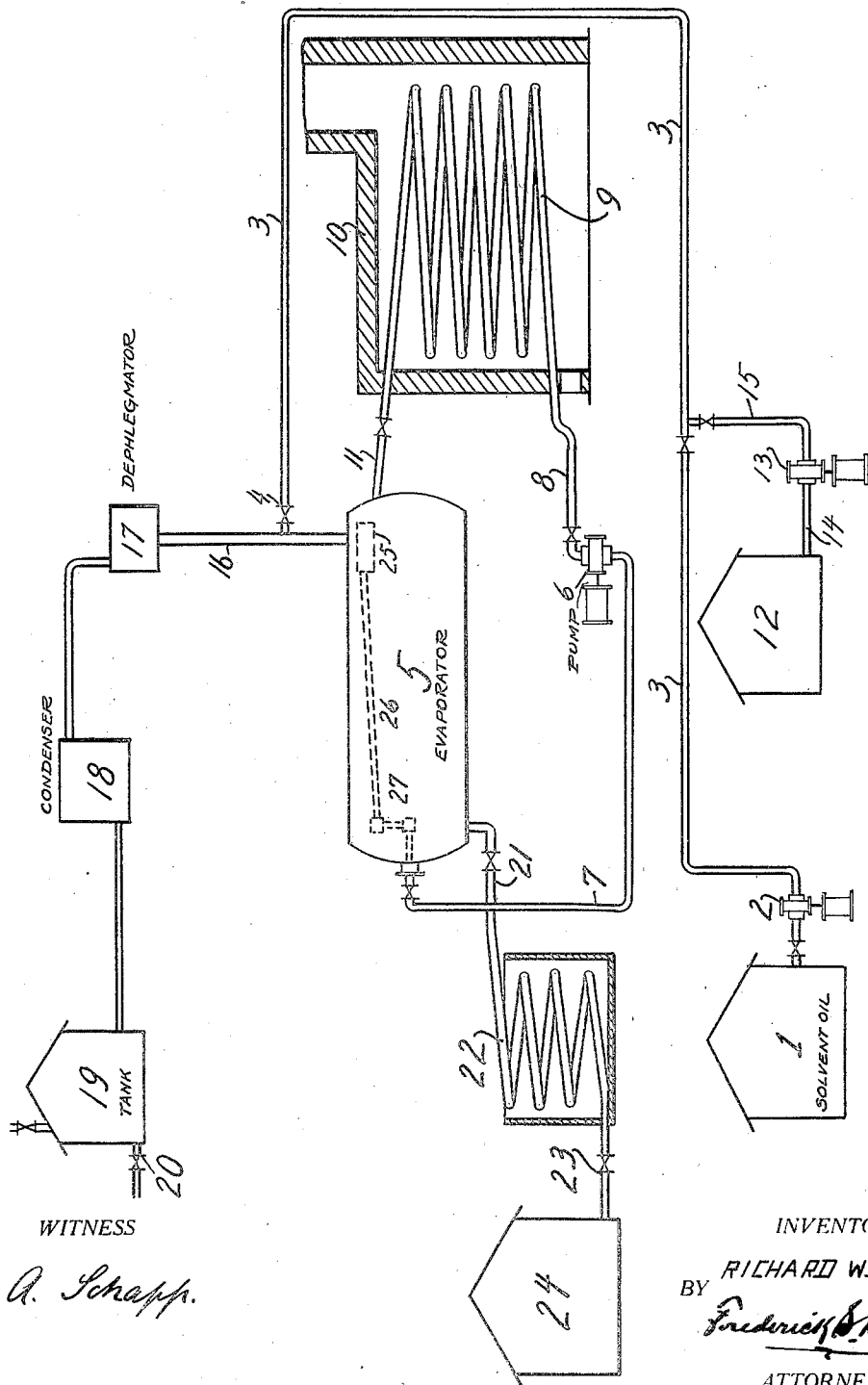


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PROCESS FOR THE CONTINUOUS PRODUCTION OF LOW BOILING POINT HYDROCARBONS FROM
PETROLEUM OILS.

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WITNESS

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PROCESS FOR THE CONTINUOUS PRODUCTION OF LOW-BOILING-POINT HYDROCARBONS FROM PETROLEUM OILS.

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Specification of Letters Patent.

Patented Mar. 7, 1922.

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To all whom it may concern:

Be it known that I, RICHARD W. HANNA, a citizen of the United States, residing at Richmond, in the county of Contra Costa and State of California, have invented a new and useful Process for the Continuous Production of Low-Boiling-Point Hydrocarbons from Petroleum Oils, of which the following is a specification.

10 My invention relates to the art of producing low-boiling point hydrocarbons from higher boiling point petroleum oils or distillates.

15 This invention provides a process whereby a substantially uniform low-boiling point hydrocarbon oil is continuously produced during the operation, without the deposit of carbons, solid hydrocarbons or tarry residues in the heating element.

20 This invention also provides a process whereby all of the solid hydrocarbons of tarry residues resulting from the cracking are kept in solution or suspension by a solvent oil and finally discharged from the apparatus.

25 I have discovered that in the cracking of hydrocarbon oils to produce low-boiling point oils carbon is produced in successive steps, primarily in the form of tarry bodies, and later by the further reduction of these tarry bodies carbon in the more concentrated forms is produced. I have found that if the formation of these tarry bodies or the further reduction thereof towards carbon can be controlled and the resultant relatively high boiling point fractions held substantially in solution, the cracking may be carried on substantially continuously, without the deposition of carbon.

40 By maintaining in the apparatus or system such a proportion of solvent oil in connection with the oil to be cracked that immediately upon the primary reduction of the oil to be cracked to relatively low boiling point oil, this solvent oil immediately holds in solution the relatively high boiling point oil or fraction produced by such cracking, so that it may be discharged from the apparatus without deposition therein.

50 Following is a detailed description of my preferred embodiment of the invention:

In its preferred form of embodiment, my

process consists in maintaining in the apparatus during the operation a substantially constant volume of the oil to be treated, continuously withdrawing the low-boiling point fraction as produced, substantially continuously withdrawing the residual oil which contains the solid hydrocarbons or tarry residues in solution or suspension, and maintaining a substantially constant pressure and temperature throughout the system.

According to present day practice, the cracking of petroleum oils is accompanied by the deposition of carbons solid hydrocarbons and the accumulation of tarry residues within the heating element of the system. The deposition and accumulation of these substances upon heated surfaces retard the conduction of heat through the metal which not only results in the loss of heat, but also in a slow destruction of the metal due to an over heated condition which in time results in the destruction of the apparatus. Also such an apparatus cannot be operated continuously as it must be shut down at intervals to clean out this accumulation, with the resultant loss of time, capacity, and efficiency.

In common practice, the oil undergoing cracking is either contained in a still, capable of withstanding a predetermined pressure, and to which the heat is directly applied or it is circulated from a reservoir through an auxiliary heating element. In either case the process is not continuous and is always accompanied by the deposition of solid hydrocarbons which must be removed at the end of each run, and the apparatus renewed after a certain period of time.

In the preferred embodiment of my invention, I overcome these difficulties by substantially continuously removing from the heating element the solid hydrocarbons and tarry residues, resulting from the decomposition of the oil therein, by the continuous introduction of a solvent oil which dissolves and keeps in solution said solid hydrocarbon and tarry residues thus preventing a deposition on the metallic surfaces of the system.

The primary feature of my method is the continuous removal of all the solid hydrocarbons and tarry residues from the heating element by the employment, conjointly

with the oil to be cracked of a continuously circulating medium relatively non-crackable. That is to say, using in conjunction with the oil to be cracked another oil which is relatively stable at the pressure and temperature of the operation, whereby solid hydrocarbons and tarry residues resulting from the cracking are held in suspension or solution without being allowed to deposit.

In practice this solvent oil which I have termed "non-crackable" may be any hydrocarbon oil which is stable to the heat and pressure employed in the process. To illustrate my invention such a stable oil may, for example, be a distillate from the so-called refractory California crude oil which is an oil of relatively low boiling points containing an unusually high percentage of naphthene and aromatic hydrocarbons, or it may be any lower boiling point fraction of the same, or any other oil, which will be substantially unaffected at the pressure and temperature employed in the cracking of the particular oil operated upon.

It is also to be understood that my method is not confined to the use of any particular non-crackable or solvent oil either produced in the system or added from any outside source, the herein mentioned oils being given merely as an example of a circulating medium relatively unaffected by the pressure and temperature required to crack the oil to be treated.

With the foregoing preliminary explanation the preferred embodiment of my method will now be more fully described, by reference to the accompanying drawing showing an apparatus in which it may be carried out.

In the drawing is shown a general diagrammatic view of such an apparatus, in which 1 represents a storage vessel for the "solvent" oil. 2 is a pump for handling this stock and 3 is a pipe connecting through a valve 4 with a vessel 5 I term an "evaporator." 6 is a circulating pump connecting, on its suction side, with a pipe 7 from the evaporator 5 and on its discharge side with a pipe 8 leading to the heating element, which is here shown as a coil 9 in a furnace 10, said coil 9 leading through a pipe 11, back to the evaporator. 12 is a reservoir for the oil to be cracked. 13 is a pump connected by a pipe 14 with the reservoir 12 and by a pipe 15 with the solvent oil pipe 3. 16 is the vapor line from the evaporator 5. 17 is a dephlegmator in said line 16. 18 is a condenser connected with said dephlegmator. 19 is a receiver connected with the condenser and 20 is a valve where pressure is released and the condensate delivered for storage. 21 is a discharge pipe from the evaporator 5. 22 is a cooler to which pipe 21 leads. 23 is a discharge valve from the cooler, and 24 is

a reservoir. 25 is a receiving pan connected to a pipe 26. 27 is a T with an open end into evaporator 5 and connected through the end of evaporator 5 to the pipe 7, the suction side of circulating pump 6. Preferably the fresh stock-to-be-cracked and solvent oil drop into the pan 25 and are conducted by the pipe 26 through the T 27 and then mix with the suction from the evaporator 5 in the suction pipe 7 of the pump. The pipe 26 is connected with one end of the T and the suction pipe 7 with another opening, leaving the third opening open into the liquid in the evaporator 5. Obviously, the vapor space can never extend below the opening of the T into the evaporator 5. Preferably the vapor space of the evaporator is approximately one-third; the liquid two-thirds filling the evaporator to ensure positive suction to the pump at all times.

My method may be carried out in this apparatus as follows:

Preferably in starting the operation the evaporator 5 may be charged to a predetermined level, leaving suitable vaporization space, from the storage vessel 1, by the pump 2, through the pipe 3, with the solvent oil, which in practice is a relatively non-crackable oil, by which is meant an oil not subject to cracking under the pressure and temperature required for cracking the oil to be treated, from which latter relatively low boiling point fraction is to be obtained by distillation. When the evaporator 5 has been charged with the solvent oil as aforesaid, the circulating pump 6 is started, causing said solvent oil to circulate from the evaporator 5, through the T 27, pipe 7, pump 6, pipe 8, heating element coil 9, and pipe 11 back to the evaporator 5.

Heat is then applied to the coil 9, and the total charge of solvent oil is heated and during this period, a certain amount of the oil to be cracked is fed from the reservoir 12, by the pump 13 and pipes 14, 15 and 3, into the evaporator 5, and a pressure of vapor sufficient to permit the oil to be raised to the required temperature for cracking is developed.

From the reservoir 12 the oil to be cracked is pumped by means of pump 13 through line 15 into line 3 where it meets and is mixed with the solvent oil supplied to the line 3, from reservoir 1 by means of pump 2. With the apparatus, as indicated in this drawing, from line 3 the oil to be cracked mixed with the solvent oil passes through valve 4 into vapor line 16 where it serves as a scrubber oil for the upcoming oil vapors from evaporator 5 and partly condenses the relatively higher boiling point portions of the vapors and which then mixed together fall into pan 25 and flow through pipe 26 into pipe 7, the suction line of circulating pump 6,

which discharges into line 8 and heating coil 9, where the mixture is brought to the desired temperature to crack the crackable oil into the desired relatively lower and higher boiling point oils. Upon the cracking of the crackable oil into such relatively high and low boiling point fractions the solvent oil immediately takes into solution and holds such higher boiling point fractions, thus preventing their further reduction, while the lower boiling point fractions pass off. From coil 9 the oil products are discharged into evaporator 5, where the low boiling point oil vaporizes and passes into vapor line 16. The vaporized oils passing up through line 16 are scrubbed as heretofore described and pass into dephlegmator 17, which is maintained at such a temperature that the solvent non-crackable oils produced by the destructive distillation and which were not condensed in the scrubbing are now condensed and fall back into pan 25. The desired low boiling products pass from dephlegmator 17 into condenser 18 where they are condensed and flow into receiver 19.

From the evaporator 5 the solid hydrocarbons and tarry residues in the solvent oil are discharged through the valve 21 and cooler 22, valve 23 and into receiver 24 at such rate as to keep the saturation of the solvent oil with the heavy hydrocarbons and tarry residues below such a degree of concentration that upon further circulation and heating such solvent oil may take into solution the further high boiling point fractions produced from the crackable oil without permitting the heavy hydrocarbons to become too concentrated in the apparatus. If the solvent oil is permitted to become overcharged with such heavy hydrocarbons deposition takes place as these heavy hydrocarbons take the brunt of the heat and unless held in solution by the solvent oil become further reduced to carbon. The degree of concentration, (of the solvent oil and high boiling point fractions produced by the cracking of the crackable oil,) which may be permitted in the system without danger of deposition will, of course, depend upon the oils charged into the system, as for example, the carbon residue test should not exceed ten times that in the charged oils. This is merely an example and will vary with the oils.

In the cracking of certain petroleum distillates there may be produced from the operation sufficient solvent or non-crackable oil of unsaturated form to keep the solid hydrocarbons and tarry residues in solution so that no deposit will form on the metal surface of the heating element, in which case it is unnecessary to add a solvent or non-crackable oil from an outside source. I, therefore, do not limit myself to the use of a solvent or non-crackable oil to be introduced

from an outside source, since sufficient may be produced in the operation when certain petroleum oils are used.

A certain amount of non-crackable or solvent oil passes off with the solid hydrocarbons and tarry residues in solution, which is replaced from the storage as needed.

As an example of the proportion of oil to be treated with the solvent oil, I add one volume of the former to as much as three or five volumes of the latter in the system at any moment; and as an example of a desirable cracking pressure and temperature for the oil to be cracked, I give 105 to 120 pounds absolute and 745-800° F., but it is to be understood that these proportions and the pressure and temperature may vary according to the oils used.

In the foregoing example I have described the starting and charging of the apparatus with solvent oil and the introduction of the oil to be cracked into the system to produce and secure the required pressure and temperature. In practice the solvent oil and the oil to be cracked may be mixed and thus introduced, not only in charging the apparatus for starting distillation but also in continued operation.

It is also obvious that any relatively low boiling point oil may be used as the solvent oil provided it is substantially unaffected at the pressure and temperature of the operation.

By constantly feeding into the apparatus or system such a quantity of solvent oil and oil to be cracked as will maintain a substantially constant volume in the apparatus and maintain continuous cracking at substantially the determined pressure and temperature a substantially uniform fraction is continually produced during the operation of the apparatus.

While I have thus referred and do hereafter refer in the claims to the solvent oil and the oil to be cracked as two oils it will be understood that I do not limit my invention to the use of two distinct oils, but include as within my process and invention the cracking of any oil which contains fractions, one of which will be cracked at a given pressure and temperature and another fraction which will be substantially unaffected by such pressure and temperature and which will act as a solvent oil as heretofore explained.

It also is to be understood that my method is not confined to the use of any particular solvent oil, the distillate from refractory California crude mentioned being given merely as an example of a solvent oil relatively unaffected by the pressure and temperature required to crack the oil to be treated.

Finally, it is to be understood that my method is not confined to its accomplishment

in the particular apparatus shown, as this may be varied, and no claim is herein made to said apparatus, as it forms no part of the present application.

5 I claim:

1. The process of producing a low-boiling point fraction of a petroleum oil from a relatively higher boiling point oil, which consists in continuously circulating through
10 a closed system, conjointly with the oil to be cracked, a solvent oil of lower boiling point than the oil to be cracked and which solvent oil is practically unaffected at the temperature and pressure required to crack
15 said first-mentioned oil, maintaining in said system a pressure and temperature required to crack said oil, continuously passing out of the system the low boiling point vapor from the cracked oil, whereby the heavy
20 derivatives from said cracked oil are taken into solution by said solvent oil, and discharging said solvent oil solution as required to prevent deposition of carbonaceous matter in the system.

2. The improvement in cracking petroleum oils which consists in continuously circulating through a closed system, conjointly with the oil to be cracked, a solvent oil of lower boiling point than the oil to be cracked
30 and which solvent oil is practically unaffected at the temperature and pressure required to crack said first-mentioned oil, maintaining in said system a pressure and temperature required to crack said first-mentioned oil, continuously passing out of
35 the system the low boiling point vapor from said cracked oil, and continuously removing from said system the resultant solvent oil solution.

3. In the method of cracking petroleum oils, that step which consists in continuously circulating, conjointly with the oil to be cracked, a solvent oil under conditions of pressure and temperature adapted to crack
45 only the first named oil, whereby the relatively high boiling point derivatives of cracking are carried in solution by said solvent oil, said solvent oil being a lower boiling point oil than the oil to be cracked.

50 4. The process of producing a low boiling point fraction from a petroleum oil from a relatively higher boiling point fraction, which consists in continuously circulating through a closed system an oil under a substantially uniform pressure and temperature
55 adapted to crack a relatively high boiling point fraction of such oil but insufficient to crack a lower boiling point fraction of such

oil, utilizing such lower boiling point fraction as a solvent in volume sufficient to dilute
60 the higher boiling point derivatives of cracking to substantially prevent further reduction thereof ultimately to carbon, continuously withdrawing the resultant low boiling point vapor produced, maintaining a
65 substantially constant volume of oil in the system, and keeping the resultant solution by dilution and discharge from becoming sufficiently concentrated to cause deposition in the system.

5. The process of producing a substantially uniform low boiling point fraction from petroleum oil, which consists in rapidly continuously circulating an oil in a closed system, maintaining a substantially constant
75 volume of oil in the system, maintaining a substantially constant pressure and temperature in the system, whereby a high boiling point fraction of such oil is cracked and a lower boiling point fraction of the original
80 oil is used as a solvent for the resultant high boiling point derivatives of cracking produced from such first-named high boiling point fraction, continuously withdrawing the resultant low boiling point vapor, and
85 keeping the resultant solution by dilution and discharge from becoming sufficiently concentrated to cause deposition in the system.

6. The process of producing a low boiling
90 point fraction from a petroleum oil from a relatively higher boiling point oil, which consists in continuously circulating through a closed system, conjointly with the oil to be cracked, a solvent oil of lower boiling
95 point than the oil to be cracked and which solvent oil is practically unaffected at the temperature and pressure required to crack said first mentioned oil, maintaining in said system a pressure and temperature required
100 to crack said oil, continuously passing out of the system the low boiling point vapor from the cracked oil, whereby the heavy derivatives from said cracked oil are taken into solution by said solvent oil, and keeping the resultant solution by dilution with said solvent oil and by discharge of solution from becoming sufficiently concentrated to cause the reduction to carbon of such heavy
105 derivatives.

Signed at Richmond, Cal., this 12th day
of December, 1919.

RICHARD W. HANNA.

Witnesses:

ALL ELLISTE,
W. D. MASON.