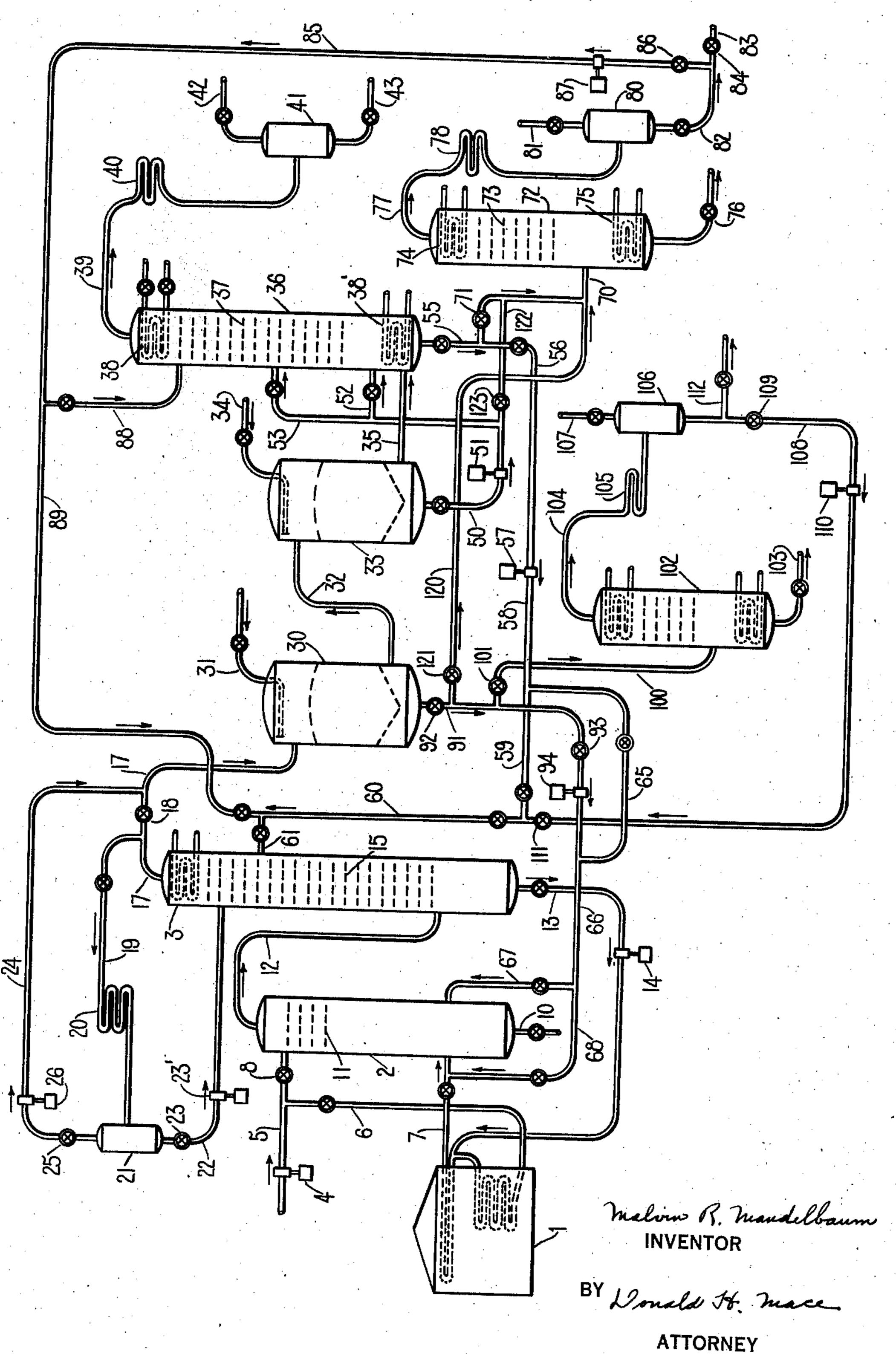
TREATMENT OF HYDROCARBON OIL

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TREATMENT OF HYDROCARBON OIL

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My invention relates to the treatment of hydrocarbon oil and more particularly to the conversion of relatively heavy hydrocarbon oil to gasoline, naphtha, or motor fuel suitable for use in internal combustion engines and the like. My invention relates more especially to the refining of distillates produced by the cracking of hydrocarbon oil under heat and pressure, by passing such distillate while essentially in the vapor phase 10 through a body of adsorbent catalytic material capable of selectively polymerizing undesirable gum-forming and color-imparting unsaturated constituents to compounds of higher boiling points which may readily be separated from the desired product, and, as set forth, for example, in U. S. Patents No. 1,340,889, 1,759,812, 1,759,813 and 1,759,814, all to Gray.

An object of my invention is to provide a process of refining distillates of the character set forth, by contact in the vapor phase with a suitable adsorbent catalytic material and having various novel and improved operating features and advantages as compared with the prior art.

A second object of my invention is to provide a novel and improved process of refining distillates of the character indicated by contact in the vapor phase in a plurality of stages with solid adsorbent material, wherein polymers and/or polymercontaining oil separated in the different stages may be segregated and individually subjected to separate treatments for the recovery and separation of the constituents thereof.

A further object of my invention is to provide a process of the character indicated, involving the preliminary fractionation of mixed hydrocarbon vapors resulting from a cracking operation for the recovery and removal of constituents heavier than gasoline, followed by vaporphase refining of the remaining constituents, wherein reflux necessary for the fractionating operation may be provided in a novel manner, and wherein gaseous constituents separated from the reflux thus provided and employed may be returned to the system for further treatment, including the recovery of valuable constituents therefrom.

My invention has for further objects such additional improvements in operative advantages and results as may hereinafter be found to obtain.

50 In order that my invention may clearly be set forth and understood, I now describe, with reference to the accompanying drawing, various preferred forms and manners in which my invention may be practiced and embodied. In this drawing,

The single figure is a more or less diagrammatic elevational view of apparatus for cracking hydrocarbon oil and for recovering a refined gasoline or motor fuel product from the vapors resulting from such cracking.

Referring now to the drawing, I have illustrated a typical cracking unit comprising in part a cracking furnace I, an evaporator 2 and a bubble tower or fractionator 3. While I have illustrated and will describe hereinbelow, for pur- 10 poses of illustration and exemplification, a particular form of cracking operation, my invention is not limited to the details of the cracking operation per se, but is readily applicable to the treatment of vapors resulting from various types of 15 oil-cracking operations.

In the particular instance described and shown in the drawing, however, a suitable charging stock, such as a gas oil, a crude petroleum oil, a reduced crude, or any other hydrocarbon oil 20 capable of being cracked to produce low-boiling distillate such as naphtha and/or gasoline is delivered by a pump 4 and lines 5 and 6 to the cracking furnace i, wherein the oil is subjected to a high temperature, ordinarily under superat- 25 mospheric pressure, and is thereby cracked. The conditions for effecting such cracking are of course well known to those skilled in the art, and my invention, at least in its broader aspects, is not limited to any particular conditions for crack- 30 ing. However, the oil to be cracked will ordinarily be heated to a temperature of from 800 to 1100° F., under a pressure of from atmospheric to as high as 1000 pounds per square inch or even higher, the exact conditions and the time of con- 35 tact being chosen according to the character of the particular oil charged and the nature of the results desired.

The cracked products from the furnace I, consisting either entirely or in part of cracked vapors, 40 pass through a transfer line 7, wherein may be located a reaction drum or soaking vessel (not shown), to an evaporator 2 where a separation of heavy liquid from gases and vapors takes place. Enough cooling is supplied in the evaporator 2, 45 for example, by admitting thereto through a valved line 8 a portion of the charging stock from the pump 4, to effect a separation of heavy residual constituents which are withdrawn from the bottom of evaporator 2 through a valved out- 50 let line 10. The interior of the evaporator 2 may be provided, as shown, with a plurality of baffles 11, which serve to assist in separating the heavy or residual constituents from the remaining vapors and to prevent undesired entrainment of 55 such constituents in the vapors and gases leaving the evaporator 2.

The remaining vapors and gases from which residual constituents heavier than gas oil have been removed then pass from the evaporator 2 through a vapor line 12 into the lower portion of the fractionator 3, the purpose of which is to rectify or fractionate the vapors to separate and remove therefrom constituents, such as gas oil, which are heavier than the desired final gasoline or naphtha product.

The separated gas oil fraction is removed from the bottom of the fractionating tower 3 through a valved line 13 and may be removed from the system, or, as shown, may be re-cycled by means of a pump 14 to the cracking furnace 1, preferably at an intermediate point in the course of travel of the charging stock therethrough.

The interior of the fractionating tower 3 is provided with suitable gas-and-liquid contact means, such as plates or trays 15. The cooling necessary to effect a separation of constituents heavier than gasoline in liquid form from the remaining gasoline vapors and gases may be variously accomplished, but I prefer to effect this cooling by condensing a portion of the vapors leaving the tower 3 and returning condensate thereby obtained to the tower 3 as a reflux medium therefor.

The remaining gases and vapors leave the fractionating tower 3 through a vapor line 17 having a valve 18 and a portion thereof may be delivered through a valved by-pass line 19 to a condenser 20. A separation of gases and con-35 densate thereby obtained is effected in a separator 21. The cool condensate is returned to the upper portion of the fractionating tower 3 through a reflux line 22 having a valve 23 and a pump 23'. The gases separated in the separator 21 may be 40 removed from the system, but are preferably passed through a gas line 24 having a valve 25 and a booster pump or compressor 26 which returns the gases to the vapor line 17, where they are commingled with the remaining vapors and 45 gases not delivered to the condenser 20.

The vapors and gases then pass through the line 17 to a clay-treating tower 30 adapted to contain a bed of adsorbent catalytic material, such, for example, as fuller's earth, de-colorizing clay or the like, as set forth in the patents to T. T. Gray recited hereinabove. The adsorbent material is preferably supported within the tower 30 in such manner as to facilitate free drainage therefrom of liquid products of polymerization as well as liquid supplied to the bed of material from an extraneous source, as, for example, from a spray line 31, and/or any condensate which is separated from the vapors, while traversing the treating bed.

60 Preferably, the vapors and gases are caused to traverse the bed of treating material in a downward direction in order to facilitate the separation and removal of liquid from the bed of treating material, thereby maintaining the bed in an active condition unhampered by the presence of excess quantities of liquid.

While my invention in some of its aspects is applicable to the treatment of the vapors in a single stage, in the preferred form illustrated in the accompanying drawing the treatment of the vapors with adsorbent material is conducted in a plurality of stages. Where this is true, the treated vapors leaving the first clay-treating tower 30 are passed through a vapor line 32 to a second clay-treating tower 33 which may conveniently be

made identical with the treating tower 30 and similarly contains a bed of solid adsorbent catalytic material supported for free drainage therein.

While I have shown separate treating towers 30 and 33 arranged in series, the treatment of 5 the vapors may be carried out in a single vessel adapted to contain a plurality of separate beds of solid treating material adapted to be traversed serially by the vapors in any desired order. Moreover, the separate towers 30 and 33, when 10 used, or the individual compartments of a tower having a plurality of treating compartments may be provided with suitable valves and connections (not shown) whereby one or the other of the beds of treating material or treating towers may 15 be by-passed whenever desired, and whereby the order in which the vapors traverse the beds may be varied at will.

According to the preferred manner of operating towers located in series, after a suitable period 20 of use, the order of the towers may be reversed, spent adsorbent being at this time discharged from the tower just previously first encountered by the vapors and fresh adsorbent being supplied thereto. The tower containing the fresh adsorbent is then replaced in the system in such manner that it becomes the last tower traversed by the vapors. This method of operating is desirable for the reason that the vapors are caused to traverse the beds in the order of increasing activity, and efficiency of conversion of undesirable constituents is enhanced.

As in the instance of the treating tower 30, the treating tower 33 may be provided with a spray line 34 for introducing into the bed of treating 35 material contained within the tower 33 a suitable liquid washing medium or solvent.

During contact of the vapors with the bed of treating material contained in the towers 30 and 33, the vapors and the treating material may 40 be maintained at a temperature above the normal condensing point of the vapors under the pressure of treatment which is preferably above atmospheric, for example, from 10 to 200 pounds per square inch. The temperature may be and 45 preferably is maintained at such a point, however, that polymers resulting from the contact of the vapors with the treating material and having boiling points higher than the boiling points of the ultimately desired product, separate out from 50 the vapors in liquid form and are removed from the beds of treating material by drainage therefrom. The separation of these higher-boiling polymers ordinarily entails the separation from the vapors of a certain proportion of desired 55 gasoline constituents, and this is the more marked because it is usually desired to provide a solvent to assist in the removal of the polymers from the beds of treating material. Such solvent may comprise a suitable oil, for example, a previously 60 treated gasoline, supplied from an external or extraneous source to the towers 30 and 33. Where desired, however, a portion of the gasoline constituents themselves may be permitted to condense in the clay-treating tower in order to act 65 as a solvent for removing polymers from the treating material.

Moreover, the gasoline vapors leaving the beds of treating material ordinarily contain a certain proportion of entrained undesired polymers. My 70 invention therefore is in part directed to the more efficient and thorough separation of desired treated gasoline products and the polymers formed as a result of the clay treatment.

I have found that when the treatment of the 75

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vapors proceeds in a plurality of stages as, for example, when the vapors are passed first through one clay-treating tower and then through a second clay-treating tower, due in 'part to dif-5 ferences between the various desired constituents which are polymerized, the polymers resulting in the several stages may differ considerably from each other. While, in the past, when series treatment in a plurality of stages has been effected, it has sometimes been the practice to combine the polymers from the several stages and to dispose of them by delivering them to some earlier point in the system where the temperature is such as to effect a re-volatilization of desired 15 constituents and a separation or even a cracking of the polymers themselves, according to my present invention the polymers or polymer-containing oils from the several stages of treatment of the vapors are preferably caused to be seg-20 regated from each other and may separately be treated for the recovery therefrom of true polymers as well as valuable constituents.

More specifically, as will be made more clear hereinbelow, the relatively strongly polymerized 25 product from a preliminary treating stage may be disposed of by delivering it to a selected portion of the system where the presence of such material will not be objectionable, while the relatively lightly polymerized product separated and re-30 covered from a subsequent stage may be treated by returning it to a different part of the system. In this manner, the more strongly polymerized products may be prevented from passing to the cracking furnace, while the more lightly poly-35 merized products may be permitted to pass to the cracking furnace. Or, where desired, the polymer oils may be separately or conjointly flashed to effect a separation of lighter from heavier constituents and the lighter flashed con-40 stituents from such flashing operation or operations may either separately or conjointly be returned to selected points in the system. Such flashing may be carried out in such manner as to produce a residual material or materials con-45 sisting to a desired extent of true polymers and constituting a suitable raw material for chemical synthesis or other manufacture.

In order to effect a separation and removal of relatively high-boiling polymers entrained in the 50 vapors leaving the treating tower 33, these vapors are passed through a vapor line 35 to a polymer-separating tower or after-fractionator 36, wherein the vapors are rectified to throw down and condense undesired and relatively 55 high-boiling polymer oil. The fractionator 36 is preferably provided with plates or trays 37, as well as suitable cooling means, such, for example, as a cooling coil 38 located in the upper portion of the tower 36. A heating or reboiling coil 38' 60 may also be provided in the inner part of the tower 36, as shown. The treated vapors, after rectification, pass from the upper portion of the tower 36 through a vapor line 39 to a condenser 40, from which condensate and uncondensed ma-65 terial pass to a separator 41 having a valved exit 42 for gases and a valved drain line 43 for condensate, this condensate comprising refined gasoline or naphtha.

Polymers formed during the passage of the vapors through the treating material contained in the treating tower 33, as well as any solvent oil condensed in or supplied to the tower 33, are removed from the latter through a valved line 50 and delivered by means of a pump 51, the conduit 50, and either a valved branch line 52

or a similar line 53 to the fractionator 36, being introduced to the latter above the point of entrance of vapors from the treating tower 33.

The rectification taking place in the tower 36 thus serves not only to remove entrained polymers from the vapors leaving the tower 33, but also to effect a separation of desired from undesired constituents present in the polymer oil withdrawn from the bottom of the tower 33. The thereby separated and reduced polymer oil collecting in the bottom of the tower 36 is withdrawn therefrom through a valved-line 55 for disposal in such manner as may be indicated hereinbelow.

According to one modification of my invention, 15 this polymer oil, which may still contain some constituents which are light enough to constitute a valuable gasoline product, is delivered through a valved line 56, a pump 57 and lines 58, 59, 60 and 61, all provided with suitable valves, to the 20 upper part of the fractionating tower 3 for use as reflux therein. When thus supplied as reflux to the tower 3, this polymer oil is caused to be fractionated in the latter with resultant separation in liquid form of polymers which com- 25 mingle with the gas oil recovered and removed from the bottom of the tower 3, while the lighter and more valuable constituents pass overhead in vapor form through the vapor line 17 and are eventually condensed in the condenser line 40. 30

As an alternative mode of procedure, this polymer oil either alone or commingled with polymer oil removed from the treating tower 30 may be delivered to the evaporator 2. When it is desired so to deliver this polymer oil, the latter may 35 be caused to flow from the line 58 through a valved line 65, a line 66 and a further line 61 directly to the evaporator 2. Or, instead of passing directly to the evaporator 2 through the line 67, this oil may be passed through a valved 40 branch line 68 which communicates with the transfer line 7, the polymer oil being thereby introduced to the stream of cracked products leaving the cracking furnace and passing to the evaporator 2.

It will be obvious to those skilled in the art that when this polymer oil is delivered to the fractionating tower 3, the polymer contents thereof will pass to the cracking furnace in the gas oil removed from the bottom of the frac- 50 tionator 3 and will be subjected to cracking in the coils within the furnace 1, whereas when the polymer oil is delivered to the transfer line 7 or directly to the evaporator 2 the passage of polymers through the cracking furnace I is avoided 55 and the heavy or residual portions of the polymer oil are largely or entirely removed from the system together with the tar withdrawn from the bottom of the evaporator 2. The introduction of this polymer-containing oil to the trans- 60 fer line 7 serves the additional purpose of quenching or rapidly cooling the products from the cracking furnace I, thus preventing undesirable continuance of the cracking reaction.

If desired, the polymer-containing oil removed 65 from the bottom of the fractionating tower 36 through the line 55 may be delivered through a branch conduit 70 having a pressure-reducing valve 71 to a polymer flash tower 72. The tower 72 is preferably provided interiorly with plates 70 or trays 73, a cooling coil or other cooling means 74 located in the upper portion of the tower 72, and a heating coil 75 located in the bottom of the tower 12. By means of the pressure reduction effected by the valve 71, the polymer-con- 75

taining oil delivered to the tower 72 is caused to be reduced substantially to atmospheric pressure or at any rate to a pressure materially lower than that obtaining in the tower 36, and under the 5 influence of this reduction in pressure the polymer-containing oil is caused to be flashed and the constituents thereof are fractionated or rectified, this action being assisted by the cooling and heating means located within the flash 10 tower **72**.

The heavier constituents, comprising principally the true polymers, remain in liquid form and are withdrawn from the bottom of the tower 72 through a valved line 76, while the lighter 15 constituents, comprising naphtha or the like, are withdrawn from the upper portion of the tower 72 through a vapor line 77 and passed to a condenser 78 where normally liquid constituents are caused to be condensed in liquid form. The con-20 densate and any gases that may be present then pass to a separator 80 wherein a separation of liquids from gases occurs, the gases passing out of the separator 80 through a line 81, and the condensate passing out of the separator 80 25 through a line 82. By means of a line 83 having a valve 84, these constituents may be withdrawn from the system for use as desired. Alternatively, however, by means of a conduit 85 having a valve 86 and a pump 87, this condensate may 30 be delivered either through a valved branch conduit 88 to the upper portion of the fractionating tower 36 or through a valved branch conduit 89 and the inlet 6! to the upper portion of the main fractionating tower 3. As a further alternative, 35 condensate recovered in the separator 80 may be returned through the lines 34 or 31 to the treating tower 33 or the treating tower 30 or both, as desired.

The polymer-containing oil removed from the 40 bottom of the first treating tower 30 is preferably not returned to the fractionating tower 3, but after being withdrawn from the tower 30 through a line 91 having valves 92 and 93, may be delivered to a pump 94 which in turn delivers this 45 polymer-containing oil through the conduit 66 and either the conduit 67 or the conduit 68 to the evaporator line 2 or to the transfer line 7, as desired.

As an alternative mode of procedure, the poly-50 mer-containing oil removed from the bottom of the treating tower 30 may be delivered through a branch conduit 100 having a pressure-reducing valve 101 to a polymer flash tower 102, the construction of which may conveniently be identical with that of the polymer-flash tower 72. Here a flashing and rectification takes place, the true polymers being withdrawn in liquid form from the bottom of the flash tower 102 through a valved line 103 while the flashed and rectified 60 lighter vapors pass through a vapor line 104 to a condenser 105. The resulting naphtha condensate is separated from any gases which may be present in a separator 106, from which gases are removed through a line 107. The naphtha 65 condensate may be passed through a line 108 having a valve 109, pump 110 and a valve 111 to the line 60 from which it flows through the inlet 61 to the fractionating tower 3 for use as reflux therein. By means of a valved-branch conduit 112, however, this naphtha condensate may be withdrawn from the system. As in the case of the naphtha condensate removed from the separator 80, this naphtha condensate may similarly be delivered to the treating tower 30, the treat-75 ing tower 33 or both as desired, either or both

of the lines 31 and 34 being used for this purpose.

Where segregation of the polymer-containing oil removed from the treating tower 30 and 33, respectively, is not desired, the polymer-contain- 5 ing oil from the treating tower 30 may be delivered to the flashing tower 72 together with the polymer-containing oil removed from the treating tower 33 and fractionating tower 36. For this purpose, I have shown a line 120 having a 10 valve [2] and leading from the line 9! to the line 70 which in turn communicates with the flash tower 72.

By means of a line 122 having a valve 123 and leading from the line 50 to the line 70, polymer- 15 containing oil from the tower 33 may be delivered to the flash tower 72 unmixed with bottoms from the tower 36, this procedure being useful when bottoms from the tower 36 are not delivered to the flash tower 72.

It will be seen that my process provides for considerable improvement in flexibility and economy of operation, especially when the vaporphase treatment of the gasoline hydrocarbons with adsorbent material is carried out in a plu- 25 rality of stages located in series along the path or flow of the vapors, and that my invention further provides for the selective disposal of polymer-containing oils drawn from the various stages in a manner best suited to the characteris- 30 tics of each.

While I have described my invention hereinabove with respect to various illustrative examples and embodiments it will be obvious to those skilled in the art that my invention is not limited 35 to the details of such illustrative examples or embodiments, but may variously be practiced and embodied within the scope of the claims hereinafter made.

I claim:

1. The process of refining gasoline which comprises subjecting the gasoline while essentially in the vapor phase to contact with solid adsorbent catalytic material in a plurality of successive treating stages, said material being effective to 45 selectively promote polymerization of unstable unsaturated constituents undesired in the final product to higher-boiling products, removing polymer-containing oils from the individual treating stages, subjecting each of said poly- 50 mer-containing oils to distillation in a separate zone removed from the flow of vapors undergoing treatment to separate them into constituents lying within a gasoline or naphtha boiling range and higher-boiling polymer products, withdraw- 55 ing said polymer products from the process, removing refined vapors from the last treating stage and condensing them to recover gasoline constituents therefrom, and returning said gasoline or naphtha constituents separated from said Ro higher boiling polymer products to said treating stages.

2. The process of refining gasoline which comprises subjecting the gasoline while essentially in the vapor phase to contact with solid adsorbent 65 catalytic material in a plurality of successive treating stages, said material being effective to selectively promote polymerization of unstable unsaturated constituents undesired in the final product to higher-boiling products, maintaining 70 said stages within a temperature range effective to cause condensation of said polymerized products while ineffective to cause condensation of the bulk of the gasoline vapors undergoing treatment, removing polymer-containing oils from the 75

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individual treating stages, subjecting each of said polymer-containing oils to distillation in a separate zone removed from the flow of vapors undergoing treatment to separate them into constituents lying within a gasoline or naphtha boiling range and higher-boiling polymer products, withdrawing said polymer products from the process, removing refined vapors from the last treating stage and condensing them to recover gasoline constituents therefrom, and returning said gasoline or naphtha constituents separated from said higher boiling polymer products to said treating stages.

3. In the method of producing refined gasoline 15 from higher-boiling hydrocarbon oil wherein said higher-boiling hydrocarbon oil is subjected to cracking conditions, the cracked products separated into vapors and residue, the vapors initially dephlegmated to separate entrained resid-20 ual constituents and the remaining vapors subjected to additional fractionation to separately condense constituents above the gasoline boiling range; the improvement which comprises subjecting uncondensed vapors from the fractionat-25 ing zone to contact with solid adsorbent catalytic material capable of polymerizing objectionable unsaturates in a plurality of successive treating stages under conditions effective to cause condensation of polymers resulting from said contact, removing polymer containing oil from an early treating stage and passing the same to the zone in which the cracked vapors are initially dephlegmated, removing polymer-containing oil from the latter treating stage and subjecting it 35 to distillation in a zone separate from the zone receiving the polymer-containing oil from the early treating stage to separate it into a fraction containing constituents lying within the gasoline boiling range and a fraction containing the highan er-boiling polymer constituents, removing refined gasoline vapors from the last treating stage and condensing the same to recover a desired gasoline product.

4. The process of refining gasoline which com-45 prises subjecting the gasoline while essentially in vapor phase to contact with solid adsorbent catalytic material capable of polymerizing objectionable gum-forming and color-imparting constituents into higher-boiling compounds, main-50 taining said solid adsorbent catalytic material at a temperature effective to cause condensation of polymerized compounds while ineffective to cause condensation of the bulk of the gasoline vapors undergoing treatment, separately removing poly-55 mer-containing oil from the vapors, subjecting said polymer-containing oil to distillation in a separate zone removed from the flow of vapors undergoing treatment to liberate gasoline constituents absorbed therein as vapors, withdrawing the remaining unvaporized polymer from the process, condensing the vapors so formed to recover the gasoline therefrom, admixing gasoline thus obtained with said vapors prior to contact with said catalytic material, and condensing 65 gasoline vapors separated from said polymercontaining oil to recover a treated gasoline product.

5. The process of refining gasoline which comprises subjecting the gasoline while essentially in the vapor phase to contact with solid adsorbent catalytic material in a treating stage, said material being effective to selectively promote polymerization of unstable unsaturated constituents undesired in the final product to higher boiling products, removing polymer-containing oils from

the treating stage, subjecting said polymer-containing oils to distillation in a separate zone removed from the flow of vapors undergoing treatment to separate them into constituents lying within a gasoline or naphtha boiling range and 5 higher-boiling polymer products, withdrawing said polymer product from the process, removing refined vapors from the treating stage, and returning the separated constituents lying within a gasoline or naphtha boiling range to the vapors 10 being treated prior to the contacting thereof with said catalytic material.

6. In the method of producing refined gasoline from higher-boiling hydrocarbon oil wherein said higher-boiling hydrocarbon oil is sub- 15 jected to cracking conditions, the cracked products separated into vapors and residue, and the vapors subjected to fractionation to separately condense constituents above the gasoline boiling range; the improvement which comprises sub- 20 jecting uncondensed vapors from the fractionating zone to contact with solid adsorbent catalytic material capable of polymerizing objectionable unsaturates in a plurality of successive treating stages under conditions effective to cause con- 25 densation of polymers resulting from said contact, removing polymer-containing oil from an early treating stage and passing the same to the zone in which the cracked products are separated into vapors and residue, removing polymer-con- 30 taining oil from the latter treating stage and subjecting it to distillation in a zone separate from the zone receiving the polymer-containing oil from the early treating stage to separate it into a fraction containing constituents lying within 35 the gasoline boiling range and a fraction containing the higher-boiling polymer constituents, removing refined gasoline vapors from the last treating stage and condensing the same to recover a desired gasoline product.

7. In the method of producing refined gasoline from higher-boiling hydrocarbon oil wherein said higher-boiling hydrocarbon oil is subjected to cracking conditions, the cracked products separated into vapors and residue, and the vapors 45 subjected to fractionation to separately condense constituents above the gasoline boiling range; the improvement which comprises subjecting uncondensed vapors from the fractionating zone to contact with solid adsorbent catalytic mate- 50 rial capable of polymerizing objectionable unsaturates in a plurality of successive treating stages under conditions effective to cause condensation of polymers resulting from said contact, removing polymer-containing oil from an 55 early treating stage and passing the same to a separate distillation zone to separate it into a fraction containing constituents lying within the gasoline boiling range and a fraction containing the higher-boiling polymer constituents, admix- 60 ing gasoline constituents thus obtained with said vapors prior to the contacting thereof with said catalytic material, removing polymer-containing oil from the latter treating stage and passing polymers thus obtained to the zone 65 wherein the cracked products are separated into vapors and residue, removing refined gasoline vapors from the last treating stage and condensing the same to recover a desired gasoline product.

8. In the method of producing refined gasoline from higher-boiling hydrocarbon oil wherein said higher-boiling hydrocarbon oil is subjected to cracking conditions, the cracked products separated into vapors and residue, and the vapors 75

subjected to fractionation to separately condense constituents above the gasoline boiling range; the improvement which comprises subjecting uncondensed vapors from the fractionating zone to contact with solid adsorbent catalytic material capable of polymerizing objectionable unsaturates in a plurality of successive treating stages under conditions effective to cause condensation of polymers resulting from said con-10 tact, removing polymer-containing oil from an early treating stage and admixing same with products of cracking prior to the treatment of said vapors with said catalytic material, removing polymer-containing oil from the latter treating stage and subjecting it to distillation in a zone separate from the zone receiving the polymercontaining oil from the early treating stage to separate it into a fraction containing constituents lying within the gasoline boiling range and a 20 fraction containing the higher-boiling polymerconstituents, removing refined gasoline vapors from the last treating stage and condensing the same to recover a desired gasoline product.

9. In the method of producing refined gasoline 25 from higher-boiling hydrocarbon oil wherein said higher-boiling hydrocarbon oil is subjected to cracking conditions, the cracked products separated into vapors and residue, and the vapors subjected to fractionation to separately condense 30 constituents above the gasoline boiling range; the improvement which comprises subjecting uncondensed vapors from the fractionating zone to contact with solid adsorbent catalytic material capable of polymerizing objectionable un-35 saturates in a plurality of successive treating stages under conditions effective to cause condensation of polymers resulting from said contact, removing polymer-containing oil from an early treating stage and passing the same to a 40 separate distillation zone to separate it into a fraction containing constituents lying within the gasoline boiling range and a fracion containing the higher-boiling polymer constituents, admixing gasoline constituents thus obtained with said 45 vapors prior to the contacting thereof with said

catalytic material, removing polymer-containing oil from the latter treating stage and passing polymers thus obtained for admixture with products of cracking prior to the treatment of said vapors with said catalytic material, removing refined gasoline from the last treating stage and condensing same to recover a desired gasoline product.

10. In the method of producing refined gasoline from higher-boiling hydrocarbon oil wherein 10 said higher-boiling hydrocarbon oil is subjected to cracking conditions, the cracked products separated into vapors and residue, and the vapors subjected to fractionation to separately condense constituents above the gasoline boiling range; the 15 improvement which comprises subjecting uncondensed vapors from the fractionating zone to contact with solid adsorbent catalytic material capable of polymerizing objectionable unsaturates in a plurality of successive treating stages under 20 conditions effective to cause condensation of polymers resulting from said contact, removing polymer-containing oil from an early treating stage and passing the same to a separate distillation zone to separate it into a fraction con- 25 taining constituents lying within the gasoline boiling range and a fraction containing the higher-boiling polymer constituents, admixing gasoline constituents thus obtained with said vapors prior to the contacting thereof with said 50 catalytic material, removing polymer-containing oil from the latter treating stage and passing polymers thus obtained to the zone wherein said vapors are subjected to fractionation, removing refined gasoline from the last treating stage and 35 condensing same to recover a desired gasoline product.

11. A process in accordance with claim 6 wherein a part of the uncondensed vapors from said fractionating zone is passed through a cool- 40 ing zone to obtain a condensate, condensate thus obtained being returned to the fractionating zone as reflux therefor, while uncondensed vapors are passed to said treating stages.

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