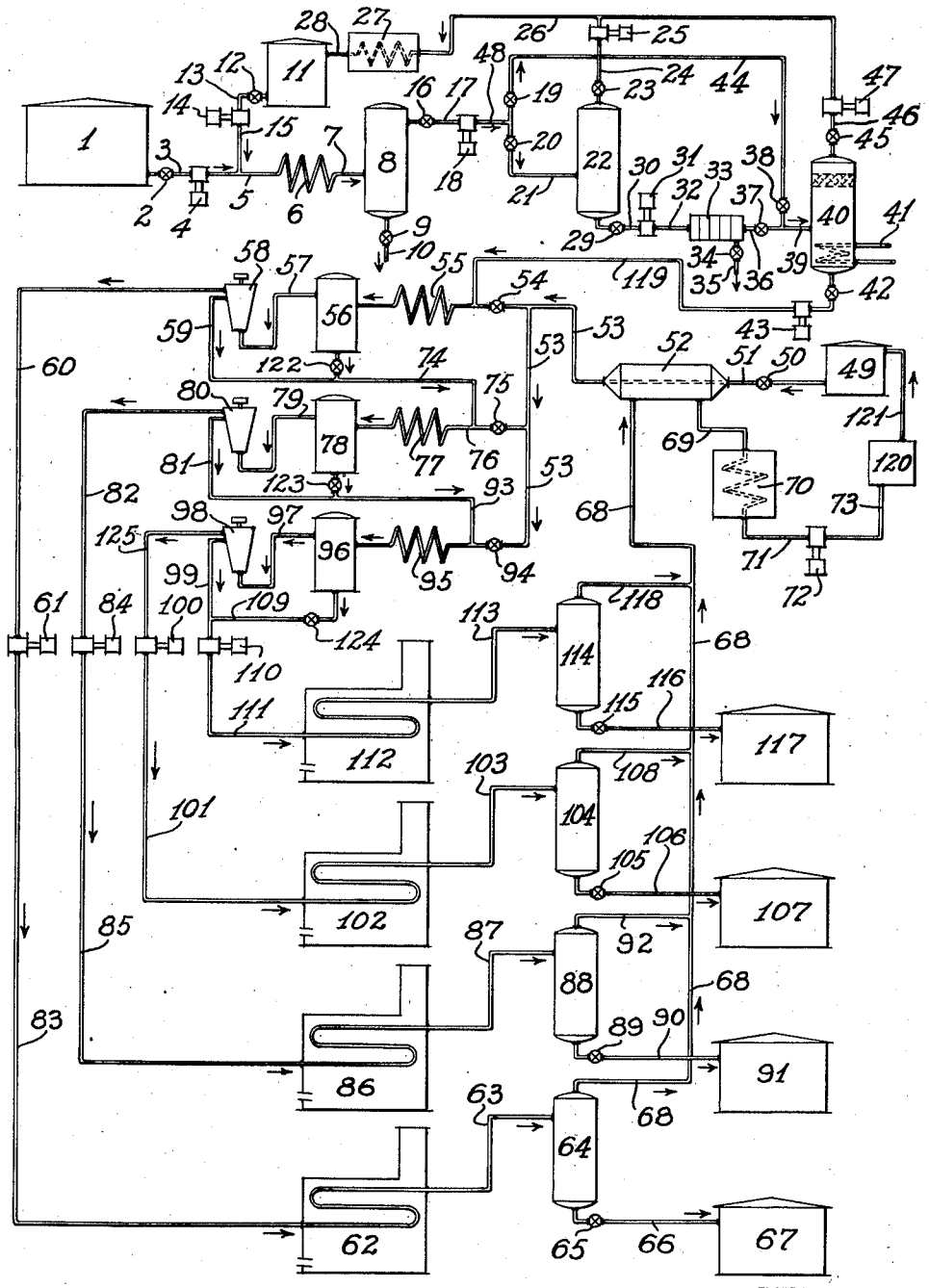
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FRACTIONATION OF MINERAL OIL

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FRACTIONATION OF MINERAL OIL

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9 Claims. (Cl. 196—13)

This invention relates to a process for the production of lubricating oil. More specifically, it relates to a process for the production of lubricating oil from oil containing asphalt or apshalt and wax.

At the present time it is customary to produce lubricating oil from asphaltic crude oil by distillation. The crude oil is first subjected to fractional distillation for the removal of the light fractions present, such as gasoline, kerosene and gas oil, after which the lubricating oil fractions remaining in the still residue are distilled away from the asphaltic still residue. These lubricating oil distillates are then given such treatment as may be required for the production of finished lubricating oil.

Providing the crude oil contains wax this material is partially separated from the still residue by the distillation along with the lubricating oil fractions. The presence of wax in the lubricating oil fractions causes the finished lubricant to have a high pour point or high congealing temperature which is undesirable. It, therefore, becomes necessary to separate a substantial portion of the wax from these distillates in order to produce a lubricating oil having the desired low pour point characteristics. Any of the methods conventional in the art, such as cold settling, cold pressing or centrifuging may be employed to separate the wax from the oil.

It has been pointed out in a patent application, filed by U. B. Bray, Serial No. 466,189, dated July 7, 1930, that distillation methods cannot be employed for separating the heavy lubricating oil fractions from asphaltic crudes without an impairment of certain valuable characteristics possessed by these fractions in the original undistilled crude oil. Distillation of the lubricating oil constituents of crude oil, and especially crude oil containing asphalt, appears to render the overhead fractions or distillates more susceptible to a change in viscosity with a change in temperature. Just what happens during the distillation of these fractions to produce the above is not known, however, it is thought that the high temperatures necessary for vaporizing the oil causes some change in the molecular configuration of the oil which renders it more susceptible to a change in viscosity with a change in temperature. Furthermore, this increase in the temperature viscosity susceptibility of the oil appears to be more pronounced where the distillation is carried out in the presence of asphalt. In order to conserve these valuable inherent characteristics possessed by the lubricating oil fractions the inventor has caused the separation of the oil from the asphalt by the use of certain selective solvents which have a high solvent power for oil but a poor solvent power for asphalt. Thus the crude oil is first subjected to distillation for the separation of the light hydrocarbons present and then the residue is extracted with such solvents as liquid propane or other light liquid hydrocarbons for the separation of the asphalt from the oil. The solvent solution of oil is then distilled to separate the solvent from the oil after which the oil may be treated by methods conventional in the art for the production of a highly refined product. When it is desired to vary the viscosity of the final product this may be done in either of two manners. First, by varying the extent of the distillation of the crude oil prior to extraction and second, by blending the extracted heavy residual oil with varying quantities of the lighter distilled overhead fractions. The first method is quite inflexible and the variations in viscosity of the final products are quite limited. The second method is open to objection because the light overhead distillates used for blending usually are highly susceptible to a change in viscosity with a change in temperature and when mixed with the extracted heavy residual oils have this same undesirable effect upon the temperature viscosity susceptibility of the blended product.

A more flexible method of separating the lubricating oil constituents of asphaltic oil into fractions of varying viscosity consists in treating such oil with suitable solvents which are capable of successively extracting oil fractions of increasing viscosities. Thus when a residual asphaltic oil, produced by distilling off the light fractions from asphaltic crude oil is successively extracted with alcohol, alcohol and ether, or alcohol and benzol, there are produced a series of oil fractions with ascending viscosities. The undesirable feature in this process, however, resides in the solubility of certain of the asphaltic bodies in the solvent solution of oil. Thus the oil fractions which are produced by successively extracting an asphaltic oil with such solvents are characterized by an undesirable dark color due to the presence of asphalt in the oil. This undesirable constituent in the lubricating oil fraction must be removed before a finished lubricant can be produced. The removal of the asphalt can be affected by the use of acid or other chemicals capable of coagulating the asphaltic bodies present or by a combination of acid treatment and bleaching with clay but such

treatment is expensive and requires much costly equipment.

I have discovered that asphaltic oil can be separated into fractions of varying viscosity by solvent extraction with a combination of solvents which eliminates the undesirable features described in the foregoing process. My process consists in commingling asphaltic oil with a solvent in which the asphalt is substantially insoluble and the oil substantially completely soluble, separating the solvent solution of oil from the undissolved asphalt, removing the solvent from the substantially asphalt-free oil and then separating the extracted oil by the use of appropriate solvents into fractions of varying viscosity.

The asphaltic oil which I extract is obtained from those crude oils which contain asphalt. The crude oil containing asphalt is first distilled under carefully controlled conditions with fire and steam for the separation of gasoline, kerosene and gas oil present. Care is exercised in removing these light constituents from the crude oil as quickly as possible and without employing excessive temperatures which would be injurious to the valuable lubricating oil constituents present. The residue so produced is then cooled and extracted with a solvent capable of dissolving the oil but in which asphalt is substantially insoluble.

For the separation of the asphalt from the oil I find the light hydrocarbons which are vaporous at ordinary temperature and pressure very satisfactory. Such hydrocarbons include methane, ethane, propane, butane and isobutane. These hydrocarbons may be obtained by rectification of casinghead gasoline by the so-called "stabilizing" method now conventional in the natural gasoline industry. They are the overhead thus obtained. They are liquefied by compression and cooling in the conventional manner and drawn off into pressure chamber 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 this fraction in a liquid state is approximately 125 pounds per square inch gauge at 70° F.

After the separation of the asphalt from the solvent solution of oil the latter is distilled to remove the solvent and recover the substantially asphalt-free oil. The oil is then subjected to successive extraction with alcohol for the production of a series of oil fractions of varying viscosity. Methyl, ethyl, propyl, isopropyl, butyl and isobutyl alcohol or mixtures of these alcohols may be employed to a good advantage in separating the substantially asphalt-free oil into fractions of varying viscosities. I find in general, however, that the alcohols of the higher molecular weights are more suitable for carrying out my process than the alcohols of the lower molecular weights. I may also employ solutions of these alcohols in ether or benzol to a good advantage. Furthermore, I find that it is only practical to employ alcohols which are substantially free from water as the presence of this material in the alcohol decreases its solvent power for oil. Alcohols which contain less than 0.75% of water, however, have proven to be satisfactory. Where larger amounts of water are present I find it advisable to dehydrate the alcohol by any of the methods common to the art. Thus the alcohol may be commingled with calcium oxide or anhydrous copper sulphate and subsequently distilled for the production of a solvent alcohol sufficiently free from water to be employed in my process.

It is, therefore, an object of my invention to produce lubricating oils of varying viscosity from crude oils containing asphalt.

It is another object of my invention to separate the lubricating oil components from asphaltic oil under conditions which will conserve the inherent temperature viscosity susceptibility characteristics of the oil and then separate the oil into fractions of varying viscosity.

It is another object of my invetnion to commingle asphaltic residual oil with liquid propane, separate the oil from the asphalt and then separate the asphalt-free oil into a plurality of fractions of varying viscosities with alcohol.

It is still another object of my invention to separate wax and asphalt bearing oils into asphalt, wax and a plurality of oil fractions under such conditions that the inherent viscosity temperature susceptibility characteristics of the oils are not impaired during the process of separation.

The accompanying drawing is a schematic arrangement of apparatus in which I may carry out my process.

In the drawing, crude oil in tank 1 is withdrawn through valve 2 and line 3 to pump 4 which forces it through line 5 into agitator 6 where it is mixed with a stream of liquid propane coming from tank 11 through valve 12, line 13, pump 14 and line 15. The thoroughly mixed mass in agitator 6 is removed through line 7 to settling chamber 8 where the insoluble asphalt is allowed to settle out and is removed through valve 9 and line 10.

The propane solution of oil is substantially free from asphalt and is removed from settling chamber 8 through valve 16 and line 17 to pump 18 which forces it through line 43, valve 19, line 44, valve 38 and line 39 to vaporizer 40 where by aid of steam introduced through closed coil 41 the propane present in the oil is vaporized and passes by means of valve 45 and line 46 to compressor 47 which forces it through line 26 to condenser 27 where it is liquefied and passes by means of line 28 to propane storage tank 11.

Where wax is present in the oil under treatment the following modification in the process is employed:

After removal of the insoluble asphalt in settling chamber 8, the propane solution of wax and oil passes by means of valve 16, line 12 to pump 18 which forces it through line 43, valve 20 and line 21 to chiller 22 where sufficient liquid propane is allowed to vaporize at reduced pressure to obtain a temperature sufficiently low to cause thorough precipitation of the wax. The vaporized propane in chiller 22 is removed through valve 23 and line 24 to compressor 25 which forces it through line 26 to condenser 27 where it is liquefied and passes by means of line 28 to propane storage tank 11. The chilled propane solution of oil carrying precipitated wax is removed from chiller 22 through valve 29 and line 30 to pump 31 which forces it through line 32 to filter press or wax separating means 33 where the wax is separated from the propane solution of oil and is removed through valve 34 and line 35. The propane solution of oil, substantially free of wax is removed from wax separation means 33 through line 36, valve 37 and line 39 to vaporizer 40 where the propane present is removed from the oil in the same manner as has previously been described.

The oil, substantially free from asphalt, in vaporizer 40 is removed through valve 42 to pump

43 which forces it through line 119 to agitator 55 where it is thoroughly mixed with hot alcohol coming from alcohol storage tank 49 through valve 50, line 51, heat exchanger 52, line 53 and valve 54. In case insufficient heat is supplied by the alcohol vapors in heat exchanger 52 to raise the liquid alcohol in line 53 to the proper temperature I may supplement other heating means not shown. The mixture of oil and hot alcohol passes to separating tower 56 where the oil dissolved in alcohol separates as the upper phase and the undissolved oil separates as the lower phase. The alcohol solution of oil constituting the upper phase is removed through line 57 to centrifuge 58 where any entrained undissolved oil globules are removed through line 59. The alcohol solution of oil from centrifuge 58 passes by means of line 60 to pump 61 which forces it through line 83 to heater 62 where the temperature of the mass is raised sufficiently high to vaporize the alcohol. The heated mass passes from heater 62 through line 63 into separating tower 64 where the unvaporized oil separates from the alcohol vapor and is removed through valve 65 and line 66 to storage tank 67. The alcohol vapor in separator 64 is removed through line 68 through heat exchanger 52 where a portion of the heat in the alcohol vapor is utilized to raise the temperature of the liquid alcohol passing to the extraction process. The partially cooled alcohol vapor in heat exchanger 52 is removed through line 69 to condenser 70 where it is liquefied and passes by means of line 71 to pump 72 which forces it through line 73 to any suitable means of dehydration 120, such as has been previously described. The dehydrated alcohol passes from dehydrator 120 through line 121 into alcohol storage tank 49.

The insoluble oil phase in separator 56 is removed through valve 122 into line 74 where it is combined with the separated entrained oil in line 59. This oil passes to line 76 where it meets a stream of hot alcohol coming through line 53 and valve 75 and the mixed stream of oil and hot alcohol passes to agitator 77 where they are thoroughly mixed and then pass to separating tower 78, where the alcohol solution of soluble oil is allowed to separate as the upper phase and is removed through line 79 to centrifuge 80 where the entrained insoluble oil globules present are separated and passed out through line 81. The hot alcoholic solution of oil passes from centrifuge 80 through line 82 to pump 84 which forces it through line 85 into heater 86 where the temperature of the mass is raised sufficiently high to vaporize the alcohol. The heated mass then passes through line 87 into separator 88 where the unvaporized oil is removed through valve 89 and line 90 to tank 91. The separated alcohol vapor is removed through line 92 into line 68 where it is finally returned to alcohol storage tank 49 in the same manner as previously described.

The insoluble oil phase in separator 78 is removed through valve 123 into line 93 along with the separated entrained oil in line 81. This oil passes through line 93 to agitator 95 where it is mixed with hot alcohol coming through line 53 and valve 94. The thoroughly agitated mass passes from agitator 95 into separator 96 where the alcoholic solution of oil separates from the remaining undissolved oil as the upper phase. This phase is removed through line 97 to centrifuge 98 where any undissolved oil present is separated and passes out through line 99. The alcoholic solution of oil in centrifuge 98 is removed through line 125 to pump 100 which forces it through line 101 to heater 102 where the temperature is raised sufficiently high to vaporize the alcohol. The heated mass then passes through line 103 to separator 104 where the unvaporized oil separates and is removed through valve 105 and line 106 into storage tank 107. The vaporized alcohol is removed from separator 104 through line 108 into line 68 where it is returned to alcohol storage tank 49 in the same manner as previously described.

The lower insoluble phase in separator 96 is removed through valve 124 through line 109 where it is combined with the insoluble oil from centrifuge 98 in line 99 and passes to pump 110 which forces it through line 111 to heater 112 where the temperature is raised sufficiently high to vaporize any alcohol present. The heated mass then passes through line 113 to separator 114 where the unvaporized oil settles out and is removed through valve 115 and line 116 to storage tank 117. The separated alcohol vapor is removed from separator 114 through line 118 into line 68 where it is returned to alcohol storage tank 49 in the same manner as previously described.

Furthermore, when the oil contains wax I may employ wax anti-solvents to aid its separation from the oil. For example I may dissolve the waxy oil in a diluent such as liquid propane and then add alcohol, acetone, acetone and benzol, or methyl formate to aid in precipitating the wax. If necessary the waxy oil dissolved in liquid propane and containing a quantity of wax anti-solvent may be chilled to cause thorough precipitation of the wax. The chilling may be accomplished by vaporizing some of the liquid propane diluent under reduced pressure or by liquid ammonia or other refrigerating means.

As an example of the preferred method of carrying out my process, an asphaltic residual oil obtained by carefully distilling out the gasoline, kerosene and gas oil present in tank 1 is mixed with a light volatile liquid hydrocarbon such as liquid propane in the proportion of one part of residual oil to five parts of liquid propane. The insoluble asphalt is separated from the propane solution of oil through line 10 of chamber 8 and the propane solution of substantially asphalt-free oil is then passed to vaporizer 40 where the propane is separated from the oil.

The hot oil in vaporizer 40 is removed through valve 42, pump 43 and line 119 from whence it passes to the foregoing described means for successive extraction with alcohol. The extraction is preferably carried out at a temperature near the boiling point of the alcohol. The predetermined temperature of the oil entering the extraction apparatus may be obtained by the use of the steam coil in vaporizer 40. After the preheated oil enters the extraction apparatus no further heat is required to maintain the proper temperature other than that furnished by the preheated alcohol withdrawn from heat exchanger 52. The ratio of the oil and alcohol entering the extraction apparatus will depend largely upon the character of the fractions desired. Any one of the succesive fractions may be enlarged by maintainng a high ratio of alcohol to oil in that particular extraction step. After separation of the oil into the desired number of fractions the particular grades obtained may be stored in tanks 67, 91, 107 and 117 and where intermediate products are desired these fractions may be blended.

The foregoing examples are merely illustrative of my process and are not to be construed as limiting the invention which I claim.

I claim:

1. A method for the fractionation of oil containing asphalt which comprises commingling said oil in a light hydrocarbon solvent, separating the light hydrocarbon solvent to separate asphalt solution of oil from the undissolved asphalt, separating the light hydrocarbon solvent from the substantially asphalt-free oil, successively extracting said substantially asphalt free oil with an alcohol to form a plurality of fractions and separating said fractions.

2. A process for the fractionation of oil containing wax which comprises dissolving said oil under superatmospheric pressure in a light volatile hydrocarbon, vaporizing a portion of said solvent to chill the oil and precipitate the wax, separating the precipitated wax from the solvent solution of oil, separating the solvent from the wax-free oil and successively extracting said wax-free oil with alcohol to produce a plurality of fractions and separating said fractions.

3. A process for the fractionation of oil containing wax which comprises dissolving said oil under superatmospheric pressure in liquid propane, releasing the pressure and lowering the temperature of the oil sufficiently to precipitate the wax, separating the precipitated wax from the propane solution of oil, separating the propane from the wax-free oil and separating said substantially wax free oil into a plurality of fractions by successive extraction with alcohol and separating said fractions.

4. A process for the fractionation of oil containing wax which comprises commingling said oil under superatmospheric pressure with liquid propane containing a wax anti-solvent, releasing the pressure and vaporizing propane to chill the oil sufficiently to precipitate the wax, separating the precipitated wax from the oil dissolved in propane and wax anti-solvent, separating the oil from the propane and wax anti-solvent and separating the wax-free oil into a plurality of fractions by successive extraction with alcohol.

5. A process for the fractionation of oil containing asphalt and wax which comprises commingling said oil with a light hydrocarbon solvent capable of dissolving the oil and wax but not the asphalt, separating the solvent solution of oil and wax from the undissolved asphalt, chilling the solvent solution of oil to a temperature sufficiently low to precipitate the wax, separating the precipitated wax from the solvent solution of oil, removing the solvent from the oil and subsequently separating the oil into a plurality of fractions by successive extraction with alcohol.

6. A process for the fractionation of oil containing asphalt and wax which comprises commingling said oil under superatmospheric pressure in liquid propane, separating the propane solution of oil and wax from the undissolved asphalt, releasing the pressure and vaporizing liquid propane to chill the oil and precipitate the wax, separating the precipitated wax from the propane solution of oil, separating the propane from the oil, extracting the oil with alcohol to form a plurality of fractions and subsequently separating the alcohol from said fractions.

7. A process for the fractionation of oil containing asphalt which comprises commingling said oil with a normally gaseous hydrocarbon solvent to separate the asphalt, separating the asphalt from the oil dissolved in said solvent, separating the solvent from the oil, extracting said substantially asphalt free oil with alcohol to produce an oil phase dissolved in said alcohol and an oil phase insoluble in said alcohol and separating said phases.

8. A process for the separation of oil containing asphalt into fractions which comprises commingling said oil with liquid propane to separate the asphalt, separating the asphalt from the oil dissolved in liquid propane, separating the propane from the oil, extracting the substantially asphalt free oil with alcohol to form an oil phase dissolved in alcohol and an oil phase insoluble in said alcohol and separating said phases.

9. A process for the separation of oil containing asphalt into fractions which comprises commingling said oil with a liquefied normally gaseous hydrocarbon solvent to separate asphalt, separating the asphalt from the oil dissolved in said solvent, separating the solvent from the oil and extracting the substantially asphalt free oil into a plurality of fractions having successively higher viscosities with a solvent and separating said fractions.

CLAUDE E. SWIFT.

CERTIFICATE OF CORRECTION.

Patent No. 2,031,234. February 18, 1936.

CLAUDE E. SWIFT.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, lines 8 and 9, claim 1, strike out the words "to separate asphalt" and insert the same after "solvent" and before the comma in line 7, same claim; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of February, A. D. 1937.

Henry Van Arsdale
Acting Commissioner of Patents

(Seal)