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PROCESS FOR CRACKING HYDROCARBON OILS DISTILLED FROM CRUDE PETROLEUM, SHALE OIL, AND OIL OBTAINED FROM GILSONITE OR SIMILAR HYDROCARBON BEARING MATERIALS, AND APPARATUS THEREFOR.

APPLICATION FILED AUG. 28, 1922.

1,435,652.

Patented Nov. 14, 1922.

2 SHEETS—SHEET 1.

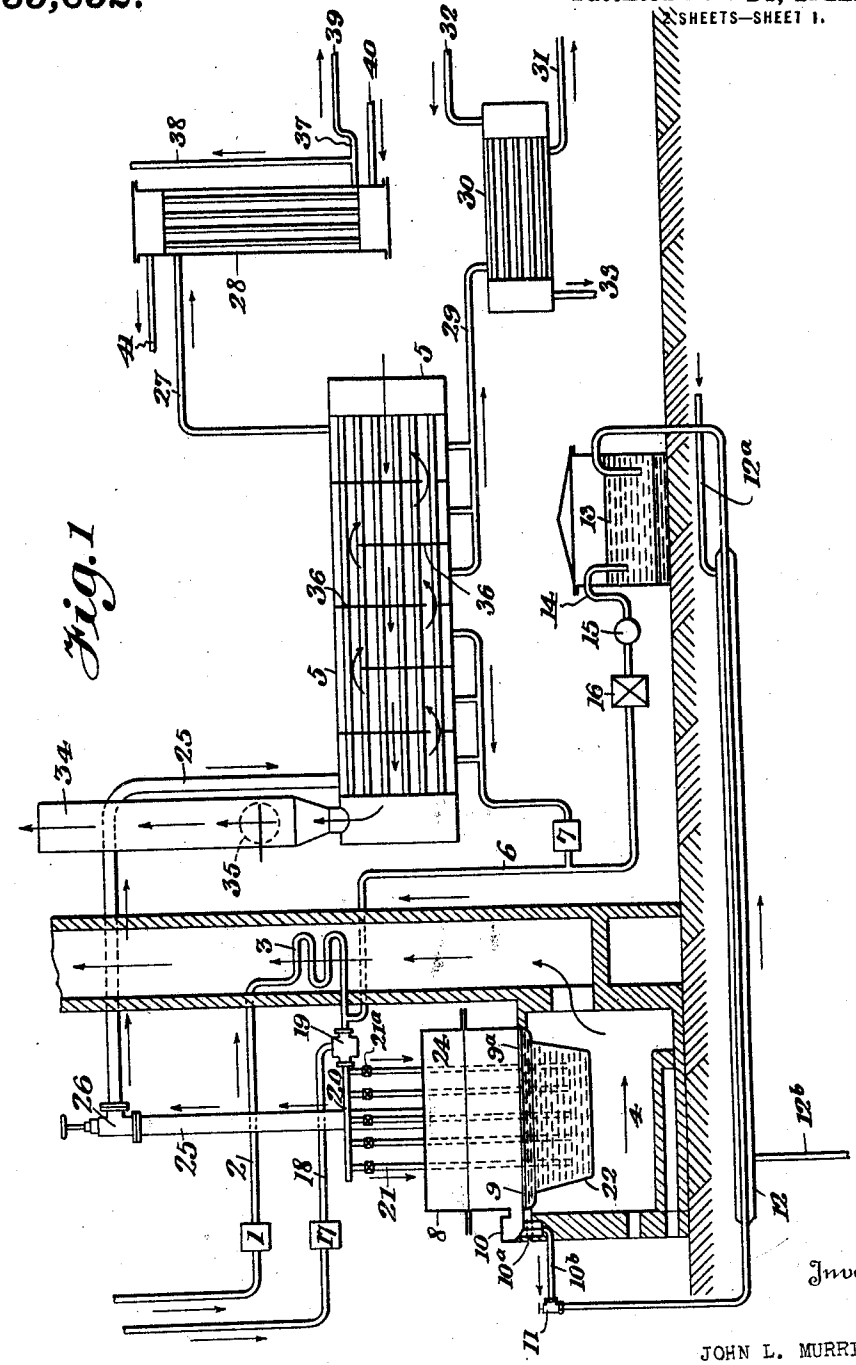

Fig. 1

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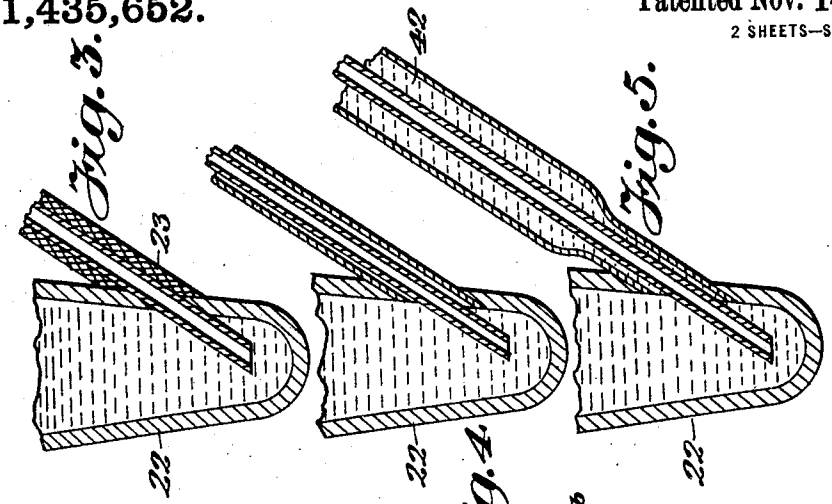

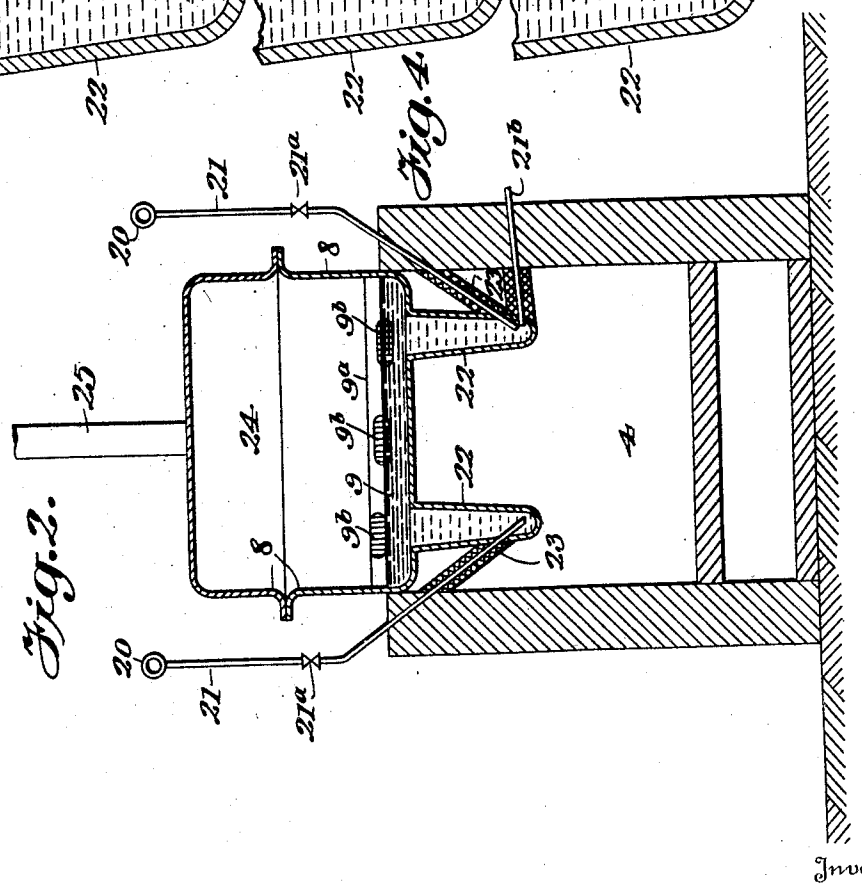

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UNITED STATES PATENT OFFICE.

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PROCESS FOR CRACKING HYDROCARBON OILS DISTILLED FROM CRUDE PETROLEUM, SHALE OIL, AND OIL OBTAINED FROM GILSONITE OR SIMILAR HYDROCARBON-BEARING MATERIALS, AND APPARATUS THEREFOR.

Original application filed May 12, 1920, Serial No. 380,719. Divided and this application filed August 28, 1922. Serial No. 584,679.

To all whom it may concern:

Be it known that I, JOHN L. MURRIE, a citizen of the United States, and a resident of the city of Yonkers, county of Westchester, and State of New York, have invented a new and improved process for cracking hydrocarbon oils distilled from crude petroleum, shale oil, and oil obtained from gilsonite or similar hydrocarbon-bearing materials, and apparatus therefor, of which the following is a specification, reference being had to the accompanying drawings.

This application is a division of an application filed by me May 12, 1920, Serial Number 380,719.

Generally stated, the objects of my invention are to provide means for removing the carbon and other impurities from the cracked oil, to regulate the pressure in the retort, to expedite the cracking operations, to increase the quantity of the desired products, to maintain uniformity of temperatures in the bath and in the retort, to simplify and reduce the cost of repairs and to reduce the generation of fixed gases and the formation of unsaturated compounds.

My process and apparatus are adapted for decomposing hydrocarbon oils, distillate and heavy petroleums by mixing them with a fixed hydrocarbon gas and passing the mixture through a molten metal bath in order to produce an increased yield of motor spirits or other low boiling point, high gravity liquids, and by the practice of my process the reduction of heavy oils to light oils is very greatly expedited and the quality and quantity of the resulting products improved and increased.

Although my process and apparatus are peculiarly adapted to the treatment of heavy oils for the extraction therefrom of the various well known lighter compounds, yet it will be understood that during the operation the temperature, the pressure, the rate of flow of oil, etc., should be regulated according to the character of the oil being cracked in order to yield the desired results, these changes being made as occasion may require.

The processes heretofore employed in the cracking of oils, by passing the oil through a molten metal bath in a closed retort, result in the accumulation of deposits of carbon, which reduce the efficiency of the process and are difficult to remove from the retort, and in most cases require that the operation of the retort be interrupted for a period to enable the operator to remove them.

In the practice of my invention the mixture of gas, oil and vapors rising rapidly through the molten metal bath keep it vigorously agitated and prevent accumulation of carbon within that portion of the retort filled with molten metal. As the particles of carbon formed in the metal bath rise to the surface thereof they are there held in suspension in a layer of oil made up of the condensed heavy fractions which flow back from the vapor line, the heavy fractions condensed on the walls of that portion of the retort above the furnace and the unvaporized heavy hydrocarbons rising through the metal bath. The layer of oil with the carbon in suspension flows continuously and of course automatically from the retort through a device, hereinafter described, which forms part of this invention and which I call the depth adjusting overflow header, to the carbon settling tank, thereby making my process a continuous one, because it is not necessary to interrupt its operation in order to remove the carbon. The depth adjusting overflow header is provided with a number of valve controlled openings at different elevations, whereby the operator is able to maintain the preferred depth of the layer of oil in order to remove the carbon particles rising to the surface of the molten metal.

Likewise those processes heretofore employing a molten metal bath have been imperfect in their operation on account of the unsatisfactory temperature regulation. This difficulty is largely due to the practice of injecting the oils into a molten metal bath contained within a vertical tube or its equivalent. Upon the oil being injected into the bottom of such tube it immediately breaks into vapors, which rapidly expanding expel a large portion of the molten metal from the tube, and there being no body of metal of the desired temperature immediately at hand to replace that which has been thus expelled, the somewhat cooled metal drops back into the tube and must be again brought up to the required temperature. Therefore, in processes where tubes or the like are used,

the rate of cracking of the oil is relatively slow as rapid injection of the oil into the metal bath under these conditions will additionally reduce its temperature so that a point is soon reached where only a very small portion of the oil is cracked, and consequently a small yield only of the desired products produced.

I find that my new construction, which embodies a melting pot as hereinafter described, is superior to the tube form, as a plurality of oil injection pipes may be used to conduct the oil to the pot without expelling the molten metal therefrom by the expansion of the vapors because the molten metal is not confined in the immediate vicinity of the points at which the oil is injected; therefore molten metal of the desired and practically uniform temperature can freely circulate throughout the entire interior of the melting pot, because of the absence of impeding piping or other obstructions. My construction is also superior to the tube form in that as the melting pot is preferably wider at the top than at the bottom, more room is thereby provided for the expansion of the vapors in the metal bath, thus causing a greater degree of cracking and less violent agitation of the molten metal.

Another important feature of my construction is the location of the oil inlet and thermometer pipes upon the outside of the retort and near the bottom of the melting pot, whereby I obviate the difficulty encountered in operating certain cracking apparatus in which the oil injection and thermometer pipes descend through the top of the retort into the molten metal bath, in which construction great difficulty is experienced in maintaining tight joints because these joints are subjected to high temperatures and are also in the vapor zone, and furthermore, it is extremely difficult and dangerous to remove the top or cover section of the retort to which the vertical oil pipes are attached, as they are of necessity immersed in the molten metal bath which adheres firmly to the pipes when cooled. Under my invention all the before-mentioned difficulties are avoided; and it will be especially noted that since, as above stated, the oil and thermometer pipes enter the wall of the melting pot near its bottom, they form no obstruction to the free circulation of the molten metal within the retort, as do the vertical pipes used in said other types of apparatus.

Under my improved process and apparatus described and illustrated herein, I pass through the molten metal bath, which is preferably lead, within the melting pot of the retort, a mixture of oil and natural gas, or other gas of the permanent hydrocarbon class. The gas in the presence of the oil reduces the vapor pressure of the oil, permitting a much more rapid expansion of the oil into vapor in the melting pot or the cracking zone, and also presents the oil in a more finely divided state to the heating element for cracking. Also injecting the gas with the oil through the molten metal bath saturates the cracking zone and retort with preferably an excess of permanent hydrocarbon gases, thereby lessening the tendency to form fixed gases from the oil when it is cracked. Thus the generation of fixed gases from the oil is reduced and the oil is presented to the heating element in a more finely divided form for cracking, thereby increasing the yield of valuable products containing a small percentage only of unsaturated hydrocarbon compounds.

My process may be practiced and my apparatus operated under atmospheric pressure, or from atmospheric pressure up to approximately 125 pounds per square inch and at varying temperatures as the character or quality of the material being treated requires. The pressure in the cracking retort is determined and regulated to obtain the maximum yield of light hydrocarbon products with the smallest amount of unsaturated hydrocarbon compounds from the heavy hydrocarbon oils.

Referring to the drawings, which illustrate apparatus adapted for use in practicing my process, Figure 1 is a longitudinal view, partly in vertical section, of the complete apparatus; Figure 2 is a vertical sectional view of the furnace and cracking retort taken at right angles to Fig. 1; Figures 3, 4 and 5 are vertical sectional views of three modified forms of pipe for injecting the heavy hydrocarbon oils and gas into the molten metal.

Referring to Figs. 1 and 2, 1 represents a suitable pump whereby the heavy hydrocarbon oil or distillate to be cracked is drawn from a tank (not shown) and pumped under constant pressure through a pipe line 2 into a preheater 3, located where preferred, and heated preferably by the waste gases from a combustion furnace 4 under the cracking retort 8. The incoming heavy hydrocarbon oil after being preheated is mixed in the line leading from the preheater 3 as shown, with the heavier fraction or fractions condensed out of the vapors in aerial condenser 5 and with the uncracked oil, which comes from the surface of the molten metal bath in the cracking retort 8.

For a more clear understanding of the invention the orderly description of the procedure will be interrupted to give a description of the operation showing the method by which the heavier fraction or fractions from aerial condenser 5 and the uncracked oil from the surface of the molten metal in the cracking retort 8 are or may be, if desired, joined with the incoming preheated

heavy hydrocarbon oil coming from the preheater 3. The heavier fraction or fractions condensed out of the vapors in aerial condenser 5 are pumped by pump 7 through line 6 into the line leading from the preheater 3 and mixed with the incoming heavy hydrocarbon oil as shown. The uncracked oil from the cracking retort 8 comes from a layer 9^a upon the surface of the molten metal bath 9, which layer holds the carbon particles in suspension, and flows automatically from the surface of the molten bath through openings 9^b, see Fig. 2, made at different elevations in the depth adjusting header 10, and controlled by suitable valves 10^a, into the draw-off pipe 10^b, which is provided with pressure regulating valve 11, water jacket 12, water inlet pipe 12^a, and water outlet pipe 12^b, for cooling the oil below the vaporization point, to the carbon settling tank 13, where the carbon precipitates as shown, and the uncracked oil free from carbon is drawn through the line 14 and carbon strainer 15 by a suitable pump 16 and is discharged through line 6 into the line leading from the preheater 3, together with the heavy fractions condensed from the vapors in the aerial condenser 5, as shown. The openings 9^b in the depth adjusting header 10 are made at different elevations as shown so that the depth of the layer of oil above the molten metal bath may be regulated by the appropriate manipulation of the said valves 10^a through which the oil will automatically overflow when the valve at the selected level has been reached. Although I have illustrated the depth regulating device on one side of the apparatus only, obviously, especially if the size or shape of the melting pot makes it desirable, there may be as many depth regulating devices as may be deemed necessary to effect the desired removal of the uncracked oil and heavy fractions holding the carbon impurities in suspension, suitable piping therefrom being arranged to pass the overflow material through the carbon settling tank 13.

Having shown the sources of the oils which are introduced into the cracking retort, I will now proceed with the orderly description of the process. The natural or other permanent hydrocarbon gas is drawn from a suitable receptacle, not shown, and pumped by a suitable pump 17 under constant pressure through a pipe 18 into a mixing chamber 19, where the gas is mixed with the preheated heavy hydrocarbon oil from the preheater 3, the condensed heavy fraction or fractions from the aerial condenser 5, and the uncracked and cleansed oil from the settling tank 13.

The mixture of heavy hydrocarbon oils and gas from the mixing chamber 19 passes into manifolds 20 and thence by pipes 21, under constant pressure and regulation by suitable valves 21^a, into the melting pot 22, which may beneficially be made of cast or other steel welded or otherwise attached to the bottom of the cracking retort 8, and within which is contained the bath of molten metal 9.

In the particular embodiment of my apparatus herein illustrated two melting pots are shown for the same furnace in the bottom of the same retort. Obviously one or more than two may be provided for the same furnace and retort. The melting pots are illustrated in the form of troughs, preferably from five to ten feet in length, about two feet in depth and having an internal width of say four inches at the bottom and six inches at the top; but obviously the special shape and dimensions may be varied to suit the requirements of the plant. They may be oblong, square, round or other shape, so long as the horizontal dimensions of the surface of the bath are greater than its depth, and preferably, although not necessarily, they should be wider at the top portion than at the bottom portion, as stated above.

The portion of the pipes 21 which passes through the combustion chamber 4 is insulated with suitable material 23, and the pipes may be spaced along the melting pot say from eight to twelve or more inches apart, and may be a single pipe as shown in Fig. 3, or one pipe fitted inside of another as shown in Fig. 4, or one pipe inside of another pipe with molten metal 42 between them, as shown in Fig. 5. 21^b is the usual thermometer pipe, preferably insulated as by the material 23.

The melting pots 22 are heated by the combustion of suitable fuel, such as gas, coal or fuel oil, in the furnace 4, the desired cracking temperature being maintained.

The heavy hydrocarbon oils from line 2, condensed heavy fractions from aerial condenser 5, and cleansed oil from tank 13, and the natural or other permanent hydrocarbon gas, injected into the melting pots 22, ascend through the molten metal, the oil decomposing or cracking and forming the light hydrocarbon compounds. The light and heavy hydrocarbon vapors and gases accumulate in the vapor space 24 above the molten metal bath 9, and leave the cracking retort 8 through a vapor pipe 25. The particles of carbon and unvaporized portion of the oil rise to the surface of the bath and leave the retort through the depth adjusting header 10 as heretofore described. The vapor pipe 25 is equipped with a suitable valve 26 for regulating the pressure in the cracking retort 8. A portion of the uncracked oil, which, as stated, removes the carbon from the surface of the molten metal bath, condenses in the vapor pipe 25 and

flows back into the retort, as is well understood. A portion of the light and heavy hydrocarbon vapors and gases which enter the aerial condenser 5 from the vapor pipe 25 is condensed by fractional cooling, in the example shown, into six fractions. The light hydrocarbon vapors and gases which are not condensed therein leave the aerial condenser by a vapor line 27 and enter a water-cooled condenser 28. One part of the six condensed fractions is a heavy hydrocarbon fraction and is pumped back to the cracking retort by pump 7 as heretofore described. The other part is a light hydrocarbon fraction suitable for distilling for motor spirits, and flows through a line 29 into a water-cooled cooler 30 and thence when cooled through a line 31 to the run-down tanks, not shown. Water for the water-cooled cooler enters through a line 32 and leaves by a line 33, flowing counter current to the hydrocarbon fraction.

The aerial condenser 5 may be a steel shell with boiler tubes inside. It is preferably so constructed that the air flows through the tubes and leaves by the stack 34. A damper 35 is installed in the stack for air control which regulates the amount of condensed fractions produced. The vapors and gases are on the outside of the tubes and the condensed fractions are separated by the baffles 36.

The cooled gas and condensed fractions resulting from the condensation of the light hydrocarbon vapors and gases in the water-cooled condenser 28 pass therefrom through a pipe 37 and the condensed fractions are trapped off through a line 39 to the run-down tanks, not shown. The non-condensable gases are carried off through a pipe 38 and may be run to an absorption plant or to a gas holder for such use as desired. The water for cooling the condenser 28 enters through a line 40 and leaves through a line 41, flowing counter current to the hot liquid and gases. The water-cooled condenser and the water-cooled cooler may be of any suitable construction, but I prefer to use the tubular form as shown. The water is inside of the tubes and the hot gases or liquid on the outside thereof.

It will be noted that by my process I secure a series of very important and valuable results:

1. By the use of the depth adjusting overflow header the depth of oil holding the carbon in suspension will automatically be regulated as desired. This is a very necessary feature as I find that in cracking different kinds of oil, some of them produce more carbon than others, and therefore a greater depth of oil is required to carry it away.

2. The herein described form of melting pot is of distinct advantage as it permits more rapid cracking due to its provision for vapor expansion without expelling the molten metal from the cracking zone.

3. By the use of oil injection tubes located outside of the retort and discharging directly therefrom into the bottom of the melting pot, I eliminate all obstructions to the circulation of the molten metal and the expansion of the vapors, and furthermore the packing glands on the oil tubes are removed from the vapor zone and are readily accessible, for adjustment, without danger from escaping vapors.

4. By the introduction of a permanent hydrocarbon gas with the oil to be cracked very important results are obtained, namely, the gas in the presence of the oil reduces the vapor pressure of the oil, permitting a more rapid expansion of the oil into vapor in the cracking zone and also presents the oil in a more finely divided state to the heating elements for cracking, and furthermore, the saturation of the entire cracking retort with fixed hydrocarbon gas tends to reduce the generation of fixed gas from the oil and the formation of unsaturated compounds.

5. By operating the retort under pressures varying from atmospheric to approximately one hundred and twenty five pounds the pressure and corresponding temperature may be regulated to produce the maximum yield of hydrocarbon products with the smallest amount of unsaturated hydrocarbon compounds.

It will be obvious to those who are familiar with such matters that the details of mechanical construction of the several parts of the apparatus herein described and illustrated, the piping connections, valving, etc., may be quite extensively modified without departing from the essentials of the invention, either as to the apparatus or the process, and I therefore do not limit myself to the mechanical details described and illustrated.

I claim:

1. In the cracking of hydrocarbon oils the described process consisting in introducing the material to be treated in conjunction with a permanent hydrocarbon gas into the lower part of a molten metal bath in a retort, collecting the resulting vapors and gases in the upper part of the retort, conveying them away and condensing them, and continuously supplying to and withdrawing from the surface of the bath a layer of the heavy fractions and unvaporized hydrocarbons which holds the carbon impurities in suspension.

2. In the cracking of hydrocarbon oils the described process consisting in introducing the material to be treated in conjunction with a permanent hydrocarbon gas into the lower part of a molten metal bath in a retort, collecting the resulting vapors and

gases in the upper part of the retort, conveying them away and condensing them, continuously supplying to and withdrawing from the surface of the bath a layer of the heavy fractions and unvaporized hydrocarbons which holds the carbon impurities in suspension, and adjusting the thickness or depth of the layer as required.

3. In the cracking of hydrocarbon oils the described process consisting in passing the oil to be treated through a molten metal bath in a retort, collecting the resulting vapors and gases in the upper part of the retort, conveying them away and condensing them, continuously supplying to and withdrawing from the surface of the bath a layer of the heavy fractions and unvaporized hydrocarbons which holds the carbon impurities in suspension, and regulating the thickness or depth of the layer as required by adjusting the height of the overflow at the outlet end of the retort and separating the carbon.

4. In the cracking of hydrocarbon oils the described process consisting in incorporating with the oil to be treated a percentage of fixed hydrocarbon gas adapted to finely divide the oil, causing the oil and gas to pass through a molten metal bath in a retort, continuously maintaining upon the surface of the bath a layer of heavy hydrocarbons, predetermining and assuring the preferred depth of said layer by adjusting the height of the outlet at the delivery end of the retort, collecting the resulting vapors and gases in the upper part of the retort, and conveying them away and condensing them.

5. In the cracking of hydrocarbon oils the described process consisting in introducing the materials to be treated into the lower part of a molten metal bath in a retort, collecting the resulting vapors and gases in the upper part of the retort, conveying them away from the retort through an upwardly extending duct, condensing the vapors, continuously supplying to and withdrawing from the surface of the bath a layer of the heavy fractions and unvaporized hydrocarbons, among them the condensate and backflow from said duct, which layer holds the carbon impurities in suspension, and regulating the thickness or depth of the layer as required by adjusting the height of the overflow at the outlet end of the retort.

6. In the cracking of hydrocarbon oils the described process consisting in introducing the material to be treated into the lower part of a molten metal bath in a retort, collecting the resulting vapors and gases in the upper part of the retort, conveying them away through an upwardly extending duct, regulating the pressure in the retort and duct, condensing the vapors, continuously supplying to and withdrawing from the surface of the bath a layer of the heavy fractions and unvaporized hydrocarbons, among them the condensate and backflow from said duct, which layer holds the carbon impurities in suspension, and regulating the thickness or depth of the layer as required by adjusting the height of the overflow at the outlet end of the retort.

7. In the cracking of hydrocarbon oils the described process consisting in passing the material to be treated through a molten metal bath in a retort, continuously supplying to and withdrawing from the surface of the bath a layer of unvaporized hydrocarbons which holds the carbon impurities in suspension, and regulating the thickness or depth of the layer by adjusting the height of the overflow at the outlet end of the retort.

8. In an apparatus of the class stated a retort, a melting pot having greater horizontal surface dimensions than depth located in the bottom of the retort, means to heat the melting pot and the retort, conduits discharging through the wall of the melting pot near its bottom without going through the retort, means to inject the material to be treated through said conduits into the melting pot, means whereby the vapors and gases may escape from the upper part of the retort, means to regulate the pressure in the retort and a condenser for the vapors.

9. In an apparatus of the class stated a retort, a melting pot located in the bottom of the retort, means to heat the melting pot and the retort, a pipe for the conveyance of the material to be treated, another pipe for the conveyance of a permanent hydrocarbon gas, a mixing chamber in which the material to be treated and the hydrocarbon gas are combined, a pre-heating coil in the line conveying the material to be treated, conduits leading from the mixing chamber and discharging into the lower part of the melting pot, and means to inject the material to be treated from the mixing chamber into the melting pot through said conduits.

10. In an apparatus of the class stated a retort, a melting pot located in the bottom of the retort, means to heat the melting pot and the retort, a mixing chamber, a pipe for conveying the material to be treated to the mixing chamber, another pipe for conveying a permanent hydrocarbon gas to the mixing chamber, conduits leading from the mixing chamber to the lower part of the melting pot, means to inject the material to be treated and gas through said conduits, means whereby the gases may escape from the upper part of the retort under pressure, a condenser adapted to separate the heavy from the light fractions, means to return the heavy fractions under pressure to the material to be treated prior to its introduction into the mixing chamber, means to continuously supply a layer of the heavy

fractions and unvaporized hydrocarbons upon the top of the molten metal bath in the melting pot, means to predetermine and assure the preferred depth of said layer, means to automatically carry the layer away, means to cool the layer, means to precipitate its impurities, and means to convey the cleansed residue of heavy fractions and unvaporized hydrocarbons and discharge the same into the line which conveys the material to be treated.

11. In an apparatus of the class stated a melting pot, means to continuously supply to and withdraw from the surface of the contents of the melting pot a layer of unvaporized hydrocarbons and means to regulate the depth of the layer by adjusting the height of the overflow at the outlet end of the retort.

12. In an apparatus of the class stated a retort, a melting pot having greater horizontal surface dimensions than depth located in the bottom of the retort, means to heat the melting pot and the retort, conduits discharging through the wall of the melting pot near its bottom without going through the retort, means to inject the material to be treated through said conduits into the melting pot, means whereby the vapors and gases may escape from the upper part of the retort, means to regulate the pressure in the retort and a condenser for the vapors.

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