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METHOD FOR PRODUCING OXIDIZED ASPHALTS

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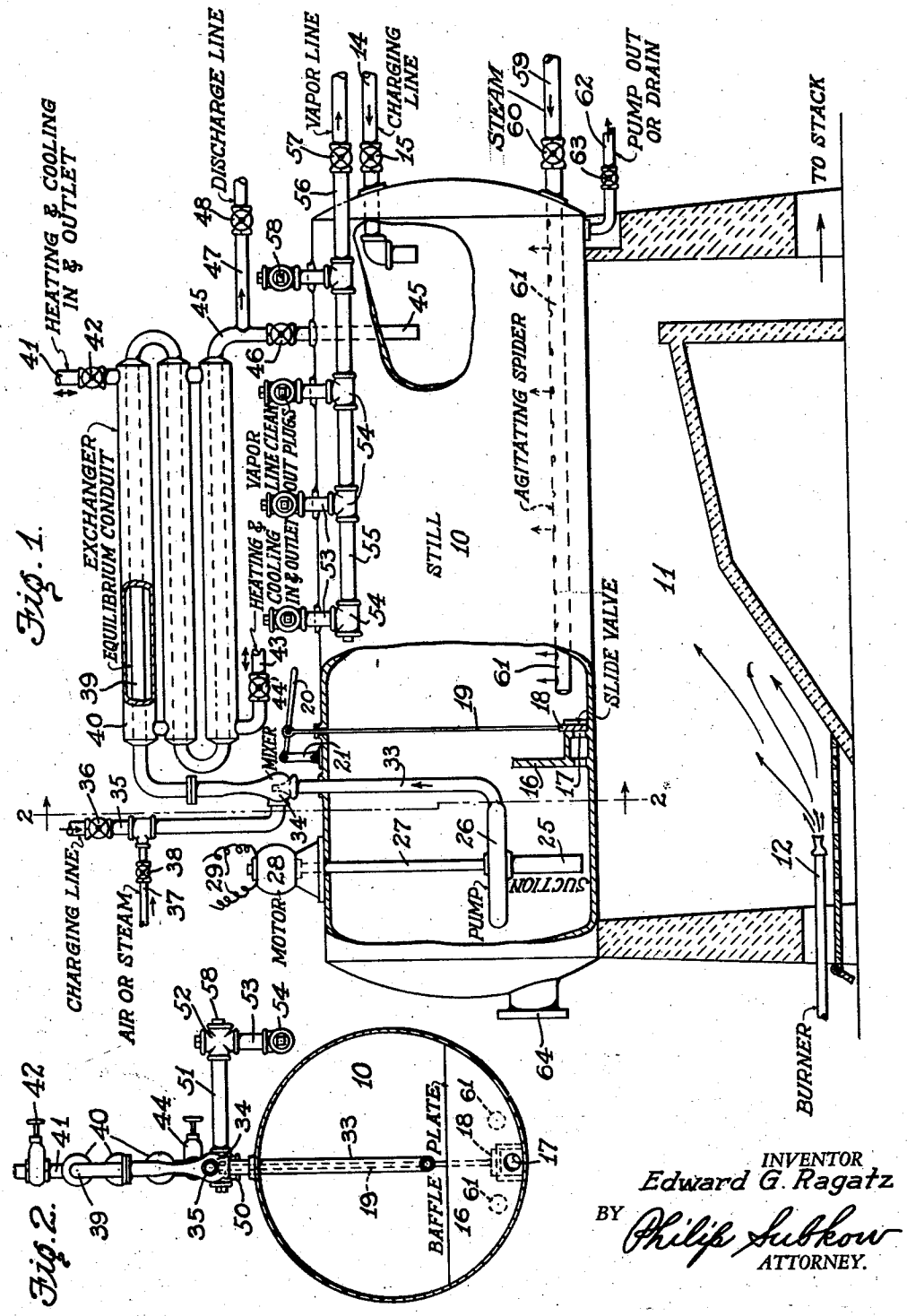


Fig. 1.

Fig. 2.

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METHOD FOR PRODUCING OXIDIZED ASPHALTS

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This invention relates to a process for treating petroleum oils, such as asphaltic residues. In particular, the invention relates to the production of oxidized or air blown asphalts.

It is an object of my invention to improve upon prior processes of oxidizing petroleum oils or residues to produce asphaltic products of improved qualities.

It is a further object of my invention to retain in the oxidized charge of asphaltic fractions which polymerize into ductile asphaltic products and which are ordinarily distilled as overhead fractions by the conventional steam blowing following oxidation of the charge.

In one method for producing an air blown asphalt, such as a coating asphalt by oxidation, air is introduced into the bottom of the cylindrical still containing a charge of asphaltic oil. At the same time the charge is heated to a temperature sufficiently high to obtain the necessary oxidation reaction. This temperature will vary from about 340 to 400° F., depending upon the type of product desired and the charge treated. Usually the oil is initially heated to about 350° F. and then air is introduced into the charge which causes the oxidation reaction to take place. The oxidation is an exothermic reaction and gradually increases the temperature of the charge. When the desired oxidizing temperature of about 450–500° F. has been reached, the charge is maintained at this temperature until completion of the oxidation reaction into asphalt. The oxidation reaction is usually continued for about 18 to 36 hours, depending upon the character of the original stock and the characteristics desired of the finished product. The oxidation increases the melting point and decreases the penetration and ductility of the charge.

Immediately following the oxidation reaction, the supply of air is discontinued and the oxidized charge is steam blown for about one to five hours. The steam blowing operation results in removing light oils present in the charge and formed by the oxidation reaction and also heavy wax bearing lubricating oil distillate-like fractions. Their removal raises the flash point of the oxidized asphalt and improves its quality.

I have observed that the production of air blown asphalt results from the dehydrogenation of a portion of the charge by the oxidation reaction and by the polymerization of the dehydrogenated fractions together with some of the original charge. I have particularly observed that this polymerization continues through the steam blowing period. As a consequence of the steaming operation, however, considerable amounts of fractions which are polymerizable into ductile asphaltic fractions are lost in the overhead distillate.

I have discovered that the polymerizable fractions which are ordinarily lost during the aforesaid steaming operation can be recovered and retained in the finished asphalt if the charge, subsequent to completion of the oxidation reaction, is held at an elevated temperature and pressure and agitated for a period by mechanical means. The charge may then be steam blown to obtain the desired specification of melting point and penetration of the asphalt. In other words, by introducing a polymerizing step intermediate the air blowing and steaming cycles, considerable polymerizable fractions which are now lost would be retained in the asphalt to its ultimate advantage which comprises not only an increase of yield of asphalt but also an improvement in the quality of the product. These polymerizable fractions polymerize into ductile products which improve the ductility of the finished product.

Therefore, briefly stated, my invention relates to a process for producing air blown or oxidized asphalt which comprises commingling oil with an oxygen containing gas at an elevated temperature sufficient to oxidize the oil into asphalt and subsequently retaining the oxidized charge at an elevated temperature with or without an elevated pressure for a period sufficient to permit polymerization. During the polymerizing cycle, temperatures of 600 to 750° F. with pressures sufficient to suppress distillation of the lighter fractions remaining in the charge may be employed.

Other objects and features of my invention will be better understood by reference to the drawing which contains a more or less schematic embodiment of the apparatus and in which Fig. 1 is a flow view of the apparatus with parts broken away and Fig. 2 is a cross-sectional view taken along line 2—2 of Fig. 1.

In the drawing, 10 is a cylindrical still for containing the bulk supply of oil to be treated. 11 is a fire box or furnace on which still 10 is positioned. 12 is a burner for supplying heat to the fire box 11. 14 is a line controlled by valve 15 for introducing oil into the still 10. 16 is a baffle plate extending across the bottom of the still to form two compartments at the botom of the still. 18 is a slide valve positioned in the extreme bottom of the baffle plate 16 to allow oil to flow from one side to the other of the baffle plate 16 through opening 17. 19 is a rod connected to slide valve 18 and valve lever 20 to open or close the slide

valve. 21 is a fulcrum support so that the valve handle 20 may be operated properly.

25 is a suction line extending into the bottom of the still and leading to pump 26 which is preferably of the centrifugal type. Pump 26 is provided with shaft 27 connected to motor 28 which is driven electrically from leads 29. 33 is a discharge line from pump 26 and is connected at its other end to mixer or injector 34. 35 is a line controlled by valve 36 for introducing oil into the mixer 34. This line may be employed for introducing steam into the mixer. 37 is a line controlled by valve 38 for introducing an oxygen containing gas such as air, oxygen or ozone into the mixer. This line may also be used for introducing steam into the mixer 34. 39 is an equilibrium conduit in which the oxidation of the oil by means of air takes place. 40 is a heat exchanger of which the equilibrium conduit is a part and is used for heating or cooling the oil during its passage through the equilibrium conduit. Heating or cooling media may be introduced into the jacket of the exchanger 40 via line 41 controlled by valve 42 and may exit therefrom via line 43 controlled by valve 44. If desired, the heating or cooling media may be introduced into the jacket via line 43 in which case it will exit via line 41. Any desired material may be used for cooling or heating in the heat exchanger such as steam, air, oil or water. It is obvious that instead of using a jacketed pipe for the equilibrium conduit and heat exchanger, any other type of cooling means may be employed as, for example, an aerial cooler including means for regulating the flow of air over the coil 39. The oil passing through equilibruim conduit 39 may be heated by placing the conduit in a furnace heated by means of hot combustion gases.

45 is a line controlled by valve 46 for returning oil, vapor and gases from equilibrium conduit 39 to the still 10. Line 47 controlled by valve 48 is connected to line 45 and is employed for discharging the oil from still 10 to storage. Still 10 is provided with a vapor outlet 50 which is connected to the vapor line 56 controlled by valve 57 by means of pipe sections 51, 53 and 55. Crosses 52 connect pipe sections 51 and 53, while T's 54 connect the pipe sections 53 to pipe sections 55. The vapor lines are provided with vapor line clean-out plugs 58. Steam for agitating and distillation purposes may be introduced into the still 10 via line 59 controlled by valve 60 and agitating spider 61. Line 62 controlled by valve 63 is employed for pumping out or draining the still 10. 64 is a manhole for cleaning the still.

In operation, a hydrocarbon oil, preferably a residuum obtained by distilling of lighter oils, such as kerosene and perhaps gas oils from asphaltic crude oils is introduced into the still 10 via line 14 and valve 15. When the required charge is in the still pump 26 driven by shaft 27 and motor 28 connected to an electrical circuit by leads 29 is started and the oil in still 10 is pumped into line 33 and into mixer 34 and is then forced through equilibrium conduit 39 of heat exchanger 40 where it is heated by any heating medium such as steam, air or hot oil entering through line 41 and valve 42 and exiting from the heat exchanger via line 43 and valve 44 or vice versa. The oil then flows through line 45 controlled by valve 46 and drops back into the still 10. During the heating period, slide valve 18 located in the baffle plate 16 and operated by connecting link 19 connected to handle 20 which is supported by fulcrum 21, is opened. The fire under the still 10 is lighted and the oil is additionally heated by hot combustion gases in fire box 11, the temperature being controlled by burners 12. The oil is circulated and additional material is introduced into the still through line 14 or preferably through line 35 controlled by valve 36.

As soon as the required amount of oil, for example about 300 bbls., is charged into the still, valve 36 is closed and about 200 cu. ft. of air per minute is admitted into the mixer 34 through line 37 and valve 38. The oil is now circulating at a rate between 1500 and 2000 bbls. per hour by pump 26. This rate of air admission is continued until the oil in still 10 reaches a temperature of around 350° F. This should require about one hour. The air is then increased to about 300 cu. ft. per minute and continued at this rate until the oil reaches a temperature of about 450 to 500° F. This should require about four hours. As soon as the required amount of oil has been charged into the still and circulation established, slide valve 18 is closed. This causes the oil to flow over baffle 16 in order to break up the bubbles of air in the oil and to give a quiet zone around the suction of the pumps. This allows the pump to take a full suction and avoids a gas-locked and air-bound pump.

In still 10 the vapors and gases are separated from the oil and pass via openings 50 through vapor lines 51, 53, 55 and 56 out of the still to a suitable condenser or to a fractionating tower where the oil condensate may be separated from the gases and returned to the still 10 for further oxidation. The rate of circulation of the oil through the equilibrium conduit 39 may be controlled by varying the speed of pump 26 through shaft 27 and motor 28. The cooling medium, such as steam, air or water or oil in heat exchanger 40 may be circulated in any desired amount in order to obtain the proper degree of cooling by heat exchange out of contact with the reacting materials.

It is preferable to maintain a slight vacuum in the still of about 5 inches of water in order to facilitate removal of gases.

When the charge has been oxidized to the desired degree, the air introduction via line 37 is discontinued. Pump 26 continues to pass the charge through the equilibrium conduit and a heating medium such as steam, air or oil is circulated through exchange 40 to raise the temperature of the oxidized charge to approximately 650° F. If desired, the heating may be augmented by increasing the fire in the fire box 11. The circulation at about 650° F. through the equilibrium conduit 39 and back into the still 10 is continued for about 3 hours. A superatmospheric pressure of approximately 25 lbs. per square inch is maintained in the still 10 by the proper operation of valve 57 on the vapor line 56. This pressure should be sufficient to prevent substantial distillation of oil fractions. The increase in temperature, the maintenance of pressure in the still 10 and the agitation caused by the circulation from the still through the equilibrium conduit and back to the still permits polymerization of the lighter polymerizable fractions which would otherwise be lost.

Upon completion of the polymerizing process, the pressure in still 10 is removed by controlling valve 57 and the charge in still 10 is steam blown for one-half hour or more for controlling the flash point of the asphalt and removing any remaining waxy distillates. If desired, the charge may be circulated by a pump 26 through equi-

librium conduit 39 during the steaming period. When the charge has been brought to proper specification, it may be withdrawn from still 10 either through line 47 controlled by valve 48 or it may be pumped out via the drain 62 controlled by valve 63.

The following is a specific example for carrying out the present invention in order to produce an oxidized asphalt: An asphaltic residuum obtained preferably by distilling from asphaltic base oil the light oils and intermediate boiling oils but retaining preferably fractions of 100 Saybolt viscosity and up at 100° F. and specifically a Torrance reduced residuum of 14.6° A. P. I. gravity is preferably preheated and then charged into the still via line 14 as previously described above. As soon as the oil is in the still, the circulating pump is started and the oil is circulated at a high rate through the heat exchanger and back into the still. The heating medium is passed through the heat exchanger and the still is fired until the oil reaches a temperature of about 350° F. When the charge has reached this temperature, air is forced or passed into the oil passing into the mixer 34 and the temperature of the charge is gradually increased by oxidation until a temperature of approximately 480° F. is reached. This temperature is then maintained throughout the oxidation reaction and is controlled by circulating a cooling medium through the heat exchanger to absorb the heat of reaction. The air introduction or air blowing of the oil is continued at an average temperature of 480° F. for approximately 15 hours or until that melting point and penetration is reached which experience has shown will subsequently produce asphalt of the desired finished specifications. For example, on the above type of oil, the air blowing is continued until the oil reaches a melting point of about 175° F. and a penetration of 40.

The air supply is then discontinued and the oxidized charge is heated to approximately 650° F. by circulating the oil through the equilibrium conduit and maintaining an appropriate temperature in the heat exchanger and also by increasing the heat in the furnace. The circulation through the equilibrium conduit and back into the still of the oxidized charge is continued for approximately 3 hours at the aforesaid temperature of 650° F. during which time the polymerizable fractions of the charge polymerize into ductile asphaltic products. A superatmospheric pressure of approximately 25 lbs. per square inch is maintained by the proper operation of the valve 57. Extremely high pressures are not necessary to retain the polymerizable fractions as liquid fractions. This cycle of operation or polymerization cycle will cause the oxidized charge to increase in melting point to approximately 208° F. and reduce the penetration to about 25 at 77° F. During the polymerizing cycle, steam or other inert gas for agitating purposes may be introduced through the agitating spider, or if desired, other mechanical agitation such as paddles may augment the agitation effected by the circulation with the pump in the still.

The pressure is then released on the charge and the steam is introduced through the agitating spider for approximately one-half hour which will permit light oils and light waxy fractions to vaporize from the oxidized charge and thus bring the charge to proper specification, such as for example, to a melting point of approximately 214° F., a penetration of 18 and a flash point of 465° F.

It will be observed that for determining the melting point, penetration and flash point, the following methods outlined by the American Society for Testing Materials were used:

Melting point	D-36-26
Penetration	D- 5-25
Flash point, Cleveland open cup method	D-92-24

If desired, the circulation by pump 26 may be continued during the steaming process and steam may be introduced through line 37 to aid in the vaporization of the light fractions and to reduce the charge to proper specification of melting point, penetration and flash point.

It will be observed that many variations of the above procedure can be made without departing from the spirit of the invention. Thus, the cooling can be obtained by cooling the oil in still 10 by passing the cooling medium through a coil situated in the still. The agitation of the oil in the still may be effected by circulation, by mechanical means or by injection of an inert gas or by the air used in the process. The equilibrium conduit may be positioned either within the still or in an external heating zone, such as a furnace, or the oil may be withdrawn from the still, passed through a cooler and then conducted through the conduit 39 prior to its introduction into the still. In each case, the oil in the equilibrium conduit on its reaction with air is not permitted to exceed a predetermined temperature. While the precooling of the oil before its introduction into the conduit 39 may have some advantages, the cooling of the oil during reaction with air is preferred. It is believed that of these methods for accomplishing this, i. e. cooling the coil itself or cooling the oil in still 10 when the coil 39 is immersed in the still 10, the former is preferred. Instead of employing the equilibrium conduit with its heat exchanger for increasing the temperature subsequent to the oxidation reaction and to permit polymerization as aforesaid, an independent tubular still positioned in a heating furnace may be provided for raising the temperature of the oxidized charge rapidly to the required polymerizing temperature.

Instead of completing the oxidation of the oil before proceeding with the polymerizing cycle, I may alternate the oxidation and polymerization cycles for short periods during the reduction of the oil to asphalt, that is, I may oxidize the oil for a short period of time and then heat the oil to the higher temperature and agitate the charge to permit polymerization of polymerizable fractions, then cool the charge to the oxidation temperature and repeat these cycles of operation until the charge has been reduced to the proper melting point and penetration. Of course, higher pressures will be necessary during the polymerizing cycle, particularly during the first polymerizing cycles due to the fact that the charge will contain considerably more oil fractions which will vaporize more readily. However, the pressure will be gradually reduced as the oxidation proceeds towards the finished product. The introduction of a plurality of polymerizing cycles during the oxidation of the oil will permit less oil of polymerizable nature to be distilled as overhead fractions.

While the present invention has been illustrated as a batch system, it will be observed that the process may be carried out continuously. Thus, by providing a plurality of units such as those described above and connecting them in series and by connecting a pair of polymerizing and grading stills in parallel with the last unit,

the oxidation process may be carried out continuously in the first mentioned units and the polymerizing and grading stills may be used alternately as batch stills to effect polymerization and grading and to finish the asphalt.

The above description is not to be taken as limiting but merely as illustrative of the invention and as one mode of carrying it out. Many changes can be made within the scope of this invention which is set forth in the following claims:

1. A process for producing asphalt which comprises commingling oil with oxygen containing gas at an elevated oxidizing temperature sufficient to oxidize the greater part of said oil into asphalt and subsequently maintaining said oxidized asphalt at a higher elevated temperature sufficient to polymerize oil fractions in said oxidized asphalt and under sufficient pressure to prevent material distillation of vaporizable oil fractions.

2. A process for producing asphalt which comprises commingling liquid oil with oxygen containing gas at an elevated oxidizing temperature sufficient to oxidize said oil into asphalt and subsequently maintaining said oxidized asphalt at a higher elevated temperature and under pressure sufficient to prevent material distillation of vaporizable oil fractions for a period of time sufficient to polymerize vaporizable oil fractions in said oxidized asphalt but without material distil'ation of oil fractions.

3. A process for producing asphalt which comprises commingling oil with oxygen containing gas at an elevated oxidizing temperature sufficient to oxidize the greater part of said oil into asphalt and subsequently agitating said oxidized asphalt at a temperature higher than that during said oxidation to permit polymerization of oil fractions in said oxidized asphalt and under sufficient pressure to prevent material distillation of vaporizable oil fractions.

4. A process for producing asphalt which comprises commingling oil with oxygen containing gas at an elevated oxidizing temperature sufficient to oxidize greater part of said oil to asphalt, discontinuing said oxidation and increasing the temperature of said oxidized asphalt immediately following said oxidation and maintaining said oxidized asphalt at an elevated temperature for a period of time sufficient to permit polymerization of oil fractions in said oxidized asphalt and at an elevated pressure sufficient to prevent material distillation of vaporizable oil fractions and subsequently distilling oil fractions from said oxidized and polymerized asphalt.

5. A process for producing asphalt which comprises oxidizing liquid oil to asphalt with an oxidizing gas at an elevated oxidizing temperature, agitating said oxidized asphalt while maintaining said oxidized asphalt under superatmospheric pressure and at a temperature higher than said oxidation temperature to permit polymerization of polymerizable fractions in said oxidized asphalt into ductile asphaltic fractions, said superatmospheric pressure being sufficient to prevent material distillation of vaporizable oil fractions and subsequently vaporizing oil fractions from said oxidized and polymerized asphalt.

6. A process for producing asphalt which comprises maintaining a bulk supply of oil at an elevated oxidizing temperature, introducing an oxygen containing gas into said bulk supply of oil to oxidize said oil into asphalt, discontinuing said supply of oxygen containing gas and maintaining said oxidized asphalt at a higher elevated asphalt producing temperature and under pressure producing temperature and under pressure sufficient to prevent material distillation of vaporizable oil fractions for a period of time sufficient to polymerize oil fractions in said oxidized asphalt to further asphaltize said oil and subsequently steaming said oxidized and polymerized asphalt.

7. A process for producing asphalt which comprises commingling oil with an oxygen containing gas at a temperature of approximately 450 to 500° F. to oxidize said oil into asphalt, increasing the temperature of said oxidized asphalt to approximately 650° F. and agitating said oxidized asphalt while maintaining said temperature and a pressure of approximately 25 lbs. per square inch to permit polymerization of oil fractions in said oxidized asphalt to further asphaltize said oil and subsequently distilling oil fractions from said oxidized and polymerized asphalt.

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