

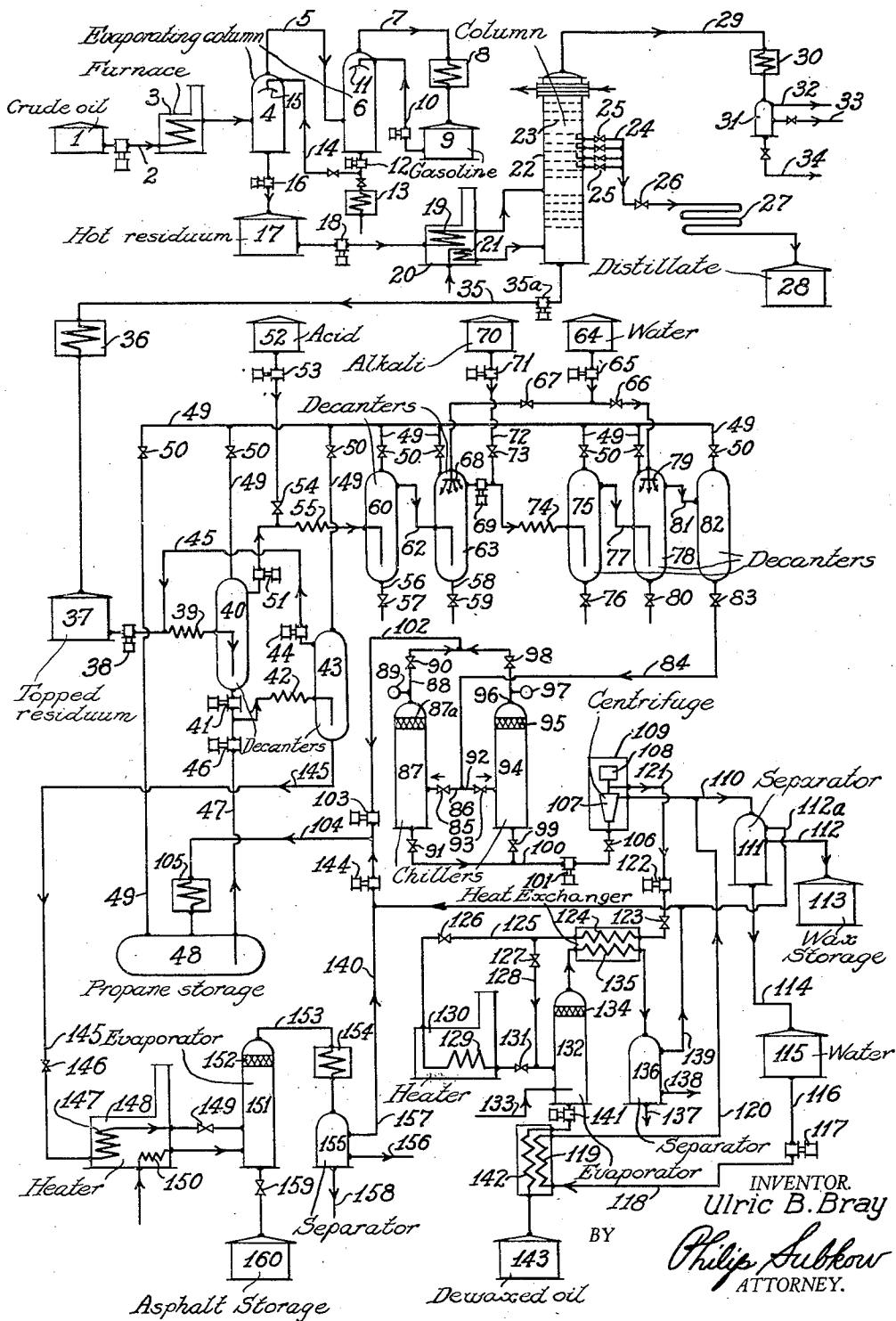
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U. B. BRAY

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PROCESS FOR TREATING OIL

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PROCESS FOR TREATING OIL

Ulric B. Bray, Palos Verdes Estates, Calif., assignor to Union Oil Company of California, Los Angeles, Calif., a corporation of California

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19 Claims. (Cl. 196—13)

This invention relates to a process for the production of lubricating oil. More specifically it relates to a method of producing lubricating oil from oil containing asphalt and is a division of my patent application Serial No. 466,189, filed July 7, 1930.

In the aforesaid patent application, filed by me on July 7, 1930, I pointed out that the lubricating oil components of asphaltic crude cannot be separated from the asphalt by ordinary distillation methods without an impairment of the temperature viscosity susceptibility of the oil. The high temperature necessary for separation of the oil from the asphalt appears to render the oil distillates more susceptible to a change in viscosity with a change in temperature than is characteristic of the oil prior to its separation from the asphalt. Furthermore, in the classification of oils according to their respective temperature viscosity slopes I described oils which exhibited a low temperature viscosity susceptibility as having a high percentage of paraffin base characteristics and oils which exhibited a high temperature viscosity susceptibility as having a low percentage of paraffin base characteristics. In other words the paraffin base characteristics of an oil are those properties which cause its viscosity temperature susceptibility to resemble that of a paraffin base oil.

Since the separation of asphalt from the oil by distillation of the oil cannot be accomplished without destruction of the paraffin base characteristics of the oil, the process devised by me for removal of the asphalt comprises its precipitation by means of solvents. Asphalt may be precipitated from oil by chemicals, such as sulfuric acid. I find, however, that it is best precipitated by use of solvents in which the lubricating oil fractions are soluble but in which the asphalt is insoluble. Such solvents are alcohol, ether, mixtures of ether and alcohol, acetone, volatile hydrocarbon solvents, such as casinghead gasoline and light naphthas. I find, however, that the process is best carried out by the use of hydrocarbons which are normally in the vapor state at atmospheric pressure and temperature. Such hydrocarbons include propane, isobutane, butane, ethane, methane and mixtures thereof. These may be obtained by rectification of casinghead gasoline by the so-called "stabilizing method" now conventional in the natural gas industry. They are the overhead thus obtained. They are liquefied by compression and cooling in the conventional manner and drawn off into pressure chambers where they are main-

tained in the liquid state until they are used. A typical analysis of such a fraction is 6.72% ethane, 72.20% propane, 19.91% isobutane and 1.17% normal butane and the necessary pressure to maintain the fraction in a liquid state is approximately 125 lbs. per square inch gauge at 73° F. This mixture has an average molecular weight substantially equal to propane. The oil stock containing asphalt is mixed with this liquid solvent under pressure, the mixture is allowed to settle to permit the precipitation of the asphalt. The solution of lubricating oil in the liquid solvent is withdrawn from the pressure precipitator and expanded through heating coils to vaporize the solvent, leaving behind the liquid lubricating oil free of asphalt. The vapors are recompressed and cooled to liquefy them and are then returned to the system. The lubricating oil fraction produced may then be distilled at atmospheric pressure by conventional methods of distillation, such as the tube still or the shell still with proper rectification or fractionating equipment to produce any desired cut of lubricating oil.

Any contained wax may be extracted and the oil treated with acid. I prefer to distill the oil to leave a residue which contains the fractions having a viscosity above 400 to 500 seconds Saybolt Universal at 100° F. In other words, the degree of distillation should leave a residue such that if it were redistilled the first fractions taken overhead would be about 600 to 800 seconds Saybolt Universal at 100° F. These figures are by their very nature approximate since they must overlap and the spread of the cut will be dependent on the percentage taken overhead. This will result in a minimum deterioration of the desirable temperature viscosity characteristics. Obviously the oil may be more deeply topped, i. e., higher viscosity oils may be taken overhead if a partial sacrifice of those desirable qualities is not uneconomic. It is to be noted that the above criteria will hold both for batch and for flash distillation within reasonable commercial limits. It is preferred to top the crude so as to leave behind a residue which on extraction, as above, leaves a lubricating oil of the desired viscosity. However, the process may be run as well by topping the crude as far as possible, i. e., without injuring the paraffin base characteristics, extracting the residue to remove the asphalt, treating the distillate and residue with acids, alkali and/or clay and then blending to the desired viscosity.

It is characteristic of this extraction process that the asphalt containing oil used for the extraction and the asphalt free lubricating oil pro-

duced have substantially the same paraffin base characteristics. In other words, the asphalt while it affects the absolute viscosity of the oil does not affect the variation of the viscosity with temperature, i. e., the slope of the temperature viscosity curve is unchanged. This is made possible by the fact that the present process removes the asphalt without affecting the characteristic oils. All of the paraffin base components present in the asphalt containing oil are found unchanged in the extracted oil.

The following is a description of a preferred method for treating a mixed base oil, i. e., one containing asphalt and wax, wherein the asphalt is precipitated under conditions such as to leave the wax and oil in the propane solution. Advantage is taken of the propane solution to permit a continuous acid treatment and alkali treatment of the oil. This is a particular advantage of this process since it permits rapid settling of the sludge. The extreme volatility of the propane is used to act as a refrigerant to cause separation of the wax. The process will be more particularly described by reference to the drawing.

Referring to the drawing, the crude oil to be used as a source of lubricating oil is taken from the crude oil storage tank 1 and sent through coil 2 in furnace 3, whence it is sent to evaporating column 4. The temperature in coils 2 and 19 and the duration of heating in the still system, 2, 4, 17, 19 and 22, is so regulated that the amount of "conversion" i. e., the destruction of inherent paraffin base characteristics is minimized. As a convenient criterion the temperature should not be raised beyond 600-650° F. The vapors passing through 5, consisting of gas oil, kerosene and gasoline vapors, go to dephlegmator 6 where they are fractionated into gasoline line overhead and kerosene and gas oil bottoms, which may be re-run or handled in any conventional manner. The vapors pass through 7, are condensed in 8, condensate, i. e., gasoline, is collected in 9. A part is returned through 10, to distributor 11, to act as a reflux. The dephlegmator bottoms pass through 12, and are cooled in 13. These consist of gas oil and kerosene. Part is returned as a wash via line 14 and spray 15. The bottoms from evaporator 4, consisting of oil containing lubricating fractions and asphalt, pass through the rundown line 16 to the hot residuum storage tank 17 which may serve only as a surge tank in the continuous operation of the process. The hot residuum from tank 17 is passed through pump 18 which sends the hot residuum through coil 19 in furnace 20, where the residuum is heated to about 625° F. Care is taken at this point not to overheat the residuum because of the danger of injuring the quality of the lubricating oil to be obtained later, i. e., its paraffin base characteristics. The temperature to which the oil may be heated has been adequately described above. The heated residuum passes to fractionating column 22. Steam, superheated in coil 21, is introduced in column 22 to aid in the flashing of the volatile oils which are taken off in one or more side streams and as an overhead. The oil is fractionated by fractionating plates 23 and a number of side streams are removed through lines 24 controlled by valves 25, reflux is generated by means of a cooler positioned at the top of the column. The various oils pass through valve 26 and are cooled in 27 and collected in 28. If desired as many tanks as there are side streams may be employed. The side

stream distillates may be processed in any suitable manner to produce desirable products. The overheads from the column pass through line 29, are condensed in condenser 30 and cooled in rundown tank 31. Uncondensed vapors are removed through 32, condensed oils composed of light lubricating oils are removed through 33 and the condensed water removed through 34. The bottoms from column 22 are run through line 35 by means of pump 35a to cooler 36 from which it is delivered to the topped residuum tank 37. The operation of coil 19 and column 22 is so regulated as to produce the predetermined extent of topping necessary to give the proper viscosity oil in the later extraction with propane. The topped residuum stored in tank 37 is sent by pump 38, meets liquid propane containing a small amount of oil coming through line 45. The preferred fraction is that obtained as an overhead in the stabilization of natural gas gasoline as previously mentioned. The mixture of propane and residuum pass through mixing coil 39 into decanter 40, where the asphalt in the topped residuum is precipitated and settles rapidly as a slurry. From the bottom of decanter 40, the asphalt slurry is pumped by pump 41 to meet fresh liquid propane introduced by pump 46 via line 47 from propane storage 48. The asphalt slurry and fresh liquid propane are sent through mixing coil 42 into decanter 43. The asphalt propane slurry from the bottom of decanter 43 is drawn off through line 145, and valve 146 and discharged at a lower pressure into a still, as will be discussed hereafter.

The overflow from decanter 43, containing the oil and wax is sent by pump 44 through line 45 to be mixed with the topped residuum and sent into decanter 40, as explained above. The overflow from decanter 40 consisting of propane and lubricating oil stock in the desired ratio is sent through pump 51 for the acid and alkali treatment of the extracted lubricating oil stock. The countercurrent washing of the precipitated asphalt illustrated by the above method of operation may be extended to as many steps as desired, but in general two decanters giving two countercurrent washings will be sufficient to produce an asphalt satisfactorily free of wax and oil.

To the propane solution of extracted lubricating stock, acid from tank 52 is added to mixer 55 by means of pump (or acid egg) 53, and the flow is controlled also by valve 54. The propane solution and acid are forced by pumps 51 and 53 through mixing coil 55 into decanter 60 where the acid sludge settles rapidly. The addition of the acid in several dumps without drawing the sludge between dumps may be accomplished by tapping mixing coil 55 at various points and introducing acid at these points. The addition of acid in several dumps with the withdrawal of sludge between dumps may be accomplished by means of additional mixing coils and acid decanters. The acid treated oil solution from decanter 60 flows continuously through line 62 into decanter 63, where water is introduced as a spray through line 68 from water storage 64 through pump 65 and valve 67 and acid reaction products are withdrawn through line 56 controlled by valve 57. The water washed oil overflows from decanter 63 and is sent by pump 69 to be treated. Water is withdrawn via line 58 controlled by valve 59. The soda solution contained in tank 70 is introduced by pump 71 through line 72 controlled by valve 73. The mixture of oil solution and aqueous alkali solution is forced through mixing

coil 74 into decanter 75 where the caustic solution separates from the propane solution of the oil, and is withdrawn through valved line 76. The overflow from decanter 75 goes through line 77 to decanter 78, where water is introduced through spray 79 by means of pump 65 through valve 66. The separated water wash is withdrawn through valved line 80. The use of propane as a solvent permits the continuous and rapid treatment of lubricating stock in the manner just described.

The neutralized and water washed oil solution overflowing from decanter 78 is carried by line 81 to tank 82, the latter acting as a reservoir or surge drum between the acid treating and dewaxing operation.

Treated oil solution in tank 82 is sent through valve 83 and line 84 to line 86 or 92 where it is sent into low pressure column 87 or low pressure column 94 by the proper operation of valves 85 and 93. Considering valves 91 and 93 closed and valves 85 and 90 open, the propane solution flows into low pressure column 87. Valves 85 and 93 are pressure reducing valves separating the low pressure columns 87 and 94 from the high pressure treating and decanting vessels. In low pressure column 87, sufficient propane vaporizes to reduce the temperature of the remaining material to a predetermined dewaxing temperature. The desired dewaxing temperature is obtained by controlling the pressure in column 87 by the proper operation of valve 90 and propane compressor 103, which is connected to the evaporator by line 102. The pressure to be maintained in column 87, as shown by gauge 89, will be, generally, about 0 lb. gauge which corresponds to a temperature of approximately -40°F .

As the propane solution passes through valve 85, its pressure is reduced so that a portion of the propane evaporates in column 87 and the vapors pass out of the top, through mist extractor 87a through line 88 controlled by valve 90. The solution from tank 82 continues to flow into column 87 until a predetermined quantity has accumulated. Valves 85 and 99 are then closed and valve 93 opened. Production then flows into column 94 until the predetermined quantity of solution has passed into the second column. The propane is vaporized, passes through mist extractor 95 through line 96, valve 98 being controlled so that the proper reading is obtained on gauge 97. In the meantime, the vapor pressure of the propane in column 87 has been reduced to approximately 0 lb. gauge by the operation of valve 90 and propane compressor 103, thereby reducing the temperature of the material remaining in column 87 to approximately -40°F . When this temperature is reached in column 87, valve 91 is opened and the cooled material is passed through line 100, pump 101 and valve 108 into the gas tight centrifuge 107 in box 109. Motor 108 is for the centrifuge. The centrifuge is of conventional type. The dewaxed propane solution of lubricating oil discharged from the center of the centrifuge through line 121 is sent by pump 122 through valved line 123 and heat exchanger 124. In passing through heat exchanger 124, heat is absorbed from the vapors coming from the top of the evaporator 132. The propane solution of dewaxed oil may be passed directly to evaporator 132 through line 128 by the proper operation of valves 127 and 126 positioned in lines 125 and 128. If it is desired to supply all or a portion of the heat required for vaporization of the propane by fire rather than by steam, the propane solution may be passed through coil 129 in furnace

130 by the proper manipulation of valves 126, 127 and 131 into evaporator 132. Open steam is introduced into evaporator through 133 to complete the vaporization of the propane and to reduce the oil to satisfactory flash and fire specifications. In general, however, the function of the steam will be to complete the vaporization of the propane. The vapors passing through the mist extractor 134 pass from the top of evaporator 132 through heat exchanger coil 135 where water is condensed by the cold propane solution of lubricating oil coming from the centrifuge. Leaving heat exchanger coil 135, the condensed steam and any light oil removed from evaporator 132 pass into separator 136 with the uncondensed propane vapors. The uncondensed propane vapors leave the separator 136 through line 139 and pass to line 140 from which they enter the suction of propane compressor 144 to be compressed and sent through line 104 to propane cooler 105 where the propane vapors are liquefied and returned to propane storage 48. Light lubricating oil is removed through 138 and water removed through 137. The bottoms from evaporator 132, consisting of the treated and dewaxed oil, are drawn off by pump 141 and passed through heat exchanger coil 142 where heat is imparted to the water used to melt the wax in the wax discharge line from the centrifuge, as will be later described. Leaving heat exchanger 142, the treated and dewaxed oil passes into storage tank 143.

The wax discharged from the centrifuge through line 110 is mixed with warm water, at about 140°F . The melted wax and water pass into separator 111 and the wax is withdrawn through line 112 to wax storage 113. The water from separator 111 is passed through line 114 to water storage tank 115 and then through line 116, pump 117 and line 118 to heat exchanger coil 119 where it is heated by the bottoms from evaporator 132, as explained above. The warm water leaving heat exchanger coil 119 is passed through line 120 to line 110 to complete the cycle. The vapors from the top of separator 111, consisting of propane discharged with the wax from the centrifuge, are conserved by compressing and returning to high pressure propane line 104 going to propane cooler 105 by passing through line 112a into line 140 and compressor 144. The vapor space in the gas tight centrifuge should be connected with the suction of a propane compressor discharging into the high pressure propane system. Provision for this latter conservation of propane is made by connecting either the dewaxed oil discharge line 121 or the wax discharge line 110 with the gas space in the centrifuge, as will be understood by those skilled in the art.

The asphalt material from separator 43 is passed through line 145, flashed through valve 146 and heating coil 147 in furnace 148 and pressure reduction valve 149 into evaporator 151, which operates at a lower pressure. Steam superheated in coil 150 is introduced into 151 to supply additional heat and to reduce the asphalt to proper specifications, generally only as regards flash and fire points. The asphalt is taken from the bottom of the evaporator 151 and sent through the valved rundown line 159 to asphalt storage 160. The overhead from evaporator 151 passing through mist extractor 152 is sent through line 153, to cooler 154, and then to separator 155. The uncondensed propane from separator 155 is sent through line 157 to line 140 to

the suction of propane compressor 144 where its pressure is raised to that in the high pressure system and then sent to line 104 to propane cooler 105 where it liquefies and runs down into propane storage tank 48. Any condensed light oil is withdrawn through line 156 and condensed water through line 158.

From the standpoint of convenience and operation, it may be desirable to connect all of the high pressure vessels containing liquid propane to a pressure equalizing line 49 controlled by valve 50, as shown in the drawing. Without provision for equalizing the pressure in the different vessels, flow of liquid will be controlled entirely by pump pressure.

In the operation of the centrifuges, it is desirable to maintain a higher pressure upon the propane, oil, wax mixture than corresponds to the vapor pressure of the mixture at that temperature. The reason for this increased pressure is to prevent foaming or gas evolution in the liquid. This pressure is applied by pump 101. If it is desirable to operate the centrifuge at atmospheric pressure or at only slightly increased pressure, the pressure maintained in cooling column 87 or 94 before the liquid in that column is sent to the centrifuge should be less than atmospheric pressure, so that when the pressure is raised to atmospheric before passage through the centrifuge, the liquid may warm up several degrees without "boiling" or foaming.

Evaporator 132 may be operated at a sufficiently high pressure to cause liquefaction of the propane vapors when cooled, and in this manner eliminate the use of a compressor on the vapors from the top of separator 136. When operating column 132 at high pressure, pump 122 is operated at a higher discharge pressure and heat exchanger 124 is operated so as to cause condensation of only steam and oil vapors.

The above description is merely illustrative of one mode of employing my invention and is not to be construed as limiting as many variations will appear to those skilled in the art within the scope of my invention which I claim to be:

1. A process for separating asphalt from oil containing same which comprises washing precipitated asphalt with fresh solvent to dissolve residual oil from said precipitated asphalt and mixing the solution of residual oil and solvent with fresh oil containing asphalt to produce the aforementioned precipitated asphalt.

2. A process for separating asphalt from oil containing same which comprises mixing asphalt containing oil with a solvent to precipitate asphalt, separating the precipitated asphalt from the solution of oil and solvent, mixing the precipitated asphalt with a liquefied normally gaseous hydrocarbon solvent to separate residual oil and employing the solution of residual oil and solvent as the solvent to precipitate the asphalt from the asphalt containing oil first mentioned.

3. A method for separating asphalt from an oil containing asphalt which comprises extracting said oil with a normally gaseous liquid hydrocarbon solvent a major portion of which solvent consists of hydrocarbons of less than four carbon atoms to cause a separation of the asphalt and separating the asphalt from the oil dissolved in said hydrocarbon solvent.

4. A method for separating asphalt from oil containing asphalt which comprises extracting said oil with a normally gaseous liquid hydrocarbon solvent, the major portion of which sol-

vent consists of propane and ethane, to separate asphalt and separating the asphalt from the oil dissolved in said hydrocarbon solvent.

5. A method for separating asphalt from an asphaltic oil which comprises extracting said oil with a liquid hydrocarbon solvent, the major portion of which is propane, to separate asphalt, and separating the asphalt from the oil dissolved in said hydrocarbon solvent.

6. A process for separating asphalt from oil containing asphalt which comprises commingling said oil with a normally gaseous hydrocarbon under super-atmospheric pressure sufficient to maintain said hydrocarbon liquid and at a temperature sufficiently elevated to dissolve the oil in said hydrocarbon solvent and to separate asphalt and separating the oil dissolved in said hydrocarbon solvent from the separated asphalt under superatmospheric pressure.

7. A process for separating asphalt from oil containing asphalt, which comprises commingling the oil with a normally gaseous hydrocarbon solvent, consisting of a major proportion of hydrocarbons of less than three carbon atoms, under superatmospheric pressure sufficient to maintain said hydrocarbon liquid and at a temperature sufficiently elevated to dissolve the oil in said hydrocarbon and to separate asphalt and separating the oil dissolved in said hydrocarbon solvent from the separated asphalt.

8. A process for separating asphalt from oil containing asphalt, which comprises commingling the oil with a normally gaseous hydrocarbon, the major proportion of which is propane, under superatmospheric pressure sufficient to maintain said hydrocarbon liquid and at a temperature sufficiently elevated to dissolve the oil in said hydrocarbon, to separate asphalt and separating the oil dissolved in said hydrocarbon solvent from the asphalt.

9. A process for separating asphalt from asphaltic oil which comprises commingling the oil with a normally gaseous hydrocarbon solvent, the major portion of which consists of propane and ethane and under superatmospheric pressure sufficient to maintain said hydrocarbon solvent liquid and at a temperature sufficiently elevated to dissolve the oil in said hydrocarbon, and to separate asphalt and separating the oil dissolved in said hydrocarbon from the separated asphalt.

10. A process for separating asphalt from oil containing asphalt, which comprises commingling the oil with propane under superatmospheric pressure sufficient to maintain said propane liquid to dissolve the oil in said propane and to separate asphalt and separating the oil dissolved in said propane from the separated asphalt.

11. A method for separating asphalt from oil containing asphalt which comprises commingling said oil with ethane under superatmospheric pressure sufficient to maintain said ethane liquid to dissolve the oil in said ethane and to separate asphalt and separating the oil dissolved in said ethane from the separated asphalt.

12. A method for separating asphalt from asphaltic oil containing asphalt which comprises extracting said oil with a liquid hydrocarbon solvent at least as volatile as propane to separate asphalt, and separating the asphalt from the oil dissolved in said solvent.

13. A method for separating asphalt from asphaltic oil containing asphalt which comprises commingling said oil with a liquid hydrocarbon solvent, having an average molecular weight less than butane to separate asphalt and separating

the asphalt from the oil dissolved in said solvent.

14. A method for separating asphalt from asphaltic oil containing asphalt which comprises commingling said oil with a hydrocarbon solvent, containing sufficient hydrocarbons of less than three carbon atoms to make the hydrocarbon solvent more volatile than butane, to separate asphalt and separating the asphalt from the oil dissolved in said hydrocarbon.

15. A method of separating asphalt from an oil containing asphalt which comprises extracting said oil with a liquid hydrocarbon solvent having a vapor pressure greater than butane to separate asphalt and removing the asphalt from the oil dissolved in said solvent.

16. A method for separating asphalt from an oil containing asphalt which comprises extracting said oil with a normally gaseous hydrocarbon solvent consisting of a major proportion of hydrocarbons of less than four carbon atoms, to cause separation of the asphalt separating the asphalt from the oil dissolved in said hydrocarbon solvent and chemically treating the oil dissolved in said liquid hydrocarbon to further refine the oil.

17. A process for separating asphalt from oil containing asphalt which comprises commin-

gling said oil with a normally gaseous hydrocarbon under superatmospheric pressure sufficient to maintain said hydrocarbon liquid and at a temperature sufficiently elevated to dissolve the oil in said hydrocarbon solvent and to separate asphalt, separating the oil dissolved in said hydrocarbon solvent from the separated asphalt and chemically treating the oil dissolved in said hydrocarbon solvent to further refine the oil.

18. A method for separating asphalt from an asphaltic oil which comprises extracting said oil with a liquid hydrocarbon solvent, the major portion of which is propane, to separate asphalt, separating the asphalt from the oil dissolved in said hydrocarbon solvent and chemically treating the oil dissolved in said hydrocarbon solvent to further refine the oil.

19. A process for separating asphalt from oil containing asphalt which comprises commingling the oil with propane under superatmospheric pressure sufficient to maintain said propane liquid to dissolve the oil in said propane and to separate asphalt, separating the oil dissolved in said propane from the separated asphalt and chemically treating the oil dissolved in said propane to further refine the oil.

ULRIC B. BRAY.

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