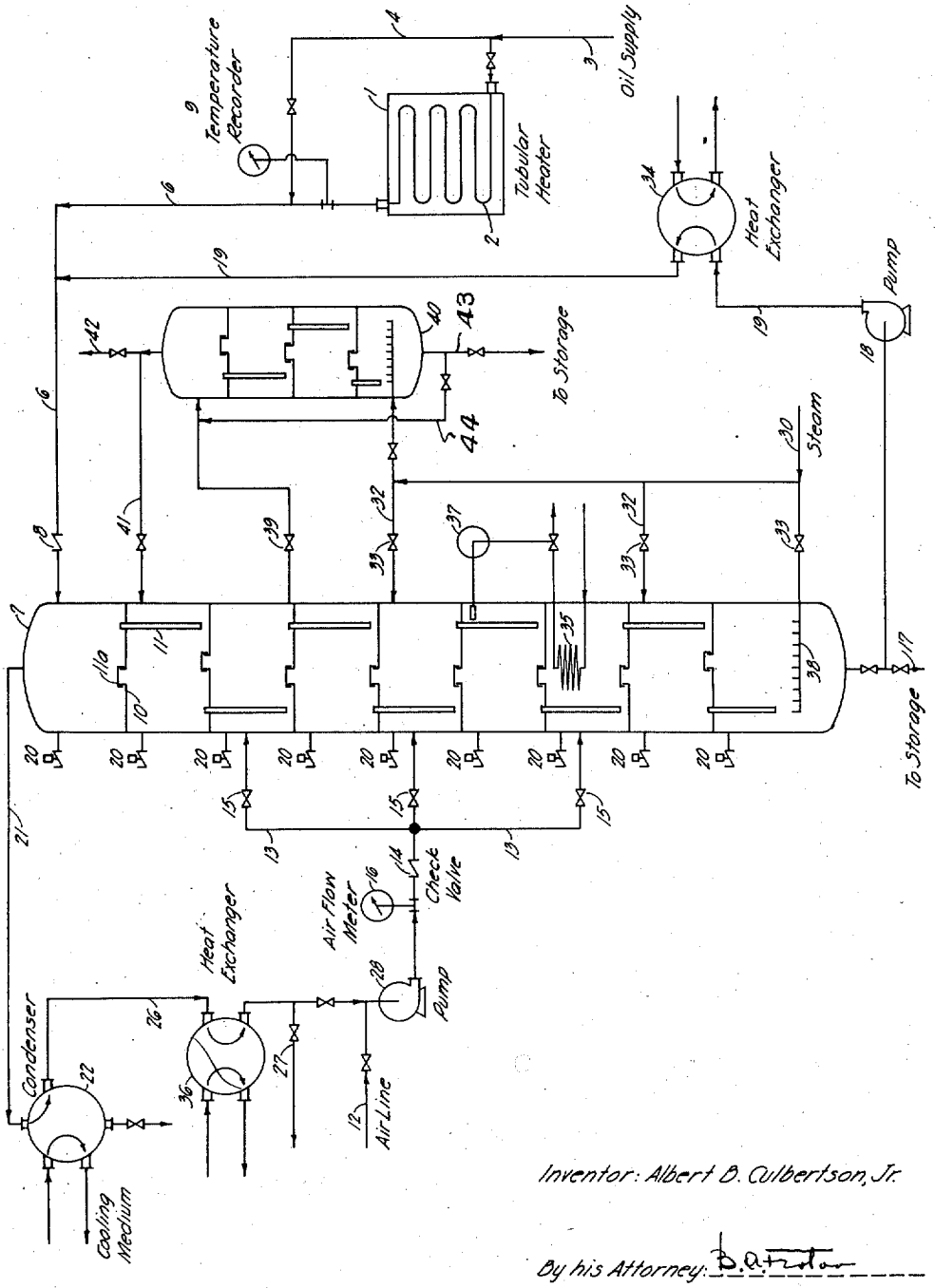
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PROCESS FOR TREATING HYDROCARBONS

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PROCESS FOR TREATING HYDROCARBONS

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14 Claims. (Cl. 196—74)

This invention relates to treating hydrocarbons, and more particularly to a process for blowing petroleum residues to produce blown asphalts and the like, and is a continuation in part of my application Serial No. 403,895, filed October 31, 1929.

An object of the invention is to provide an improved process for blowing petroleum residue with air or other oxidizing gas for transforming the base material; for example, to produce a blown asphalt from a residuum obtained in the distillation of an asphaltic base petroleum oil.

Another object of the invention is to provide a continuous process whereby a charging stock of a selected type may be subjected to an intimate contact with air or other oxygen-containing gas and whereby the composition of air and material treated as well as the reaction temperature may be conveniently controlled.

Difficulties have heretofore been experienced, when blowing petroleum oil residues, in properly regulating the reaction to produce a controlled end product, and in securing a uniform mixture of the air and material treated. The methods primarily employed heretofore may be characterized as "batch" processes, as distinguished from "continuous" processes.

It has been discovered that a successful continuous blowing of materials of the kind mentioned above may be accomplished and a uniform product may be obtained by passing the materials countercurrent to a stream of oxidizing gas, through a reaction chamber provided with means for separating the stream of treated material so as to expose a relatively large surface for contact with the oxidizing gas, and by controlling the admission of the gas to provide a selected ratio of the volume of the reacting gas with the material treated. Furthermore, by controlling the composition and the amount of the oxidizing gas, the danger of explosions may be eliminated and the temperature maintained during reaction may be kept within practical limits.

The invention will further be understood from the following description of a preferred form of apparatus in which it may be practiced. This apparatus is illustrated diagrammatically and partly in cross-section on the drawing attached. It includes a conventional tube heater 1 having coils 2, supplied with the charging stock delivered from a supply line 3.

The heated stream of the charging stock is conducted through the transfer line 6 to near the top of the reaction chamber 7 through a check valve 8, the transfer line being preferably equipped with a temperature recorder 9 for registering the transfer temperature.

The reaction chamber 7 comprises a column of suitable dimensions, containing a series of plates 10 provided with downflow pipes 11 and bubble-caps 11a. The heated stream of oil entering the top of the column gradually descends therethrough by gravity, forming a separate pool of liquid on every tray before it overflows through downflow pipes 11 to the next lower tray and is withdrawn from the column through a pipe 17.

The air or any other oxidizing gas is admitted to the column through an air conduit 12, having a pump 28 and a check valve 14. An air flow meter 16 is connected to the air line so that the volume of air entering the reaction chamber may be measured. I have often found it advantageous to inject air into column 7 at different levels, which provides a more flexible control of the oxidizing reaction taking place in the column than is attainable with the air injection only at one point. Therefore, the air line 12 is provided with a plurality of branch conduits 13 each having a valve 15, serving to control separately the amount of air admitted to the column 7 by each branch. The oxidizing gas rises within the column through the bubble caps 11a, in countercurrent flow to the stream of material under treatment descending through the overflow pipes 11.

In order to provide a sensitive means of control, I recirculate the withdrawn material, or a part thereof, through the reaction chamber by means of a pump 18 and a pipe 19, after blending it, if desired, with fresh asphalt base material admitted through pipes 3 and 6. Due to the exothermal reaction taking place within the column 7, the recycled oxidized asphalt may have a sufficient heat content to make the use of the heater 1 superfluous, in which case the raw oil is conducted through conduits 3, 4 and 6, thus by-passing the tubular heater 1. Further means for controlling the temperature of the recycled material may be provided by using a heating or cooling heat exchanger 34 in the recycle line 19. In this manner, the heat content of the asphaltic material to be oxidized can be accurately adjusted and the danger of causing either overoxidation or insufficient oxidation within the column 7, can be avoided.

An additional means of controlling temperatures within the reaction chamber may be provided in the form of coils 35, within the column 7, of which only one is shown on the drawing, although any number of such coils may be used between the plates of the column. By circulating a

cooling or a heating medium in these coils, and by automatically regulating the rate of flow of said medium by means of thermostatic control means 37, responsive to the temperatures within the column, it is possible to keep the temperature of the oxidizing reaction within desired limits. It is preferable that the coils 35 be installed in the vapor space between the plates of the column, since in that case there is less tendency for an asphaltic coating to form on coils 35 and thus impair the rate of heat transfer.

Several relief valves 20, which serve as safety devices to prevent excessive internal pressures in the reaction chamber, are connected to the vapor spaces between the plates and may be set to any predetermined safe value. These valves open automatically whenever an excessive pressure is developed within the column; for example, in case of fire within the column the destruction of the apparatus is prevented by venting expanding gases and vapors through these valves.

It is known that steam distillation is often used for reducing asphaltic materials, i. e. for removing their lighter components and otherwise modifying their compositions. I have found that this process may be particularly advantageously used as a part of my new method of producing blown asphalt. For this purpose, steam is admitted through a line 30, which enters the column at a point near its bottom and is provided with a portion 38 preferably consisting of a perforated pipe. The steam introduced by means of the pipe 38 into the bottom of the column passes through the oxidized material accumulated therein, and then ascends through the column countercurrently to and in contact with the descending oil on the plates. Since the point of injection of the steam is substantially below that of the oxidizing gas, the asphaltic material in the lower portion of the reaction chamber 7 is subjected only to the reducing action of the steam, and this portion of the chamber may be considered as a reducing section, while the upper portion of the chamber, wherein the material under treatment is in contact with both the oxidizing gas and the steam, may be considered as an oxidizing section.

If desired, steam may also be injected into the reaction chamber at various selected levels, for which purpose the line 30 is provided with manifold branches 32. The amount of steam injected at each point may be individually controlled by means of valves 33. In this way, by controlling the amounts of steam and oxidizing gas injected at various points into the column, it is possible to obtain a final product of any desired specification with regard, for example, to viscosity, penetration, ductility, etc.

If it is desired to obtain from the same reaction chamber several types of asphalt products of different specifications, this may be conveniently done by withdrawing a stream of the partly oxidized material from the main column 7 by means of a valved conduit 39 and passing it to a side column 40, which may be similar in general construction to the main column. The material in chamber 40 may be stripped with steam or any other suitable agent, the gaseous products being withdrawn from the system by means of pipe 42 or returned to the reaction chamber by means of pipe 41 at a point above the outlet for the side stream. The bottom product obtained in the side column 40 may be removed to storage through pipe 43, or, as a further means of controlling its desired specification, may be recycled through the side column 40 by means of pipe 44, connected to pipe 39, through which the stream of partly oxidized material from the main column 7 is admitted into side column 40. Valved pipe 39 between its juncture with pipe 44 and its point of entry into side column 40 may suitably contain a pump, not shown. Although only one column is shown on the drawing, any number of such side columns may be used in combination with the main column.

The gaseous mixture within the column, consisting of residual oxidizing gas, oil vapors and steam, if the latter had been injected into the column, is withdrawn from the column by means of a vapor line 21 leading out of the top of the reaction chamber to a condenser 22, to which a cooling medium is supplied at a desired rate. This condenser may be used to condense only the easily condensable, high-boiling hydrocarbons vaporized from the asphaltic mixture by the heat of the reaction in column 7, in which case both the residual air and the steam issue from the condenser in gaseous form and may be recirculated through the column 7 by means of pipe 26 and air pump 28, after their heat content has been adjusted, if desired, by passing them through a heat exchanger 36, and fresh oxidizing gases have been added by means of pipe 12. It is also possible to condense both the hydrocarbon vapors and steam in condenser 22, after which only the partly exhausted oxidizing gas is recirculated through the system, as described above. The condensed portion of the gaseous phase withdrawn from column 7 is removed from the condenser and may be directed to a separator (not shown), where the oily material is separated from water; at least a part of the condensed oily material may be combined with the recycled oil in the conduits 19 or 6.

It will be understood that the charging stock to the main reaction chamber may comprise either a residuum from topped crude petroleum oils of asphaltic base or a suitable cracked residue, or other asphalt-producing material, such as coal-tar, coal-tar residue, etc. The charging stream is brought to a desirable temperature in the heater 1 and then transferred from the heater to the reaction chamber under such conditions as to provide a suitable initial temperature for the blowing reaction in the reaction chamber. This initial temperature, of course, is subject to variations depending upon the charging stock and the end product desired. With the usual charging stock the normal initial reaction temperature is approximately 425° F., the operating temperature being within the range 425–600° F.

The reaction is exothermic and, therefore, the temperature maintained in the reaction chamber depends, to a substantial degree, upon the ratio of the volume of air or gas admitted to the reaction chamber to the volume of material undergoing treatment. The final product is also influenced to a considerable degree by the extent of oxidation and the rapidity of the reaction. By providing means for controlling with accuracy the admission of the oxidizing gas and by controlling the location of the points of injection of the oxidizing gas to the reaction chamber, the reaction may be kept under accurate control. Furthermore, by exposing a large surface of the material under treatment, a very intimate contact between the pools of material on separate trays and the oxidizing agent is accomplished.

I claim as my invention:

1. The process of blowing petroleum base materials comprising introducing a stream of material to be treated at an elevation in a reaction chamber, separating the stream into pools, said pools having a gravity downward flow, and passing separate currents of air at selected elevations into the reaction chamber.

2. A continuous process of producing blown asphalt which consists in preheating a stream of base material, causing a gravity flow of said stream in a closed chamber in such manner as to separate the stream into pools, introducing for contact with said material currents of air of controlled volume whereby the temperature within the chamber is controlled, said air being introduced at different elevations in respect of the downward moving column of the material under treatment, and continuously withdrawing the asphaltic material after treatment.

3. The process of blowing petroleum base materials comprising introducing a stream of material to be treated at an elevation in a reaction chamber, separating the stream into pools, said pools having a gravity downward flow, passing separate currents of air at selected elevations into the reaction chamber and causing the air thus introduced to pass through said pools in succession in countercurrent to the stream of material being treated.

4. A process of blowing asphalt-producing petroleum base materials comprising, introducing a stream of material to be treated at an elevation into a reaction chamber, separating the stream into pools, said pools having a gravity downward flow, injecting separate currents of an oxidizing gas at selected elevations into the reaction chamber, withdrawing the residual gases from the reaction chamber, recirculating at least a portion thereof through said chamber and withdrawing the oxidized petroleum base material from the reaction chamber.

5. A process of blowing asphalt-producing petroleum base materials, comprising, introducing a stream of material to be treated at an elevation into a reaction chamber, separating the stream into pools, said pools having a gravity downward flow, injecting separate currents of an oxidizing gas at selected elevations into the reaction chamber, withdrawing the residual gases from the reaction chamber, withdrawing the oxidized petroleum base material from the reaction chamber and recirculating at least a portion thereof through the reaction chamber.

6. A process of blowing asphalt-producing petroleum base materials comprising, introducing a stream of material to be treated at an elevation into a reaction chamber, separating the stream into pools, said pools having a gravity downward flow, injecting separate currents of an oxidizing gas at selected elevations into the reaction chamber, withdrawing the residual gases from the reaction chamber and recirculating at least a portion thereof through said chamber, withdrawing the oxidized petroleum base material from the reaction chamber and recirculating at least a portion thereof through the reaction chamber.

7. A continuous process of producing blown asphalt which consists in preheating a stream of asphalt-producing petroleum base material, causing a gravity flow of said stream in a reaction chamber in such manner as to separate the stream into pools, introducing for contact with said material currents of an oxidizing gas at different elevations with respect to the downward moving column of the material under treatment, continuously withdrawing the oxidized petroleum base material from the reaction chamber, removing a portion thereof from the system, adjusting the heat content of the remaining portion and recirculating it through the reaction chamber.

8. In the process of claim 7, the step of adjust the heat content of the oxidized asphalt-producing material withdrawn from the reaction chamber by commingling it with fresh petroleum base material before returning it to the reaction chamber.

9. In the process of claim 7, the step of adjusting the heat content of the oxidized asphalt-producing material withdrawn from the reaction chamber by commingling it with fresh cold petroleum base material before returning it to the reaction chamber.

10. A process for blowing asphalt-producing petroleum base materials comprising, introducing a stream of the material at an elevation into a reaction chamber comprising an upper or oxidizing section and a lower or reducing section, separating the stream into pools, said pools having a gravity downward flow, passing a current of steam without oxidizing gas through the pools within the reducing section and continuing the said current of steam mixed with the oxidizing gas through the pools within the oxidizing section.

11. A continuous process for blowing petroleum base materials which consists in introducing a stream of material to be treated at an elevation into a reaction chamber, separating the stream into pools, said pools having a gravity downward flow, continuously introducing a current of an oxidizing gas and a current of steam into said chamber in a plurality of separate streams at selected elevations for contact with the material under treatment, withdrawing residual gases, steam and condensable hydrocarbon vapors resulting from the reaction and conducting them through a condensing zone wherein at least a portion of said vapors is condensed and continuously withdrawing from the reaction chamber the oxidized petroleum base material.

12. A process for blowing asphalt-producing petroleum base materials, comprising introducing a stream of the material at an elevation into a first reaction chamber, separating the stream into pools, said pools having a gravity downward flow, passing a current of oxidizing gas countercurrent to the material being treated, withdrawing a part of said material intermediate the top and the bottom of the reaction chamber, conducting the withdrawn portion to a second reaction chamber and steam stripping it therein, introducing the steam and vaporized materials from the second reaction chamber into the first reaction chamber, continuing the downward flow of the remaining portion of the material in the first reaction chamber to the bottom thereof, introducing a current of steam near the bottom of the first reaction chamber below the point of introduction of the oxidizing gas, and withdrawing the blown material from the bottom of the first reaction chamber.

13. A process for blowing asphalt-producing petroleum base materials, comprising, introducing a stream of the material at an elevation into a reaction chamber, separating the stream into pools, said pools having a gravity downward flow, passing a current of oxidizing gas countercurrent to the material being treated, withdrawing a part of said material intermediate the top and

the bottom of the reaction chamber, conducting the withdrawn portion to a second reaction chamber and steam-stripping it therein, continuing the downward flow of the remaining portion of the material in the first chamber to the bottom thereof, withdrawing the blown material from the bottom of the first chamber and recirculating at least a portion thereof to the top of the first chamber.

14. A process for blowing asphalt-producing petroleum base materials, comprising, introducing a stream of the material at an elevation into a reaction chamber, separating the stream into pools, said pools having a gravity downward flow, passing a current of oxidizing gas countercurrent to the material being treated, withdrawing a part of said material intermediate the top and the bottom of the reaction chamber, conducting the withdrawn portion to a second reaction chamber and steam-stripping it therein, recycling at least a portion of the stripped material from a low point in said second reaction chamber to a high point in said second reaction chamber, continuing the downward flow of the remaining portion of the material in the first reaction chamber to the bottom thereof, withdrawing the blown material from the bottom of the first reaction chamber and recycling at least a portion thereof to a high point in the first reaction chamber.

ALBERT B. CULBERTSON, JR.

DISCLAIMER

2,099,434.—*Albert B. Culbertson, Jr.*, St. Louis, Mo. PROCESS FOR TREATING HYDROCARBONS. Patent dated November 16, 1937. Disclaimer filed June 16, 1938, by the assignee, *Standard Oil Company* (*Indiana*).

Hereby enters this disclaimer to, but only to, those claims in said specification which are numbered 4, 5, 6, 7, 8, and 9.

[*Official Gazette July 12, 1938.*]

the bottom of the reaction chamber, conducting the withdrawn portion to a second reaction chamber and steam-stripping it therein, continuing the downward flow of the remaining portion of the material in the first chamber to the bottom thereof, withdrawing the blown material from the bottom of the first chamber and recirculating at least a portion thereof to the top of the first chamber.

14. A process for blowing asphalt-producing petroleum base materials, comprising, introducing a stream of the material at an elevation into a reaction chamber, separating the stream into pools, said pools having a gravity downward flow, passing a current of oxidizing gas countercurrent to the material being treated, withdrawing a part of said material intermediate the top and the bottom of the reaction chamber, conducting the withdrawn portion to a second reaction chamber and steam-stripping it therein, recycling at least a portion of the stripped material from a low point in said second reaction chamber to a high point in said second reaction chamber, continuing the downward flow of the remaining portion of the material in the first reaction chamber to the bottom thereof, withdrawing the blown material from the bottom of the first reaction chamber and recycling at least a portion thereof to a high point in the first reaction chamber.

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