

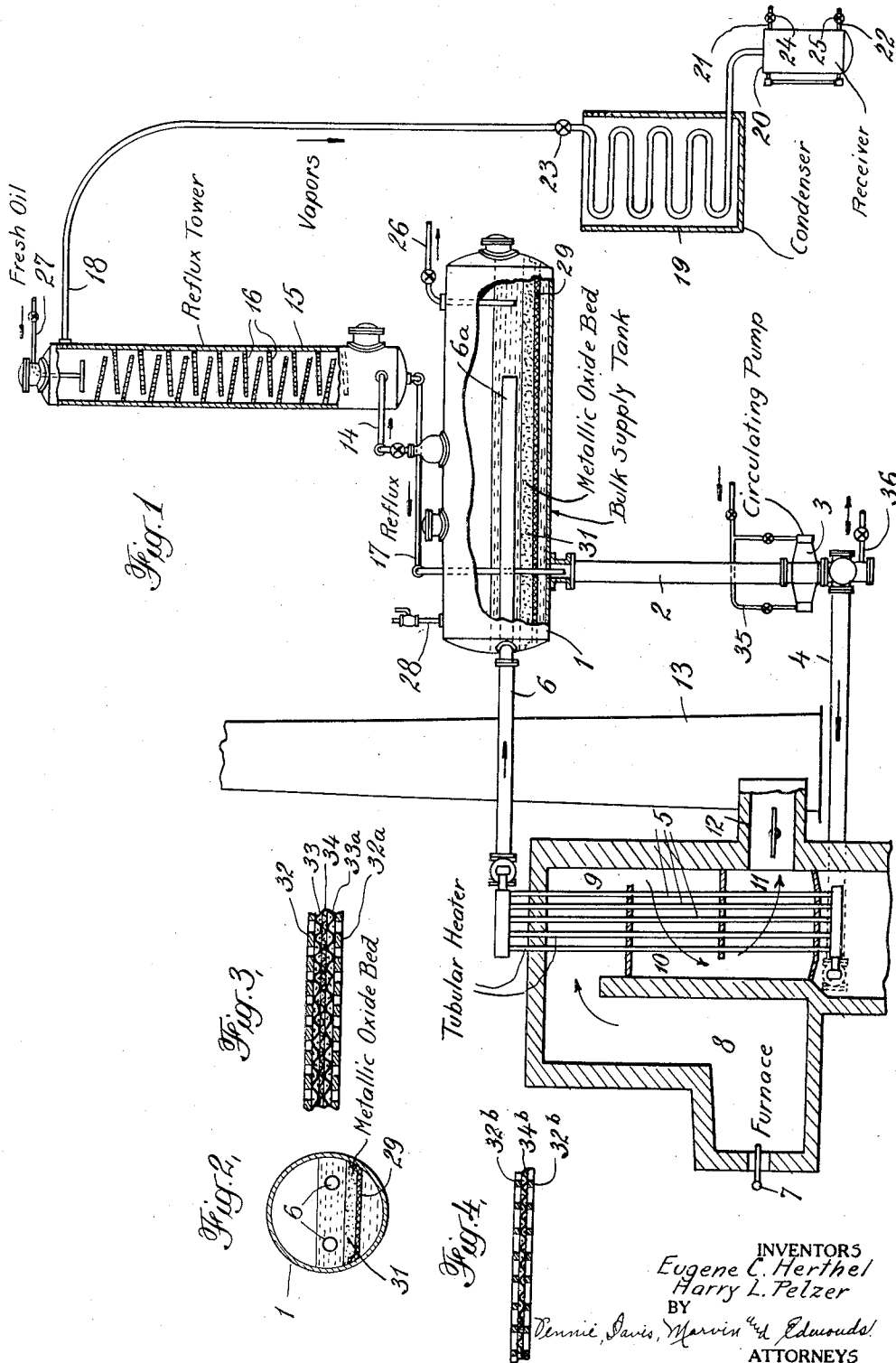
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ART OF CRACKING HYDROCARBONS

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## UNITED STATES PATENT OFFICE.

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## ART OF CRACKING HYDROCARBONS.

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This invention relates to improvements in the cracking of heavier hydrocarbon oils in pressure stills for the production of gasoline or motor spirit or pressure distillate therefrom. The invention comprises an improved process which assists in protecting the heating surfaces of the cracking still and which also enables the cracking operation to be continued for a prolonged period of time before the deposition of carbon begins or before it is necessary to shut down for cleaning purposes. This application is in part a continuation of our copending application Serial No. 704,926, filed April 8, 1924, which has issued as Patent No. 1,634,666.

In the cracking of heavier petroleum oils in pressure stills for the production of gasoline or pressure distillate therefrom there are formed during the cracking operation certain constituents of an asphaltic or pitch-like character. With the continuation of the cracking operation, the amount of such constituents increases and there is a tendency for deposits of carbon or coke to form on the heated surfaces of the still, thus necessitating the shutting down of the still for cleaning purposes between successive runs. The shutting down of a pressure still, the withdrawal of the charge therefrom, the cleaning of the still, the recharging of the still and the preliminary heating of the still to bring the fresh charge up to cracking conditions, all require time, and the total amount of time so required in ordinary commercial operations means a corresponding reduction in the proportion of the time when the still is operating for carrying out the desired cracking operation.

According to the present invention, the deposition of pitch or carbon on the heating surfaces of the pressure still is prevented or greatly reduced so that overheating or danger of failure of the heating surfaces can be effectively prevented, and the time of operation of a single run can be somewhat prolonged, with correspondingly greater continuity of operation, less loss of time, and greater production per still per day.

When a pressure still is charged with gas oil or other charging stock to be subjected to cracking, and when the charge is heated to the cracking temperature, the cracking takes place in a gradual and progressive manner. The lighter constituents produced by the cracking operation, which go to make up the

pressure distillate, are removed from the still progressively during the cracking operation. Other constituents, such as heavier hydrocarbons formed by the cracking operation, may remain and mix with the charge of the still. A small amount of asphaltic or pitch-like constituents is progressively formed. Such constituents appear to be of varying properties and characteristics. For the most part they remain in solution in the charge during the early portion of the run, and they may remain completely in solution during the early portion of the run. With gradual and progressive cracking of the charge however the amount of such asphaltic or pitch-like constituents gradually and progressively increases until sooner or later the amount of such constituents increases beyond the saturation point. Furthermore, certain of these constituents, which appear to be relatively small in amount as compared with the total amount of the pitch-like constituents formed, appear to be of a different character and to have an increased tendency to deposit on the heating surfaces of the still. Furthermore, as the charge becomes supersaturated with the less objectionable pitch-like constituents, there is an increased danger of deposit of pitch or carbon on the heating surfaces of the still, with corresponding danger of overheating and failure of the heated surfaces if the still is not shut down at more or less frequent intervals to remove this deposit.

Among the constituents produced by the cracking operation which seem to be particularly objectionable are certain sulfur-containing compounds. In charging stock which contains sulfur, certain of the sulfur compounds appear to undergo cracking to form sulfur-containing constituents, probably of an asphalt-like character, which are particularly objectionable. Analyses of the carbon deposit on the heated tubes of a cracking still indicate that certain of these sulfur-containing constituents have a preferential affinity for the heated surfaces, or tend to separate out on such surfaces, to give a deposit containing both iron and sulfur in proportions approximating those of iron sulfide.

We have found that the length of time during which the operation of the pressure still can be continued can be prolonged by maintaining within the pressure still a body of metallic oxides in direct contact with the

still charge, and by causing the still charge to circulate repeatedly through said body of metallic oxides during the progress of the cracking operation. We have also found that the maintenance of a body of metallic oxides within the still charge is of advantage in protecting the heating surfaces of the still from corrosion, overheating and burning out, and in reducing carbon deposition upon the heating surfaces, whether or not the operation is carried out over a prolonged period. The body of metallic oxides which is maintained in the still in contact with the charge, and through which the charge is continuously circulated has a selective action upon certain of these objectionable constituents, including the sulfur-containing compounds, and apparently removes those constituents which are particularly objectionable from the standpoint of forming a carbon deposit on the heated surfaces of the still. This selective action may be a desulphurizing action or it may be in part a filtering action or absorbent action removing colloidal carbon or precipitated asphalt-like constituents. Whatever the explanation of the action of the body of metallic oxides may be, it has an important protective effect in preventing objectionable carbon deposit on the heating surfaces of the pressure still.

The metallic oxides which may be employed in carrying out the present invention include iron oxide and copper oxide. The oxides may be employed alone, or they may be employed in conjunction with a supporting material, for example, a bed of metallic oxides may be supported on a bed of suitable filtering material in the still charge so that the charge is circulated through both the bed of metallic oxides and the bed of filtering material. The use of a supporting material in this manner is particularly advantageous with finely divided metallic oxides or with oxides which otherwise tend to be carried with the circulating oil. The metallic oxides may also be precipitated upon the filtering or supporting material and the still charge circulated through a body of this composite material. Suitable filtering materials which may be so employed include asbestos, disintegrated silo-cel brick or fire brick, sand, kieselguhr, diatomaceous earth, pumice, glass wool or mineral wool, and ground coke or charcoal. Fuller's earth or similar absorbent clays, acid treated clays, and silica gels may also be used. Circulation of the still charge through such filtering or supporting material also assists in the removal of objectionable constituents from the charge by a filtering action or selective absorbent action therein in addition to the action of the metallic oxides associated therewith.

The provision of a body of metallic oxides in direct contact with the pressure still charge arranged for circulation of the pres-

sure still charge therethrough may assist in prolonging the cracking operation in several ways. The body of metallic oxides apparently has a filtering action in removing suspended pitch or asphaltic constituents and other objectionable constituents. It also apparently reacts with sulfur-containing constituents of the charge to form insoluble sulphides which are retained in the body of metallic oxides, or where a supporting body of filtering or similar material is employed also on the filtering material. The sulphides may be absorbed or filtered out as formed or they may be removed from the circulating charge as it circulates through the body of metallic oxides and any associated material. A part of the metallic oxides may dissolve in the circulating oil and may react while dissolved with the sulfur-containing constituents of the still charge to form insoluble sulphides which are filtered out as the oil is recirculated through the body of metallic oxides. Where a part of the metallic oxides are so dissolved, the desulphurizing reaction may thus be effected in the zone in which the oil is subjected to the highest temperatures in an advantageous way. In some cases, the saturation concentration of pitch and asphaltic constituents in the still charge may also be increased apparently by the selective action of the body of metallic oxides on the most objectionable constituents or on constituents tending to cause deposition on the heating surfaces.

In the improved process of the present invention part of the pitch-like constituents produced during the cracking operation are thus removed by the action of the body of metallic oxides and in some cases the saturation concentration of pitch-like constituents in the charge may also be increased. The metallic oxides may also act upon certain constituents of the charge which tend to cause rapid precipitation of pitch-like constituents so that pitch-like constituents not removed and remaining in the charge are less injurious. Both the nature and the amount of asphaltic and pitch-like constituents in the oil charge circulated over the heating surfaces of the pressure still are thus regulated by the action of the body of metallic oxides, and any associated material, and the rate of formation of such constituents may also be restricted. The body of metallic oxides may remove the more objectionable constituents and may act to permit a higher concentration of less objectionable constituents in the charge. Such pitch-like constituents as remain in the circulating charge after passage through the body of metallic oxides are apparently in solution in the circulating charge.

In carrying out this invention, the entire body of oil charged into the pressure still, for example gas oil, serves to hold in solution, up to the point of saturation, the pitch-like

constituents that are formed. In the process of the present invention, however, only the pitch-like constituents which are not removed by the body of metallic oxides remain to be held in solution in the charge, and the action of the body of metallic oxides apparently increases the amount of pitch-like constituents which the charge will hold in solution. Where no tar is withdrawn during the operation, or where a relatively small amount of tar is withdrawn, the pitch content gradually increases and approaches the saturation point, and during the latter portion of the operation, the pitch concentration may reach and even greatly exceed the saturation point in the remaining oil of the still charge. When fresh charging stock is introduced during the cracking operation, this also assists in holding the pitch-like constituents in solution, but as part of the fresh charging stock is cracked and as additional portions of the charge already in the still are also cracked, the increased solvent effect of the fresh charging stock is also progressively saturated. In either batch or semi-continuous operation, the cracking operation is terminated when, or before the amount of pitch-like constituents remaining in the charge, above the amount removed by the body of metallic oxides and any amount withdrawn as tar, increases to a point where objectionable deposition will take place upon the heating surfaces.

The process of the present invention may also be carried out in a continuous manner by withdrawing pitch-laden tar from the pressure still and introducing fresh oil at a regulated rate to maintain the pitch content of the charge below saturation in the way described in United States Letters Patent No. 1,598,136, granted August 31, 1926, to the Sinclair Refining Company on an application of Eugene C. Herthel, one of the applicants herein. The concentration of pitch-like and asphaltic constituents in the still charge may thus be regulated both by the action of the body of metallic oxides and by the introduction of fresh oil and the withdrawal of pitch laden tar. In carrying out the process of the invention in this way, both the nature and the amount of asphaltic or pitch-like constituents contained in the charge circulated over the heated surfaces are regulated, the action of the body of metallic oxides removing the more objectionable constituents, and the introduction of fresh feed and withdrawal of pitch laden tar regulating the concentration of the less objectionable pitch-like constituents in the charge.

In its broader aspects and embodiments, the improved process of the invention can be carried out in stills of different constructions, including shell stills as well as tube stills. Whatever the type of still, the metallic oxides are supported in the form of a bed

through which the entire charge can be circulated, and the still is provided with circulating means for circulating the charge through the bed of metallic oxides. The bed of metallic oxides is also supported out of contact with the heating surfaces of the still, and circulation of the oil over such heating surfaces as well as through the bed of metallic oxides is provided for. The circulating charge circulated in contact with the heating surfaces thus contains only the constituents which are not removed by circulation through the bed of metallic oxides.

The provision of a large bed of metallic oxides within the pressure still itself has the advantage that a large surface area of the metallic oxides is exposed to the charge, and a large area of bed is provided for circulation of the charge therethrough. The pressure still construction need not be changed by the provision of additional external equipment; but pressure stills of present day construction can readily be provided with a perforated support extending across the interior of the still for supporting the bed of metallic oxides in contact with the still charge.

The improved process of the present invention is particularly advantageous in the cracking of oils in tubular cracking stills or so-called tube stills, with the metallic oxides maintained in the form of a bed extending across a drum or bulk supply tank containing the main charge of oil, and with circulation of the oil from such drum through heating tubes and back to the drum. The tube stills may have either horizontal or vertical tubes, and may be of the bank or continuous type, with mass or stream circulation. The tube still may thus be one in which there is stream circulation through a series of tubes in the form of a continuous stream; or the circulation may be in parallel through a large number of heating tubes. The still may be one in which thermal action is relied upon to cause the circulation of the charge through the heating tubes, or it may be one in which the circulation through the tubes is effected by mechanical forcing means, such as a circulating pump. In such tube stills the circulation of the charge through the tubes and through the bed of metallic oxides in the bulk supply tank or drum results in causing all portions of the circulating charge to pass through the bed of metallic oxides in the bulk supply tank before they recirculate through the tubes, while the entire charge in the bulk supply tank is in contact with the bed of metallic oxides through which the charge is circulated.

The invention will be further described and illustrated in connection with the accompanying drawing which shows in a somewhat diagrammatic manner, one form of tubular pressure still embodying the inven-

tion and adapted for the practice of the process of the invention; but it is intended and will be understood that the invention is not limited to the specific construction and operation so described.

In the accompanying drawing, Fig. 1 shows, in a somewhat conventional and diagrammatic manner, and with part in section and part in elevation, one arrangement of a tubular pressure still embodying the invention and adapted for carrying out the process of the invention;

Fig. 2 is a sectional view of the drum or bulk supply tank of Fig. 1;

Fig. 3 is an enlarged detailed sectional view of one form of screen support by which the fuller's earth or like material is supported in the still; and

Fig. 4 is a similar view of a modified construction of screen support.

The pressure still illustrated in the drawings is of the general type described and illustrated in United States Letters Patent No. 1,285,200 granted November 19, 1918, to the Sinclair Refining Company on the application of Edward W. Isom. The present invention is of special value and application in connection with pressure stills of this general character.

The pressure still illustrated comprises the drum or bulk supply tank 1 having an outlet pipe 2 leading to the pump 3 by which the oil is pumped through the lower connecting pipe 4 to the distributing pipes and headers of the vertical tubes 5. From these tubes the oil is returned through the upper headers and connecting pipes and the return lines 6 to the bulk supply tank 1. The vertical tubes 5 are shown as enclosed within a furnace having one or more burners 7 adapted to be heated by gas or oil, the main furnace chamber 8, and three passes 9, 10 and 11 separated by baffles for causing the furnace gases to pass over the vertical tubes in a back and forth manner before they escape through the connecting flue 12 to the stack 13. From the drum 1 of the pressure still a vapor line 14 leads to the reflux tower 15 which is shown as a baffle tower having a series of baffles 16 therein. This tower has a return pipe 17 leading from the bottom and discharging into the outlet pipe 2. The vapor line 18 leads from the top of the reflux tower 15 to the condenser 19 from which the condensate and uncondensed gas are collected in the receiver 20. Draw-off pipes 21 and 22 are provided for drawing off the uncondensed gas and the condensate respectively from the receiver 20. A pressure regulating valve 23 is provided between the still and condenser, or the pressure can be regulated by means of the valves 24 and 25 in the outlet pipes from the receiver 20. A tar draw-off line 26 is provided; as well as a safety valve 28. A feed line 27 is shown for introducing fresh

charging stock into the upper portion of the reflux tower.

Within the still is provided a perforated support 29 suitably secured to the shell of the drum, e. g., by welding, and upon this perforated screen or support is maintained a relatively deep body of metallic oxides indicated at 31. A cross-section of one suitable form of screen support is illustrated in Fig. 3. This is made up of five layers, a top layer 32 of e. g.  $\frac{3}{8}$ " thick plate with  $\frac{1}{2}$ " perforations, a 4 mesh screen 33, a 40 mesh screen 34, another 4 mesh screen 33<sup>a</sup> and another  $\frac{3}{8}$ " thick steel plate 32<sup>a</sup> with  $\frac{1}{2}$ " perforations therein. A modified and simpler form of support is illustrated in Fig. 4, made up of the upper and lower perforated plates 32<sup>b</sup> having the screen 34<sup>b</sup> between them. The nature of this support can be varied so long as it performs the function of supporting the metallic oxides without leakage. Where finely divided metallic oxides are employed, a bed of filtering material or supporting material may be arranged on the perforated support 29 and the bed of metallic oxides supported thereon.

It will be noted that the perforated support and screen form a floor over the bottom of the still. With such a screen, thoroughly sealed by welding or riveting at the joints and secured to the walls of the still, the metallic oxides placed upon the support are maintained in the upper portion of the drum above the screen.

From Fig. 1 it will be noted that the return pipes 6 extend a considerable distance into the drum 1 and terminate in extensions 6<sup>a</sup> discharging to the remote end of the drum from that at which the outlet 2 is arranged. Where the velocity of the oil discharged from the pipe 6<sup>a</sup> is such as to cause erosion of the bed of metallic oxides, this bed can be protected by a plate or screen at the point of greatest velocity so as to prevent objectionable erosion.

In the operation of the pressure still, and in the carrying out of the cracking process of the present invention therein, the still is charged and heated to the cracking temperature and pressure. The still may be charged for example through the charging line 36 which also serves as a tar draw-off at the end of the run. During the cracking operation, the oil is circulated by the circulating pump 3 from the bulk supply tank 1 through the connecting pipes 2 and 4 to the heating tubes 5 and then back through the pipes 6 and 6<sup>a</sup> to the drum 1, discharging into this drum at the far end. Vapors from the oil are released in the bulk supply tank and pass up through the vapor line 14 into the reflux tower where the heavier ends are condensed by feed introduced into the top of the reflux tower through the feed line 27, and pass with such feed through the reflux tower and the run-back line to the pump circulation. The

uncondensed vapors pass through the vapor line from the reflux tower through the pressure control valve to the usual condenser and receiver. Additional feed can be introduced through the bearings of the pump by means of a feed line 35.

The charge is withdrawn from the drum below the perforated support and is circulated through the heating tubes and back to the drum or bulk supply tank above the perforated support. The unvaporized portion of the charge, before it can again be withdrawn and passed through the heating tubes, must pass downwardly through the bed of metallic oxides, and the bed of metallic oxides thus has an opportunity of exerting its action upon the objectionable asphaltic or pitch-like constituents of the charge. In the apparatus illustrated it will be noted that the bed of metallic oxides is completely submerged or immersed in the body of the charge and that it provides a large surface area in contact with the charge and a large sectional area through which the charge can flow downwardly at a relatively reduced rate as compared with the rate of circulation through the heating tubes. Ample opportunity is thus provided for the metallic oxides to act on the charge as it is slowly circulating or filtering downwardly therethrough.

In the apparatus illustrated it will be noted that the fresh feed introduced through the reflux tower and also the refluxed vapors from the still are returned to the outlet pipe 2 from the bulk supply tank and that additional feed may be introduced through the pipe 35 and the pump bearings. The circulating charge, therefore, is made up of the fresh feed and reflux together with such portion of the still charge itself as percolates downwardly through the bed of metallic oxides. The reflux and admixed fresh feed from the reflux tower may also be discharged into the bulk supply tank above the bed of metallic oxides so that substantially all of the oil circulating to the heating tubes is first subjected to the action of the bed of metallic oxides. The oil after circulation through the heating tubes is discharged into the upper compartment of the bulk supply tank above the bed of metallic oxides. The cracking operation may also be prolonged by withdrawing through the line 26 from the body of oil above the bed of metallic oxides part of the pitch-laden oil formed by the cracking operation as the pitch content of the charge increases.

The action of the metallic oxides is such that an increased percentage of the charge, including any fresh oil introduced during the operation, can be taken off as pressure distillate, and the pitch-content of the circulating charge can be carried to an increased amount during the run without objectionable carbon deposit on the heating tubes or surfaces. As

the pitch content of the charge approaches saturation, the removal from the circulating charge of the constituents which are removed by the metallic oxides prolongs the period of operation preceding saturation and enables the operation to be continued for a much longer period of time without objectionable carbon deposit on the heating tubes. Even where the pitch content is carried to a point considerably above saturation, the metallic oxides will remove from the circulating charge objectionable constituents which would otherwise tend to separate out on the heating tubes.

In carrying out a run according to the present invention, the still can be charged with fresh charging stock in the usual way. The charging stock may be, for example, gas oil or other suitable charging stock which is to be cracked for the production of gasoline or pressure distillate therefrom. The still charge is brought to the required cracking temperature and pressure in the usual manner. After the cracking temperature is reached, cracking begins and takes place in a gradual and progressive manner, the lighter vapors forming the pressure distillate passing off and being removed from the still, while the heavier vapors are refluxed back to the still. The asphaltic or pitch-like constituents formed are in part removed by the metallic oxides and in part held in solution in the remaining constituents of the charge. As the reaction proceeds, the pitch constituents formed which are not removed by the metallic oxides continue to dissolve in the oil and may progressively approach, or pass, the saturation point. Fresh oil may be introduced as the operation progresses, and the solvent capacity of fresh oil so introduced further assists in holding the unabsorbed pitch constituents in solution. The action of the metallic oxides may also be supplemented by withdrawing part of the pitch laden oil formed by the cracking reaction as the operation progresses. For example, a part of the pitch laden oil may be withdrawn during the period just preceding the time at which the pitch concentration reaches the saturation point, and the withdrawal of tar may be continued for all or part of the remaining period of operation until the operation is terminated. Before the pitch content reaches the saturation point, the withdrawal of tar through the line 26 may be begun and the rate of introduction of fresh oil into the still may be proportionately increased to maintain approximately a uniform level in the still, and the rate of tar withdrawal and of increased introduction of fresh feed so regulated that the pitch content is held below the saturation point in the still. The circulating charge may thus be kept of a regulated pitch content, while it is also subjected to the action of the bed of metallic

oxides in the still, and the action of the metallic oxide bed thus supplemented by the maintenance of a regulated pitch concentration.

Where the withdrawal of tar, even though in relatively small amount, is omitted the period during which the operation can be carried out without objectionable carbon deposit is somewhat reduced. The operation is preferably conducted to a point such that the charge remaining in the still can be withdrawn in a fluid condition. Where the operation has been carried to a point such that the unabsorbed pitch in the oil materially exceeds the saturation point, part of the pitch-like constituents present in the remaining charge will be in solution and part in suspension.

In another way of carrying out the invention, the metallic oxides may be precipitated on a supporting material and a body of this composite material employed in the pressure still. For example, fuller's earth may be treated with a suitable salt solution, for example an aqueous solution of iron chloride or iron sulphate, and the corresponding metallic hydrate precipitated on the earth by suitable treatment with an alkaline solution, for example an aqueous solution of sodium carbonate or of ammonia, and the earth and precipitate dried and dehydrated by roasting or the like.

The metallic oxide employed may be revived after use in the process of the invention by burning or roasting. The metallic content of the original oxide material may thus be reconverted to oxide and the revived or regenerated metallic oxide reused in the process of the invention. Sulfur present in combination with the oxide material may be converted to sulfur dioxide and separated as a gas which can also be recovered if desired.

It will be evident that the pressure maintained during the cracking operation can vary, depending upon the character of the charging stock and other considerations. For example, with a gas oil charging stock, a pressure in the neighborhood of 90 to 100 lbs. or up to 125 lbs. or more can be used. With a lighter kerosene charging stock, a higher pressure, for example, from 125 lbs. up to 300 lbs. or more is used with advantage. The pressure can be regulated by a pressure reducing valve arranged between the still and condenser, or the condenser can be maintained under still pressure and the pressure regulated by a pressure regulating valve arranged in the outlet of the receiver. The character of the charging stock used in the process can also be varied. In particular, a charging stock which contains constituents which otherwise would tend to cause an increased deposit of carbon or coke on the heating surfaces can be used in the process and the apparatus of the present invention and their

objectionable tendency in this respect overcome or greatly reduced by the action of the bed of metallic oxides.

We claim:

1. In the cracking of hydrocarbon oils by distillation under pressure in pressure still systems in which the charge of oil is circulated from a bulk supply tank through an externally heated tubular heater and back to the bulk supply tank, the improvement comprising maintaining a bed of material containing uncombined metallic oxides in the bulk supply tank submerged in, directly exposed to and extending entirely across the charge of oil therein and supported upon a support adapted to retain said material but to permit free passage of the still charge, supplying oil to the heating tubes from below said bed of material, and discharging the oil from the heating tubes directly into the charge of oil in the bulk supply tank above the support and material thereon.

2. In the cracking of hydrocarbon oils by distillation under pressure in pressure still systems in which the charge of oil is circulated from a bulk supply tank through an externally heated tubular heater and back to the bulk supply tank, the improvement comprising maintaining a bed of material containing uncombined metallic oxides in the bulk supply tank submerged in, directly exposed to and extending entirely across the charge of oil therein and supported upon a support adapted to retain said material but to permit free passage of the still charge, supplying oil to the heating tubes from below said bed of material, discharging the oil from the heating tubes directly into the charge of oil in the bulk supply tank above the support and material thereon and preventing saturation of the still charge with pitch by feeding fresh oil to the pressure still and drawing off pitch-laden oil therefrom.

3. In the cracking of hydrocarbon oils by distillation under pressure in pressure still systems in which the charge of oil is circulated from a bulk supply tank through an externally heated tubular heater and back to the bulk supply tank, the improvement comprising maintaining a bed of material containing uncombined metallic oxides in the bulk supply tank submerged in, directly exposed to and extending entirely across the charge of oil therein and supported free from externally heated surfaces upon a support adapted to retain said material but to permit free passage of the still charge, supplying oil to the heating tubes from below said bed of material, and discharging the oil from the heating tubes directly into the charge of oil in the bulk supply tank above the support and material thereon.

4. In the cracking of hydrocarbon oils by distillation under pressure in pressure still systems in which the charge of oil is circu-

lated from a bulk supply tank through a heater located away from the bulk supply tank and back to the bulk supply tank, the improvement comprising maintaining a bed of material containing uncombined metallic oxides in the bulk supply tank, submerged in, directly exposed to and extending entirely across the charge of oil therein and supported upon a support adapted to retain said material but to permit free passage of oil, supplying oil to the heater from below said bed of material, heating the oil to a cracking temperature in the heater by circulating heating gases externally there-over and discharging the oil from the heater directly into the charge of oil in the bulk supply tank above the support and material thereon.

5. In the cracking of hydrocarbon oils by distillation under pressure in pressure still systems in which the charge of oil is circulated from a bulk supply tank through an externally heated tubular heater and back to the bulk supply tank, the improvement comprising maintaining a bed of material containing uncombined metallic oxides in the bulk supply tank submerged in, directly exposed to and extending entirely across the charge of oil therein and supported upon a support adapted to retain said material but to permit free passage of the still charge, withdrawing oil from below the bed of material and rapidly circulating it through heating tubes and discharging the oil from

the heating tubes directly into the charge of oil in the bulk supply tank above the support and material thereon, and circulating the oil relatively slowly through the bed of uncombined metallic oxide.

6. In the cracking of hydrocarbon oils by distillation under pressure in pressure still systems in which the charge of oil is circulated from a bulk supply tank through an externally heated tubular heater and back to the bulk supply tank, the improvement comprising maintaining a bed of material containing uncombined metallic oxides in the bulk supply tank submerged in, directly exposed to and extending entirely across the charge of oil therein and supported upon a support adapted to retain said material but to permit free passage of the still charge, withdrawing oil from below the bed of material and rapidly circulating it through heating tubes and discharging the oil from the heating tubes directly into the charge of oil in the bulk supply tank above the support and material thereon, circulating the oil relatively slowly through the bed of uncombined metallic oxide, and preventing saturation of the still charge with pitch by feeding fresh oil to the pressure still and drawing off pitch-laden oil therefrom.

In testimony whereof we affix our signatures.

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