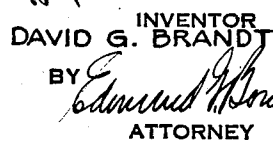


2,316,931

Filed May 14, 1940



UNITED STATES PATENT OFFICE

2,316,931

CONTINUOUS PROCESS FOR CRACKING AND
POLYMERIZING PETROLEUM OILSDavid G. Brandt, Westfield, N. J., assignor to
Cities Service Oil Company, New York, N. Y., a
corporation of Pennsylvania

Application May 14, 1940, Serial No. 335,059

12 Claims. (Cl. 196—58)

This invention relates to a continuous process for cracking and polymerizing petroleum oils by subjecting heavy residual types oils to high temperature and pressure conditions adapted to crack portions of the oil to produce gasoline, and polymerize other portions to produce a stock of high specific gravity suitable for the production of petroleum coke.

Many cracking processes produce both high and lower molecular weight hydrocarbons from the charging stock, and many coking processes have been developed for coking cracking still residuums. Some combined cracking and coking processes have been developed in which the charging stock heated in a pipe still furnace is alleged to be converted into vapors and a non-flowing carbon residue, the latter of which is collected in an enlarged coke chamber. In many of the cracking operations in which coke is produced from petroleum oil, the coke is mostly of low marketable quality, and in such processes there seems to be no consistent effort to control the quality of the coke either from the standpoint of its marketability or from the standpoint of producing a coke which can be removed from the coking chamber in a satisfactory manner. Efforts directed to the control of the cracking operation have been largely toward increasing the quality or quantity of the gasoline produced.

The primary object therefore of the present invention is to provide an improved process for cracking and polymerizing residual petroleum oil stocks to produce a hydrocarbon stock of high specific gravity which can be converted into a marketable coke.

A further object of the invention is to provide an improved continuous process for simultaneously producing gasoline and a petroleum tar or pitch of high specific gravity which is converted into marketable petroleum coke.

A still further object of the present invention is to provide an improved polymerization and cracking process for converting residual petroleum stocks into gasoline and a residue of high specific gravity suitable for coking, in which the various features of the process are correlated to produce lighter oils and marketable coke from the stock, with of course the incidental production of some gas.

Accordingly, the improved process of the present invention comprises the step of passing a heavy charging stock such as a topped crude petroleum (preferably mixed with a small proportion of hydrated lime where the oil is cor-

rosive, to prevent corrosion in the apparatus), through a heating zone comprising a heat exchanger coil mounted in a fractionating tower wherein the charging stock is heated in indirect heat exchange with vapors produced in the conversion operation, preheating the charging stock to a temperature of approximately 650° F., and subjecting it to pressure cracking and polymerization conditions in an enlarged chamber wherein the stock mixture is passed in intimate contact with high temperature vapors produced in another part of the operation to heat the stock for a substantial period of time to a temperature above 800° F., maintaining a body of the stock in the lower portion of the enlarged chamber to increase the time reaction, cracking and polymerization of stock to produce a residuum having an A. P. I. gravity of from about 2 to 15, conducting the high temperature vapors, after contact with said stock, on through said enlarged chamber and then into the lower portion of said fractionating tower wherein they are subjected to rectification to produce a reflux distillate of high boiling point and the desired lower boiling products, passing a portion of the reflux distillate from said fractionating tower into the upper part of said enlarged chamber in intimate contact with the high temperature vapors passing therethrough, conducting another portion of the reflux distillate from said fractionating tower through a pipe still furnace and therein heating the same to a high conversion temperature at a substantial superatmospheric pressure, conducting the highly heated products from said pipe still furnace through a transfer line and mixing therewith hot heavy liquid oil residue from the lower portion of said enlarged chamber to intimately contact said products, thereafter conducting the resulting mixture into the upper portion of one of a plurality of alternate enlarged coking chambers, separating vapors from unvaporized oil constituents including said residue in said coking chamber and conducting the vapors at a high temperature into the lower portion of said enlarged chamber for effecting said cracking and polymerizing operation, retaining the unvaporized liquid oil residue in said coking chamber to be converted into coke, and removing the vapors from the upper portion of said fractionating tower and recovering the gasoline constituents therefrom.

Other features and objects of the present invention will be apparent to those skilled in the art, from the following more detailed descrip-

tion thereof, taken in connection with the accompanying drawing, in which:

The single figure comprises a vertical arrangement of apparatus elements particularly adapted for carrying out the improved process.

Referring to the drawing, the charging stock to be subjected to the cracking and polymerization treatment, and which preferably comprises topped crude oil or similar residual stock, is conducted from a charge supply tank 2 through a line 4, and forced by means of a pump therein, through a heat exchange coil 6 mounted in and extending through a fractionating tower 8. If the charging stock contains sufficient sulfur or other corrosive materials to cause excessive corrosion of the apparatus, a small portion of lime may be conveniently introduced into the line 4 by a line 10 as a slurry in some of the charging stock. This lime slurry is preferably made up in suitable apparatus, not shown, by mixing a predetermined proportion of hydrated lime with a definite proportion of the charging stock.

The fractionating tower 8 is preferably of the usual bubbler type construction with the convolutions of the coil 6 mounted in the vapor space above the bubbler trays. The tower is preferably operated at a pressure of about 225 lbs. per square inch to condense all of the oil constituents produced in the cracking operation, of higher boiling point than the desired gasoline or pressure distillate product, which is removed overhead in vapor form, along with the uncondensable gases through a vapor line 12. The gasoline constituents are condensed in a condenser mounted in the line 12, and the resulting products are conducted into a gas separator 14, from which the fixed or uncondensable gases are discharged through a suitable pressure valve controlled line, while the gasoline or pressure distillate is discharged through a float valve controlled line, as shown.

By the time the charging stock has passed through the coil 6, it is heated to a temperature of from about 625° to 660° F., at which temperature it is conducted through lines 16 and 18, into the mid-portion of an enlarged pressure cracking and polymerizing chamber 20, in which the charging stock passes downwardly over a series of baffle plates in contact with high temperature vapors produced in another part of the conversion operation. In the normal functioning of the apparatus, the oil stock required for the coil 6 for cooling purposes, is considerably greater than the requirements for the chamber 20, and the process in general, so that a portion of the preheated stock in the line 16 is conducted through a valved line 22 and a cooler mounted therein, back to the charging line 4. Instead of cycling oil through the line 22, the additional cooling in the tower 8 may be effected by other means.

The reflux distillate produced in the tower 8, and which has roughly the boiling range of gas oil, is discharged through a line 24 and forced into other parts of the apparatus by means of a pump mounted therein. A portion of this reflux stock is preferably conducted through a valved line 26 and a cooler mounted therein and passed into the upper portion of the enlarged pressure chamber 20, where it passes in intimate contact with vapors as it flows downwardly over a series of baffle plates in the upper part of chamber 20.

The remainder of the reflux distillate from the tower 8 is conducted on through the line 24 to a pipe still heater 28, where the distillate is conducted at a pressure of approximately 500 lbs. per square inch, first through a convection

tube bank 30, and then through a radiant tube bank 32. In passing through these tube banks, the reflux or stock is heated from an inlet temperature of about 750° F. to a discharge temperature of from about 970° to 1010° F., at which temperature it is conducted through a discharge line 34 into a three-way valve 36, and then through a valved transfer line 38 into the upper portion of an enlarged coking chamber 40, which is one of a plurality of similar chambers used alternately to collect liquid residuum, in accordance with the process of the present invention.

The charging stock introduced into the chamber 20 through line 18 is subjected to relatively high cracking and polymerizing temperatures for a sufficient time to produce a heavy liquid polymer. The resulting mixture of heavy residual stock and lime suspended therein is conducted from the bottom of the chamber 20 through a line 42 and forced by means of a pump mounted therein through a three-way valve 44, and then through a valved line 46, directly into the transfer line 38 beyond the valve therein. The heavy polymerized stock from the bottom of the chamber 20 has a temperature of from 800° to 865° F. and is usually equal to from one-fourth to one-third by volume of the stock passing through the line 34, so that the temperature of the mixture in line 38 will be from about 915°-945° F.

The high temperature products conducted from the line 38 into the top of the coking chamber 40, comprise both liquid and vapor constituents which are separated in the chamber 40, the liquid constituents and lime being retained in the chamber to be later converted into coke, while the separated vapors are conducted through a valved vapor line 48 into a three-way valve 50, and then through a connecting line 52 into the lower portion of the pressure cracking and polymerizing chamber 20. These vapors will have a temperature of from 885° to 900° F., so that they are particularly adapted for use in cracking, polymerizing, and otherwise conditioning the heavy charging stock passed into the chamber 20 through the line 18. After the high temperature vapors contact the charging stock in the lower portion of the chamber 20, and their temperature has been substantially reduced, they are brought in contact with reflux distillate introduced through the line 26. This distillate washes the vapors and holds back occluded heavy hydrocarbons for further reaction, and is in turn largely revalorized because of the high temperature maintained in the chamber 20. The resulting vapor mixture in the top of the chamber 20 is conducted therefrom at a temperature of from 800° to 830° F. through a vapor line 54 and introduced into the lower part of the fractionating tower 8.

The operations carried out in the chamber 20 may be varied in certain details in order to produce a conditioned liquid of high specific gravity at the bottom of the chamber. For example, the control of the reactions in the chamber 20 is more readily effected by passing a portion of the heavy charging stock and lime from the line 16 through a connecting valved line 56 and introducing it directly into the high temperature vapors in the line 52. This has the effect of cooling the vapors in the line 52, contacting them with lime and of lowering the contact temperature in the chamber 20. Furthermore, the quality of the body of high gravity polymerized material collected in the bottom of the chamber 20 is affected by varying the proportions of stock

conducted respectively through the lines 18 and 56.

The cracking and polymerization of the charging stock carried out in the chamber 20 is effected at a pressure of approximately 225 lbs. per square inch, and at a temperature of from 820° to 850° F., so that substantial vaporization is prevented and there is no net loss by vaporization. In a typical operation, topped crude oil charging stock of about 24 A. P. I. gravity was supplied to the chamber 20 in the proportion of about 23 parts through the line 56 to about 57 parts through the line 18. While that portion introduced into the vapor line 52 was cracked and polymerized at a slightly higher temperature from that introduced into the chamber 20 through the line 18, the combined operations produced a product of optimum quality for conversion into a marketable coke. In ordinary practice, a considerable body of material is maintained in the lower portion of the chamber 20 to provide a suitable soaking time under pressure to give a product of from 8 to 11 A. P. I. gravity. This polymerized product contains no coke and very little free carbon, since the cracking and polymerizing operation carried out in the chamber 20 is controlled to avoid coke formation. In conditioning the polymerized material in the chamber 20, it has been found necessary to supply a rather definite proportion of the preheated charging stock to the vapor line 52. Attempts to introduce all of the stock through the line 18 have resulted in the production of a much poorer quality of coke from the polymerized stock.

The transfer line products from the line 38 are continuously introduced into the coking chamber 40 until the chamber has been filled or substantially filled with the conditioned polymerized liquid oil constituents. Thereafter, the transfer line products are directed by the three-way valve 36 through an alternate valved transfer line 58 into the upper portion of a second coking chamber 60 which is of the same structure as the chamber 40, the chamber 60, of course having been freed of coke from any previous use in the system. When the transfer line products are directed through the line 58 by the valve 36, the valve 44 will also be operated to conduct the hot heavy polymers from the line 42 through a connecting line 62 into the line 58, and the three-way valve 50 will be turned to take the vapors from the coking chamber 60 through a valved vapor line 64.

The accumulation of liquid in the chambers 40 and 60 is followed by means of thermocouples (not shown) installed in the chambers at various levels to serve as an indication of the approximate oil level. Thermocouples located in the vapor space will normally read very close to the temperature at the upper part of the chamber, for example, these couples may read from 885° to 895° F. As soon as the liquid level covers one of the thermocouples there is a marked drop in temperature from, say, 885° down to 870° F., so that an operator will know the approximate oil level and how fast the chamber is filling with the conditioned oil.

The three-way valves 36, 44 and 50 are of a well-known type, each of which may, if desired, be set to simultaneously connect into all three of their connecting lines at the same time. This may be desirable, as for example, when chamber 40 is completely cut off from the line 38, the valve 50 may be used to receive vapors from both chambers 40 and 60, and in a heating

up period supply vapors from one chamber to the other.

It will be noted that each of the lines 38, 58, 46, 62, 48 and 64, is provided with independent cut-off valves. These valves are installed as a safety feature to absolutely prevent the entrance of any high-temperature products into the coking chamber which is cut out of the system for cleaning.

The collecting chambers are operated under a superatmospheric pressure of from about 200 to 275 lbs. per square inch, so that immediately after the chamber 40 is cut out of the system and the valves in lines 38, 46 and 48 are closed, the pressure on the chamber is reduced as the first step in effecting the coking of the hot tar collected in the chamber. The pressure reduction is effected by opening a valve in a run-down line 66 which leads to a cooler and sump, not shown in the drawing (the chamber 60 is also provided with a similar line 66). Since the large body of liquid tar in the chamber 40 is at a high temperature, a considerable portion thereof, comprising the lighter constituents, is vaporized upon the reduction in pressure, and such constituents are discharged through the line 66. The pressure in chamber 40 is reduced to substantially atmospheric, and the coking of the body of oil in the chamber is partially effected, but is completed by the introduction of steam into the lower portion of the chamber, followed by the introduction of water.

When either of the chambers 40 or 60 is cut out of the system for coking, and pressure reduced thereon, as for example the chamber 40, steam (not superheated) is supplied from a valved line 68 and conducted through one of the lines 70 which connects into a short line 72 on the bottom of each of the chambers. In the case of a chamber 10 feet in diameter by 40 feet high, steam introduction is gradually increased for about one hour until 15,000 pounds per hour is being supplied. The steaming is then continued for another hour at the rate of 15,000 pounds of steam per hour. If steam is supplied at a lower rate, a longer steaming time should be used, since the steaming is very effective in furthering the coking of the heavy tarry material in the chamber. After the steaming operation has been completed, water is admitted from a valved supply line 74 to complete the coking operation; the water being admitted from the line 74 through lines 70 and 72, into the lower part of the chamber 40. The rate of water supply to the chamber is usually controlled by watching the pressure developed in the chamber and preventing the occurrence of a pressure which will in any way approach that on the water line. In the later stages of the coke production water is introduced into the chamber to effect its cooling down to a point sufficiently low that it may be opened for coke removal.

Coke removal from the chamber 40, and of course, from the chamber 60 when it was cut out of the system, is accomplished by any of the well-known methods or means.

After the chamber 40 has been cleaned of coke, the man-heads are replaced, and the chamber is filled with oil from a supply line 76 which is connected into the lines 70. This oil is the usual charging stock or other oil taken from any source and supplied rapidly to the chamber so as to fill it quickly, after which the chamber is cold tested at a high pressure, in order to insure safe operation, when it is subsequently cut back into the system in place of chamber 60. After the chamber 60 has been filled with the unvaporized tarry

residue conditioned for coking, the chamber 40 is cut back into the system, while it is still filled with the oil introduced from the line 76.

In order to avoid confusion in the supply of steam or water and oil to the lower portions of the chambers 40 and 60, a detachable L-connection 80 is provided for each of the lines 70. This L-connection 80 must be completely detached from the water line 74 or the steam supply 63 before oil can be supplied from the line 76. By changing the L-connection 80 in the manner indicated, it is impossible to supply both oil and water or steam at the same time. There is therefore no possibility of introducing water or steam into a chamber after it has been connected into the cracking system.

A few hours before chamber 60 has become filled with the conditioned tarry residue, and after chamber 40 has been cold tested, the switch valve 50 is partially turned so that the opening in the plug communicates with both chambers 40 and 60. This places full unit pressure on chamber 40, which has been previously filled with cold oil. Oil is then drawn from chamber 40 through lines 72, 77 a valved line 78 and a relief cooler (not shown) in order to slowly lower the level in the chamber. Hot vapors from chamber 60 pass through line 64, switch valve 50 and line 43, into the upper part of the chamber 40, and serve to force the oil out of this chamber and also to pre-heat the chamber. The rate at which oil is withdrawn from the chamber is controlled, so that the chamber will be almost empty by the time chamber 60 has accumulated its charge of hot tarry residue. At this time the three switch valves 35, 44 and 50 are turned simultaneously to place chamber 40 in the system and cut out chamber 60. The residue in chamber 60 is then converted to coke in the manner described above.

When chamber 40 is first cut into the system, it will not have had a chance to become heated to full operating temperature and consequently some of the vapors from line 33 will condense. The condensate collected in chamber 40 is withdrawn when, say 5 feet of oil has accumulated therein. The chamber may not be heated sufficiently when this amount of condensate has been formed, so that a second batch of condensate may be allowed to collect in the chamber. When the vapor temperature at the upper part of the chamber has reached about 890° F., any liquid in the chamber is quickly withdrawn through line 72, and the chamber is finally shut in by closing the valve in line 72. After finally preparing a chamber in this manner, the temperature of the mixed feed entering the chamber is raised about 5° in order to "dry out" the lower portion of the chamber. This latter operation reduces the tarry residue to the proper consistency so that in the subsequent coking operation the bottom of the chamber will contain coke which can be easily broken, instead of a tarry pitch. Although this method for switching chambers has been found very satisfactory and is preferred, other methods may be used. The empty chamber may be heated with superheated steam or other hot fluid prior to switching it into the system.

Repeated investigations have shown that the material collected in the coking chambers from the lines 38 and 53 is fluid, even at the bottom of the chamber. The conditioned and polymerized tarry material introduced into the transfer lines from the chamber 20 is quickly heated in the transfer line to a temperature of about 935° F., so that some further polymerization or condi-

tioning occurs after the material is deposited in the chambers 40 or 60. Samples of the tarry material collected in the chambers 40 or 60 have been removed and examined, and other tests have been made, which show that at the temperatures existing in the chambers the material is fluid. Furthermore, an analysis showed that it contained only about 12% of free carbon at the end of the filling period. The free carbon may run from 9% to about 24%.

As an example of a typical operation of the process, a topped crude oil, having a 24 A. P. I. gravity, was introduced through the line 4, containing 0.75 pound of hydrated lime per barrel of oil. This stock was introduced at the rate of about 160 barrels per hour, heated to a temperature of about 640° F. in the coil 6, and 80 barrels per hour recycled through the line 22. The remaining 80 barrels per hour were conducted through the line 16, of which about 23 barrels per hour was conducted through the line 56, and the remainder through the line 13. The reflux condensate produced in the tower 8 had an A. P. I. gravity of 19 to 21, and approximately 285 barrels per hour of this stock at a temperature of 755° F. was conducted to the pipe still furnace 28 at a pressure of 490 lbs. per square inch. From 15 to 20 barrels per hour of recycle stock was conducted through the line 26. The hot tar withdrawn from the chamber 20 was conducted at a temperature of about 815° F. through the line 42 and supplied at the rate of about 85 barrels per hour to the transfer line. A period in excess of 10 hours is required to collect the body of tar in one of the chambers 40 or 60.

In this instance, the pressure maintained in the chambers 40 and 60 was 265 lbs. per square inch, with a pressure of 235 lbs. per square inch in the pressure cracking chamber 20. Gradually lower pressures of 225 and 215 lbs. per square inch were maintained in the tower 8 and receiver 14, respectively. The transfer line temperature at the point of discharge from the pipe still furnace was 935° F., and that at the entrance to the coking chamber 935° F. while the temperature in the upper part of the coking chamber was 890° F. The vapors conducted from the chamber 20 through the line 54 were at a temperature of 820° F., while those conducted through line 12 were 420° F. This operation was carried out entirely by the use of the heavy topped crude stock introduced through the line 4, so that the recycle stock produced in the tower 8 was obtained from the heavier material by cracking, did not accumulate in the cracking operation, but was completely converted to other products.

The pressure distillate recovered amounted to 75% of the topped crude charge and had an end point of approximately 420° F. The amount of coke produced was equivalent to 55-60 lbs. per bbl. of topped crude charged to the unit. This coke was fairly hard, making it possible to recover approximately 80% in the form of lump. The coke contained 2-3% soluble matter and 8-10% volatile matter.

Having thus described the invention in its preferred form, what is claimed as new is:

1. The process of conditioning heavy residual petroleum stocks for conversion of the same into marketable petroleum coke which comprises pre-heating a residual stock of the type of topped crude oil to a temperature of approximately 650° F., conducting the preheated stock into an enlarged reaction chamber in which the stock is cracked and polymerized by bringing it in con-

tact with petroleum oil vapors having a sufficient temperature to crack and polymerize the heavy stock, maintaining a pressure of at least about 200 lbs. per square inch in said chamber and preventing substantial vaporization, accumulating a substantial body of the polymerized stock in the lower portion of the chamber at a temperature in excess of 800° F. to provide a time reaction, continuously withdrawing polymerized stock from said body and quickly heating it to a temperature of about 935° F., conducting the resulting heated polymerized stock directly into the upper portion of an enlarged collecting chamber, gradually collecting an enlarged body of liquid polymerized stock in said chamber for a substantial period of time while retaining said collected liquid body at an average temperature in excess of 800° F., maintaining a pressure of at least about 200 lbs. per square inch in said collecting chamber while said polymerized stock is collected in said body, and thereafter coking the liquid body of polymerized stock collected in said collecting chamber by the successive steps of gradually reducing the pressure thereon over a period of time, passing steam through the collecting chamber from the bottom for a substantial period of time and thereafter introducing water into the bottom of the chamber for a substantial period of time.

2. The method of converting petroleum oils, which comprises passing a petroleum distillate stock in a confined stream of restricted cross section through a pipe still furnace and subjecting it to cracking conditions of temperature and pressure, discharging the resulting highly heated products from said pipe still furnace at a temperature of approximately 1000° F. and mixing therewith a minor proportion of a very heavy polymerized oil stock having a temperature of at least 800° F., an A. P. I. gravity of from about 8 to 12 and resulting from a cracking operation in which it has been conditioned under pressure for coking, conducting the resulting mixture into the upper portion of an enlarged chamber in which the vapors and unvaporized liquid oil constituents are separated at a pressure of at least 200 lbs. per square inch, accumulating the unvaporized liquid oil constituents in said chamber under conditions adapted to prevent substantial agitation until the chamber is substantially filled with liquid, discharging the separated vapors from the upper part of said chamber and subjecting them to a fractionation operation to separate out the desired gasoline from higher boiling constituents and uncondensable gas, isolating the filled chamber from the operation cycle and immediately coking the liquid contents of the chamber by the successive steps of gradually reducing the pressure thereon over a period of time, passing steam through the chamber from the bottom for a substantial period of time and thereafter introducing water into the bottom of the chamber for a substantial period of time.

3. The method of converting petroleum oils which comprises passing petroleum distillate stock in a confined stream of restricted cross section through a pipe still heater and therein subjecting the stock to cracking conditions of temperature and superatmospheric pressure, discharging the resulting highly heated products of said distillate stock from said pipe still heater through a transfer line and mixing therewith in said transfer line a substantial but minor proportion of a very heavy polymerized oil stock

which has been conditioned for conversion to coke, conducting the resulting mixture through said transfer line at a temperature of about 950° F. into the upper portion of one of a plurality of enlarged chambers in which a pressure of at least 200 lbs. per square inch is maintained and wherein the vapors of the mixture are separated from unvaporized tarry oil constituents, continuously supplying said distillate stock to said pipe still heater and retaining said polymerized tarry oil constituents in said chamber under quiescent conditions until the chamber becomes substantially filled therewith, thereupon directing the stream of products in said transfer line into another of said enlarged chambers and isolating the filled chamber, continuing the alternate use of said plurality of chambers as collection chambers to thereby provide a continuous process, immediately upon isolating a chamber filled with liquid residue from the process cycle, effecting the coking of its tarry contents by the successive steps of gradually reducing the pressure thereon over a substantial period of time, then introducing steam into the bottom of the chamber for a substantial period, and thereafter introducing water into the chamber for a substantial period.

4. In a continuous process for converting petroleum oil, in which a reflux distillate produced in the conversion operation is passed in a confined stream of restricted cross section through a pipe still furnace and subjected to a cracking temperature of from 960° to 1010° F. at a substantial superatmospheric pressure, and in which a topped crude oil stock is subjected to a polymerizing operation in an enlarged contact chamber by heating it with high temperature gases and vapors produced in the conversion operation, the improvement which comprises subjecting said topped crude oil stock to a polymerizing operation at a temperature above 800° F. to produce a heavy polymerized tarry residuum while preventing substantial vaporization, mingling said heavy tarry residuum while at a temperature of at least 800° F. with the high temperature products resulting from the heating of said reflux distillate and thereby raising the temperature of said residuum, passing the resulting mixture into the upper portion of an enlarged collecting chamber in which vapors are separated from unvaporized liquid oil constituents under conditions adapted to prevent substantial agitation of the separated liquid oil, gradually accumulating said separated liquid oil constituents in said collecting chamber under high pressure until the chamber is substantially filled with the same, thereupon isolating the said collecting chamber from the conversion cycle by conducting the stream of mixed products into an alternate collecting chamber, coking the unvaporized liquid oil constituents in the isolated chamber by gradually reducing the pressure thereon to approximately atmospheric pressure, thereafter passing steam into the lower portion of the isolated chamber for a substantial period of time, and finally introducing water into the lower portion of the chamber until the contents of the chamber have been coked and the chamber cooled to a point sufficiently low to permit opening of the same and removal of the resulting coke therefrom.

5. A continuous process for conditioning heavy petroleum oils to be coked, which comprises introducing fresh topped crude oil into an enlarged pressure cracking and polymerizing chamber and therein intimately contacting the

topped crude oil with high temperature oil vapors and effecting the polymerization of said topped crude oil at a temperature between 800° and 900° F., continuously introducing the topped crude oil into said chamber and maintaining it therein under a pressure of approximately 200 lbs. per square inch for a sufficient period of time to polymerize the topped crude oil to a heavy tarry liquid product having an A. P. I. gravity of from 8 to approximately 11 and having a relatively low free carbon content, conducting hot tarry polymerized stock from said chamber and heating it quickly to a temperature of from about 915° to 945° F., under a pressure in excess of 200 lbs. per square inch then collecting said polymerized stock in a quiescent liquid body of the stock over a substantial period of time of at least ten hours, maintaining the collected liquid body of stock at an average temperature in excess of 800° F. and at a pressure in excess of 200 lbs. per square inch, and after a sufficient body of said polymerized stock has been collected and converted into a product not containing in excess of from about 9% to 24% of free carbon, subjecting the liquid body to coking conditions to convert the stock into marketable petroleum coke.

6. A continuous process for converting corrosive petroleum oils by the use of lime wherein the direct heating of the lime with the oil by firing is avoided, which comprises passing a mixture of high temperature vapors having a temperature in excess of 800° F. and produced in the conversion operation into an enlarged unheated contact chamber in intimate contact with a mixture of a heavy oil and lime to purify said vapors, maintaining a superatmospheric pressure of at least 200 lbs. per square inch in said contact chamber to prevent substantial vaporization of said heavy oil, passing the vapors from said contact chamber into a fractionating tower and therein producing a reflux condensate free of lime, passing said reflux condensate in a confined stream of restricted cross-section through a pipe still furnace and subjecting it to a cracking the resulting highly heated products from substantial superatmospheric pressure, conducting the resulting highly heated products from said pipe still furnace into a transfer line and introducing therein and mingling with said products a stream of the highly heated heavy oil and lime produced in said contact chamber, passing the resulting mixture of products and lime in said transfer line into an unheated separating chamber in which liquid oil constituents and lime are separated from vapors, and conducting vapors from said separating chamber to supply the high temperature vapors introduced into said unheated contact chamber.

7. In a continuous process for converting petroleum oil, in which a reflux distillate produced in the conversion operation is passed in a con-

5 fined stream of restricted cross section through a pipe still furnace and subjected to a cracking temperature in the neighborhood of 1000° F. at a substantial superatmospheric pressure, and in which a topped crude oil stock is subjected to a polymerizing operation in an enlarged chamber by heating it with high temperature gases and vapors produced in the conversion operation, the improvement which comprises subjecting said topped crude oil stock to a polymerizing operation at a temperature above 800° F. to produce a heavy polymerized tarry residuum while preventing substantial vaporization, mingling said heavy tarry residuum while at a temperature of at least 800° F. with the high temperature products resulting from the heating of said reflux distillate and thereby raising the temperature of said residuum, passing the resulting mixture into the upper portion of an enlarged chamber in which vapors are separated from unvaporized liquid oil constituents under conditions adapted to prevent substantial agitation of the separated liquid oil in said chamber, gradually accumulating said separated liquid oil constituents in said chamber under high pressure until the chamber is substantially filled with the same, thereupon isolating the chamber from the conversion cycle by conducting the stream of mixed products into an alternate chamber, and coking the unvaporized liquid oil constituents in the isolated chamber by the successive steps of gradually reducing the pressure thereon over a period of time, passing steam through the isolated chamber from the bottom over a substantial period of time, and thereafter introducing water into the bottom of the isolated chamber for a substantial period of time.

8. A continuous process as defined by claim 7 in which the topped crude oil stock subjected to the polymerizing and coking operations includes a minor proportion of lime intimately mingled therein.

9. The method of converting petroleum oils as defined by claim 2 in which a small proportion of lime is included in the heavy polymerized oil stock mixed with the highly heated products from the pipe still furnace.

10. The method of converting petroleum oils as defined by claim 3 in which a small proportion of lime is included with the heavy polymerized oil stock mixed with the highly heated products discharged from the pipe still heater.

11. A continuous process as defined by claim 4 in which a small proportion of lime is present in the topped crude oil stock in the enlarged chamber in which the stock is heated with high temperature gases and vapors.

12. A continuous process as defined by claim 5 in which a small proportion of lime is present in said enlarged chamber and brought in contact with high temperature oil vapors therein.

DAVID G. BRANDT.

CERTIFICATE OF CORRECTION.

Patent No. 2,316,931.

April 20, 1943.

DAVID G. BRANDT.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 25, for "72, 77" read --72, 70--; page 6, first column, line 46, strike out "ing the resulting highly heated products from" and insert instead --ing temperature of from 960° to 1010° F. at a--; 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 25th day of May, A. D. 1943.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)