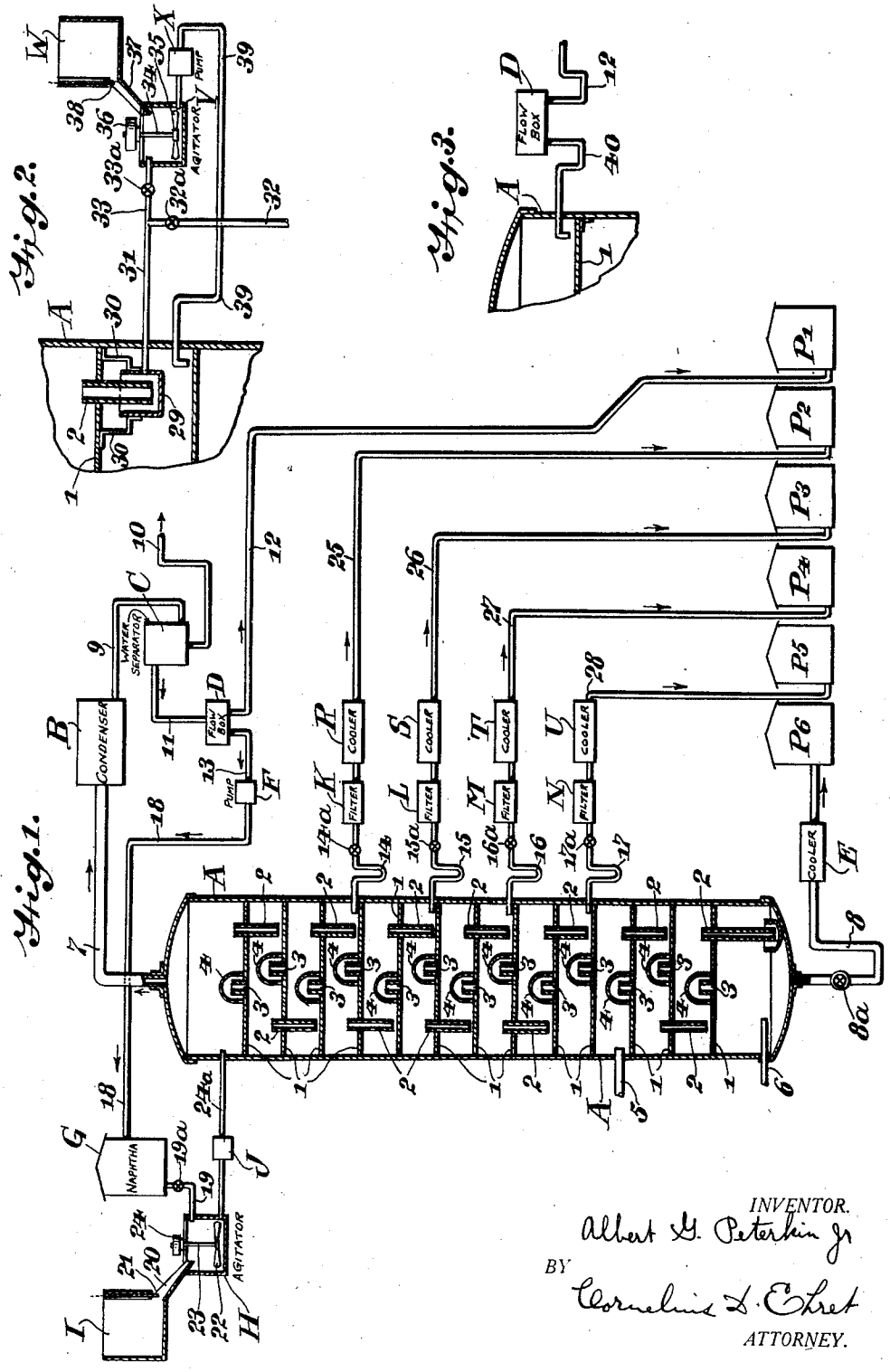
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REFINING SYSTEM

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REFINING SYSTEM

Application filed April 8, 1926. Serial No. 100,477.

My invention relates to the art of refining hydrocarbon oils with particular reference to a method of and apparatus for concurrently refining and distilling an oil of the character aforesaid.

In accordance with my invention, vapors of a hydrocarbon oil during their fractionation are brought into contact with a refining agent in mixture with hydrocarbon oil, and more particularly, the last-mentioned oil is utilizable as a refluxing liquid.

Further in accordance with my invention, oil in vapor phase is passed along a path into contacting relation with successive pools of refluxing liquid maintained at successively lower temperatures, containing in suspension a solid refining agent.

My invention is particularly applicable to the distillation of hydrocarbon oil in the manner described in Chillas Patent No. 1,612,572, December 28, 1926.

My invention resides in a method and apparatus of the character hereinafter described and claimed.

For an understanding of my method, and for an illustration of some of the various forms my apparatus may take, reference is to be had to the accompanying drawing, in which:

Fig. 1 is a schematic view of apparatus utilizable in accordance with my invention.

Fig. 2 is a fragmentary schematic view of a modification.

Fig. 3 is a schematic view of a modification of the portion of the apparatus for feeding reflux liquid into the column.

In the commonly used methods of refining hydrocarbon oils such as petroleum and coal tar oils the crude oil is first subjected to distillation and is thereby separated, frequently with the aid of a fractionating column, into fractions of different properties characterized further by differences in their boiling ranges. For example, in the distillation of crude petroleum there may be obtained fractions such as crude naphtha, crude lamp oils, gas oil, light lubricating oils and heavy lubricating oils. These fractions resulting from the distillation are in general unsuited for marketing as withdrawn from the column and are subjected to refining processes of various natures by which such desirable results may be obtained as odor removal, color stabilization, sulphur removal, etc. Among the commonest refining methods are the treatment with sulphuric acid and with clay or fuller's earth. For example, the crude lamp oil obtained by the initial distillation of petroleum is commonly refined by treatment with sulphuric acid in order to remove objectionable compounds, as unsaturated compounds, and to thereby stabilize color, and with a reagent such as sodium plumbite for the purpose of removing odoriferous compounds and rendering the lamp oil "sweet". The sulphuric acid treatment particularly produces in the oil polymerized compounds of low volatility which interfere with the burning quality of the oil. It is, therefore, common practice to re-distill the oil after these various chemical treatments.

I have found that oils may frequently be refined in the course of their normal fractional distillation process by subjecting them in the fractionating column to the action of a solid refining agent introduced at some point in the column, held in suspension in the reflux liquid passing through the column, and flowing therewith countercurrent to the rising vapors in the column. The solid reagent used may be of various types depending on the type of refining which is needed. For example, for the removal of compounds tending to produce an unstable color in the condensed distillate I may use clay, fuller's earth, bauxite, bone black, active carbons, and other equivalent catalytic or adsorbent materials, hereinafter generically termed "fuller's earth". Where sweetening or sulphur removal is to be effected, I may utilize a material, as copper oxide, lead oxide, mercuric oxide or the like, hereinafter generically termed "copper oxide," having the property chemically combining with a sulphur compound or other undesired material in the oil undergoing distillation. I may use one of these reagents alone or a mixture of two or more of them in order to accomplish several different results at the same time.

In practicing my invention I prefer to use

a column of the plate and bell or bubble type. The solid reagent used in my method may be fed in at the top of the column or at any point intermediate between the top of the column and the point of vapor inflow. It is preferably introduced as a slurry mixed with a liquid similar to the reflux liquid in the column at the point of introduction.

In the following description for purposes of description, it will be assumed that a mid-continent crude petroleum of about 35° A. P. I. gravity is being refined, although it shall be understood that my method is applicable in connection with the refining of any hydrocarbon oil.

Referring to Fig. 1, the fractionating column A of any suitable type, as for example, equipped with the bubbler plates 1 in which are the downflow pipes 2 and the vapor uptakes 3 covered by the bubbler caps 4, is utilized for the fractionation of the vapors or mixture of oil and vapors introduced from any suitable heating structure, for example, a pipe still, through the pipe 5. If desired, superheated steam may be introduced through the pipe 6. The vapors in passing through the column are fractionated and the low boiling vapors are removed through the line 7, while unvaporized liquid and reflux are removed from the bottom of the column through the line 8, controlled by the valve 8^a. The vapors pass through the line 7 to the condenser B from which liquid passes through the line 9 to the water separator C. Water present in the oil or added as steam is removed through the line 10 and discarded, while oil passes through the line 11 to the flow box D where it is separated into two streams, one of which passes through the line 12 to a suitable destination, as storage tank P^1, and the other passing along line 13, thereafter serving as a reflux for the fractionating column. The residue from the bottom of the column is passed through the line 8 to the cooler E and thence to the storage tank P^6. As suitable elevations in the column liquid drawoff lines 14, 15, 16 and 17 controlled, respectively, by valves 14^a, 15^a, 16^a and 17^a are provided to effect the removal of various intermediate cuts. In the example illustrated these cuts are lamp oil distillate, gas oil, paraffine distillate and high viscosity distillate respectively. Naphtha vapors leave the top of the column and the bottoms removed through the line 8 constitute a satisfactory asphalt.

In accordance with my invention, these various cuts are refined during the fractionation so that when passed to the storage tanks or other destinations, they will be substantially free from undesirable bodies. To this end, there is introduced into the column one or more solid refining agents which are caused to flow downwardly with the reflux. As illustrated, the solid reagent may be added to the reflux before the latter is fed to the column or if desired it may be introduced at any point below the introduction of reflux. In any event it is preferred that the solid be fed to the column in suspension in a liquid having a composition similar to that of the liquid in the column at the point of introduction.

That portion of the condensate to be used as reflux is forced by the pump F from line 13 to and through the line 18 to the tank G, from which it may be fed continuously or intermittently by way of line 19 controlled by valve 19^a to the agitator H, to which the solid reagent, as, for example, a mixture of fuller's earth and copper oxide in finely divided condition is conducted from bin I along the chute 20 controlled by gate 21. In agitator H, the mixture is agitated by the propellor 22 mounted on the shaft 23 which may be actuated by pulley 24 driven by any suitable mechanism, not shown. The mixture of naphtha and solid reagent passes under the action of pump J through the line 24^a into the top of the column A and passes downwardly through the downflow pipes 2 onto the plates 1 where it is brought into intimate contact with the rising vapors.

The solid reagent reacts with the undesirable components of the liquid with which it is brought into contact while passing through the column. In general, these undesirable constituents are the most reactive constituents, chemically, in the oil. They may be objectionable in that owing to their reactivity they may oxidize readily to produce color imparting bodies or may polymerize or oxidize with the formation of resinous bodies or may produce corrosive effects upon the metal containers, etc. These various types of compounds are more readily acted upon by such solid reagents as are used in my process and may be chemically changed, due to the action of the solid reagent, to such bodies as may be adsorbed by the solid or held in chemical combination therewith or may be converted into other compounds which are innocuous.

In ordinary fractional distillation substantial equilibrium is established between the vapor and the liquid on each plate by an interchange of constituents whereby high boiling components of the vapor pass into the liquid phase while low boiling components of the liquid pass into the vapor phase. In fractional distillation in which the vapors are refined according to my invention, there is a continual removal from the liquid of the undesirable components by the action of the solid reagent. As similar undesirable materials are present in the vapor phase, there is a tendency to establish an equilibrium in respect to these components in the two phases. The result is that compounds pass from the vapor phase into the liquid

to take the place of those removed as a result of the action of the solid reagents. Thus in passage of the vapors upwardly through the column there is a continual removal therefrom not only of high boiling components as in ordinary fractionation but also of those undesirable constituents which react with the solid reagent passing downwardly in suspension in the reflux liquid.

Since the solid material passes through substantially the entire length of the column, the various fractions removed, as through drawoffs 14, 15, 16 and 17, contain some of this material in suspension. This solid may be removed by settling or as shown by passing through the filters K, L, M, and N, of any suitable type, for example, rotary filters. The filtered fractions may then be passed through coolers R, S, T and U, from which they are led through the lines 25, 26, 27 and 28 to suitable destinations, as the storage tanks P^2, P^3, P^4 and P^5, respectively. In some cases it may be desirable to insert a preliminary cooler before the filter. With the more viscous fractions it is desirable to filter at as high a temperature as possible because of the greater ease of filtering the oil at elevated temperature.

In those cases where the residue withdrawn through the pipe 8 is of such a nature that filtering is impractical to remove the solid reagent, the entire quantity of reflux may be withdrawn through the lowermost liquid drawoff 17. The plate from which this drawoff leads is not provided with a downflow pipe. This prevents the passage of any solid material below the drawoff 17 and thus it is kept from mixing with the residue.

An alternative method of carrying out my invention is to mix the solid reagent with the reflux liquid at some point below the top of the column and cause it to flow down through the column with the reflux liquid from this point. Referring to Fig. 2, there is illustrated one form of apparatus suitable for carrying out this alternative method. By this modification the entire reflux stream may be withdrawn from the column at some particular point by causing the downflow pipe 2 of a plate 1 to discharge into the seal pan 29, supported, for example, by the rods 30 from the plate 1 above. The reflux is withdrawn from seal pan 29 through the line 31 and is divided into two streams, one of which may be passed to storage and the other mixed with the solid reagent and returned to the column. The division may be accomplished by the use of the two pipes 32 and 33 controlled, respectively, by the valves 32^a and 33^a or by a flow box or other means. The oil passing through the line 33 discharges into the agitator V into which extends the shaft 34 carrying the propeller 35, said shaft carrying the pulley 36 actuated by any suitable mechanism, not shown. Solid reagent is fed into the agitator from the bin W through the chute 37 controlled by the slide gate 38. The mixture of oil and reagent is agitated by the propeller 35 and is forced by the pump X through the line 39 to the plate 1 immediately below the seal pan 29. When introducing the solid reagent in this manner the introduction of reflux at the top of the column should be modified as shown in Fig. 3 wherein a trapped line 40 leads directly from the flow box D to the top of the column.

When my invention is performed in the manner last described, the same refining effect is produced, for, since all of the vapor passes through these plates over which the suspension of solid reagent flows, it must all come in contact with the liquid which is in contact with the refining reagent and the objectionable constituents are changed or removed in the same manner as in the first application of my process described above. This alternative arrangement has an advantage in that the streams removed from the column above the point of introduction of the solid refining reagent are not contaminated with the reagent and do not, therefore, require filtration. Furthermore these streams are free from polymerized bodies produced by the catalytic action of the solid material. In practicing this alternate method, the solid reagent is mixed with the reflux liquid preferably that which collects on the palte 1 which passes material to the draw-off 16, this being the plate from which the second heaviest distillate stream is removed. By following this procedure all of the solid comes out with the lowest stream and the various other streams are not contaminated therewith.

The refining agents removed from the oil in the filters, K, L, M and N, may be revivified by any suitable means and utilized for subsequent treatment of additional quantities of oil. For example, the spent fuller's earth and copper compound may be roasted in any suitable furnace, thereby burning the adsorbed polymerized product from the former and oxidizing the latter to copper oxide.

As a result of my invention, distillation of the oil into various fractions and refining of these fractions are accomplished in one step in the ordinary distillation apparatus without rehandling and with the use of only a small amount of extra equipment. This effects a material saving over usual refining procedure in which it is necessary to conduct separate operations involving separate agitators, stills, pumps, etc. There is also a saving in fuel required, for, by refining during the distillation, it is unnecessary to redistill the treated naphtha and lamp oil cuts as is done when they are acid treated. In effect, my invention results in the refining of the various fractions without any additional cost

over the distillation other than that incident to the use of the solid reagent.

The system herein described may be advantageously utilized in or as a part of a system of the character described in Patent No. 1,709,874, in which the petroleum charged through the pipe 5 into the column A is previously rapidly heated to high temperature in excess of the normal cracking temperature without substantial cracking; and in which superheated steam is introduced into the column at or adjacent the bottom thereof.

What I claim is:

1. Apparatus for simultaneously fractionating and purifying vapors of hydrocarbon oil comprising a fractionating column, means intermediate the top and bottom of said column for withdrawing liquid fractions therefrom, means for introducing into said column near its top liquid reflux oil, means for withdrawing at a point between the top and bottom of said column a portion of said reflux oil, a bin containing solid purifying agent, means for transferring purifying agent from said bin into mixture with a portion of said reflux oil withdrawn, and means for returning the mixture to the column as reflux liquid.

2. A method for simultaneously fractionating and purifying the vapors of hydrocarbon oil, which comprises passing the vapors upwardly in contact and interchange relation with descending liquid reflux oil, removing liquid fractions of the oil from the fractionating zone, suspending a solid purifying agent in at least a portion of a fraction so removed, and passing the oil containing the suspended material in fractionating relation with at least a portion of the ascending vapors.

3. A method for simultaneously fractionating and purifying the vapors of hydrocarbon oil, which comprises passing the vapors upwardly in contact and interchange relation with descending liquid reflux oil having in suspension therein a solid purifying agent, removing liquid fractions of the oil from the fractionating zone, and utilizing at least a portion of one of the removed fractions as refluxing liquid by passing it in fractionating relation to rising vapors in the fractionating zone.

4. A method for simultaneously fractionating and purifying the vapors of hydrocarbon oil, which comprises passing the vapors upwardly in contact and interchange relation with descending liquid reflux oil having fuller's earth in suspension therein, removing liquid fractions of the oil from the fractionating zone, and utilizing at least a portion of one of the removed fractions as reflux liquid by passing it in fractionating relation to rising vapors in the fractionating zone.

5. A method for simultaneously fractionating and purifying the vapors of hydrocarbon oil, which comprises passing the vapors upwardly in contact and interchange relation with descending liquid reflux oil, removing liquid fractions of the oil from the fractionating zone, suspending a solid purifying agent in at least a portion of one of the fractions so removed, passing said mixture of purifying agent and oil in fractionating relation to rising vapors in the fractionating zone, and during the descent of said last-named mixture removing a portion thereof from the fractionating zone.

ALBERT G. PETERKIN, JR.

CERTIFICATE OF CORRECTION.

Patent No. 1,752,455. Granted April 1, 1930, to

ALBERT G. PETERKIN, JR.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 16, after the comma and before the word "containing" insert the words "at least one of them", and line 94, before "chemically" insert the word "of"; page 2, line 42, strike out the article "a"; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of May, A. D. 1930.

M. J. Moore,
Acting Commissioner of Patents.

(Seal)