

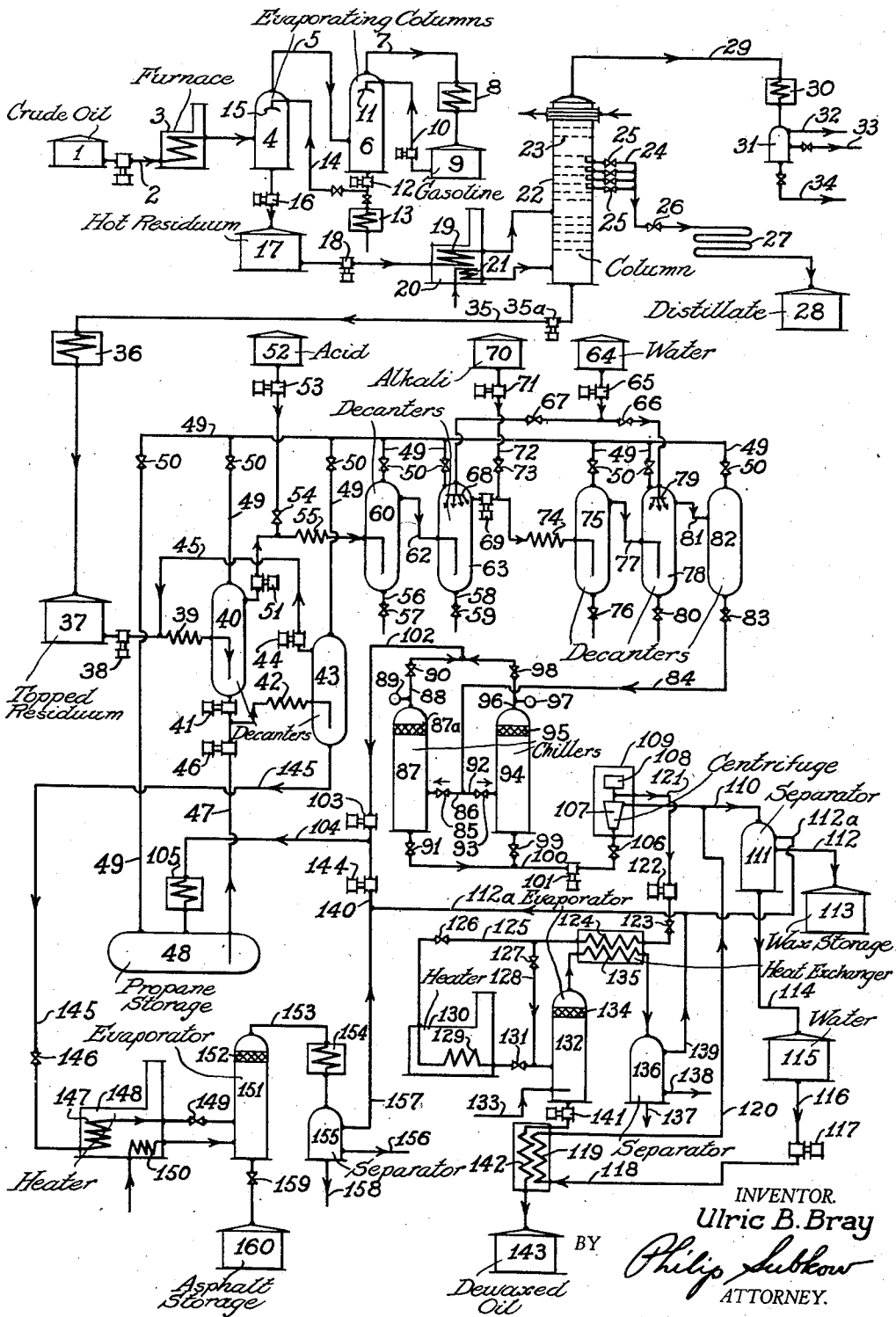
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U. B. BRAY

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METHOD FOR PRODUCING LUBRICATING OIL

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METHOD FOR PRODUCING LUBRICATING OIL

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

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14 Claims. (Cl. 196—13)

This invention relates to a method and apparatus for treating petroleum to produce lubricating oil and is a division of my patent application Serial No. 466,189, filed July 7, 1930.

It is an object of my invention to produce an asphalt and wax-free lubricating oil from an oil containing both asphalt and wax.

Briefly stated, my invention comprises a process for producing lubricating oil from an oil containing asphalt and wax by first separating the asphalt from the oil and wax and then separating the wax from the oil. One of the features of my invention resides in the use of a solvent and in particular, a hydrocarbon solvent, for the purpose of precipitating the asphalt and dewaxing the oil. Another feature resides in the acid treatment and neutralization of the solution of oil, wax and solvent subsequent to the step of separating the asphalt by means of the solvent. Thus oil containing both asphalt and wax may be processed to produce an asphalt and wax free lubricating oil by mixing the oil with a hydrocarbon solvent capable of precipitating the asphalt but dissolving the oil and wax, the precipitated asphalt is separated from the solvent solution and the latter is chilled to precipitate the wax which is then separated from the oil solvent solution. The solvent may then be separated by distillation. If desired, the solvent solution of wax and oil may be acid treated and neutralized prior to the dewaxing step. The de-asphaltizing and chemical treatment steps may be effected under a pressure above atmospheric.

More specifically, my invention comprises a process for separating asphalt and wax from an oil containing the same to produce an asphalt and wax free lubricating oil by mixing the oil under pressure with a liquefied normally gaseous hydrocarbon solvent such as propane to precipitate the asphalt but to retain the oil and wax in the propane solution, in separating the propane solution from the precipitated asphalt while under pressure, in acid treating the propane solution under pressure and separating the excess acid and products of reaction, in neutralizing the acid treated solution also under pressure, in separating the neutralizing reagent and the products of neutralization from the propane solution, in releasing the pressure on the propane solution to effect vaporization of a portion of the propane which in turn causes a chilling of the oil and consequent precipitation of the wax, in separating the precipitated wax from the propane solution and finally, in separating any unvaporized or residual propane from the oil,

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 casing-head 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 maintained 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.

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, 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.

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 vapors passing through 5, consisting of gas oil, kerosene and gasoline vapors, go to dephlegmator 6 where they are fractionated into gasoline 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. 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 106 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 40 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 method for the production of lubricating oil from oil containing asphalt and wax which comprises mixing the oil with a volatile solvent under superatmospheric pressure to dissolve the oil and wax and to separate asphalt, separating the asphalt from the oil wax solution, releasing the pressure on said solution to evaporate the solvent and cool the oil to precipitate the wax, separating the wax from the cooled oil.

2. A process for the production of lubricating oil from oil containing asphalt and wax which comprises commingling said oil in liquid propane under superatmospheric pressure to dissolve the oil and wax and separate asphalt, separating the undissolved asphalt from the propane solution of oil and wax, releasing the pressure and vaporizing a portion of the liquid propane to cool the propane solution of oil and wax to a temperature sufficiently low to precipitate the wax, separating the precipitated wax from the oil dissolved in the remaining propane and subsequently separating the remaining propane from the oil.

3. A method of producing lubricating oil from oil containing asphalt and wax which comprises contacting said oil with a hydrocarbon solvent under superatmospheric pressure to precipitate asphalt, separating the precipitated asphalt from the oil, treating the oil solvent solution with acid, releasing the pressure on the oil solvent solution and vaporizing a portion of said solvent to cool the oil and precipitate the wax, separating the precipitated wax from the cooled oil solvent solution and then separating the residual solvent from the oil.

4. A process for the production of lubricating oil from an oil containing asphalt and wax which

comprises mixing said oil with liquid propane under superatmospheric pressure, separating undissolved asphalt from the solution of oil, wax and liquid propane, treating the oil solvent solution with acid, separating the oil solvent solution from acid and acid reaction products, treating the oil solvent solution with a neutralizing agent, separating the oil solvent solution from said neutralizing agent and the products of neutralization, cooling the propane solution of oil and wax to a temperature sufficiently low to precipitate the wax by vaporizing a portion of said propane under reduced pressure, separating the precipitated wax from the oil dissolved in the remaining liquid propane and subsequently separating the oil from the remaining propane.

5. A method of producing lubricating oil from an oil containing asphalt and wax which comprises treating the oil with a solvent, dissolving the oil and wax and separating the undissolved asphalt, partially evaporating the solvent from the oil solvent solution to chill the resultant oil and precipitate wax, separating the wax and then distilling off the residue of solvent from the oil.

6. A method for the separation of asphalt and wax from oil which comprises extracting said oil with a normally gaseous liquid hydrocarbon solvent consisting of a major proportion of hydrocarbons of less than four carbon atoms to cause a separation of the asphalt, separating the asphalt from the oil and wax dissolved in said hydrocarbon solvent, chilling said hydrocarbon solvent solution of oil and wax to precipitate wax and separating the precipitated wax from the oil dissolved in said hydrocarbon solvent.

7. A method for the separation of asphalt and wax from oil 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 a separation of the asphalt, separating the asphalt from the oil and wax dissolved in said hydrocarbon solvent, vaporizing a portion of said hydrocarbon solvent from the solvent solution of oil and wax to chill the oil and precipitate wax and separating the precipitated wax from the oil and remaining solvent.

8. A process for the separation of asphalt and wax from oil which comprises commingling 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 and wax in said hydrocarbon solvent and to separate asphalt, separating the oil and wax dissolved in said hydrocarbon solvent from the separated asphalt, chilling the hydrocarbon solution of oil and wax to precipitate wax and separating the precipitated wax from the oil dissolved in said hydrocarbon solvent.

9. A process for separating asphalt and wax from oil which comprises commingling 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 and wax in said hydrocarbon solvent and to separate asphalt, separating the oil and wax dissolved in said hydrocarbon solvent from the separated asphalt, releasing the pressure and vaporizing a portion of the hydrocarbon solvent to cool the oil and precipitate wax and separating the precipitated wax from the oil and remaining hydrocarbon solvent.

10. A process for separating asphalt and wax from oil which comprises commingling said oil with a normally gaseous hydrocarbon, 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 and wax in said hydrocarbon solvent and to separate asphalt, separating the oil and wax dissolved in said hydrocarbon solvent from the separated asphalt, chilling the hydrocarbon solvent solution of oil and wax to precipitate wax and separating the oil dissolved in said hydrocarbon solvent from the precipitated wax. 80
13. A method for separating asphalt and wax from 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 and wax dissolved in said hydrocarbon solvent, chilling the hydrocarbon solvent solution of oil and wax to precipitate wax and separating the precipitated wax from the oil and hydrocarbon solvent. 85
11. A process for the separation of asphalt and wax from oil which comprises commingling said oil with a normally gaseous hydrocarbon, 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 and wax in said hydrocarbon solvent and to separate asphalt, separating the oil and wax dissolved in said hydrocarbon solvent from the separated asphalt, releasing the pressure and vaporizing a portion of said hydrocarbon solvent to chill the oil and precipitate wax and separating the precipitated wax from the oil and remaining hydrocarbon solvent. 90
14. A method of producing lubricating oil from an oil containing asphalt and wax which comprises treating said oil with a volatile hydrocarbon solvent under superatmospheric pressure sufficient to maintain the hydrocarbon liquid which solvent will precipitate the asphalt but dissolve the oil and wax, separating the precipitated asphalt from the oil solvent solution, evaporating a portion of the solvent by releasing the pressure on the oil solvent solution and thus chilling the oil to precipitate the wax and separating the precipitated wax from the oil. 95
12. A method for separating asphalt and wax 100
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