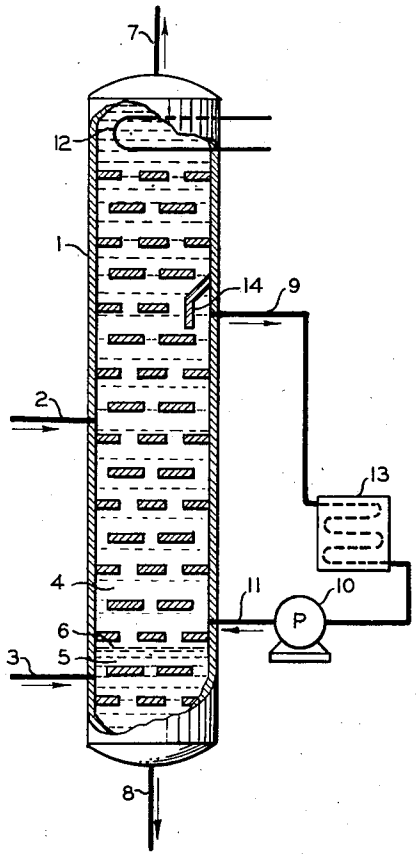
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FRACTIONATION OF REDUCED CRUDE OIL

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FRACTIONATION OF REDUCED CRUDE OIL

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This invention relates to the propane-fractionation of lubricating oil stocks. In one of its more specific aspects it relates to a method for the treatment of low asphalt-containing lubricating oil stocks for the separation and recovery of lubricating oil fractions. In a still more specific aspect it relates to a process for the separation and recovery of lubricating oil fractions from crude lubricating oil stocks containing some asphaltic material by fractionation with liquid propane wherein the asphalt is not precipitated and caked in the fractionating apparatus.

Deasphalting petroleum oils and more particularly reduced crude oils from which distillate lubricating oil fractions have been removed is old in the art. Such operations are usually carried out at temperatures between about 70° and 140° F. to take advantage of the precipitating action of propane on the heavy asphaltic constituents of the oil. It has also been recognized for many years that a fractionating effect can be obtained with propane-oil mixtures at temperatures ranging from about 140° F. up to the critical of propane. Utilizing the unique properties of liquid propane whereby increasing temperatures result in progressive rejection of hydrocarbons in such a manner that the higher molecular weight components and the more aromatic and naphthenic components are separated first and the lighter components and more paraffinic hydrocarbons last, a combination of low temperature distillation and solvent extraction is achieved. However, due to the difficulties involved in working at high pressures and in close proximity to the critical temperature of propane, commercial exploitation was unknown until quite recently.

It has been found, however, that some low-asphalt content reduced crude lubricating oil stocks may be fractionated continuously by liquid propane at a high temperature and under correspondingly high pressures, while other low-asphalt content reduced crude lubricating oil stocks can be fractionated for only short periods of time. In this latter case, it has been found that the fractionating equipment became plugged with a hard deposit of asphalt. This asphaltic material had apparently been precipitated from the oil upon contact with the high temperature liquid propane.

An object of my invention is to devise a process for the fractionation of low asphalt-containing reduced crude lubricating oil stocks for the removal and recovery of lubricating oil constituents. Another object of my invention is to devise a method for the separation of lubricating oil

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constituents from such crude oil stocks by fractionation with propane without the formation of hard asphaltic deposits in the fractionation apparatus. Still another object of my invention is to devise a continuous process for the separation and recovery of lube constituents from low asphalt-containing reduced crude oil stocks suitable for the manufacture of lubricating oils by fractionation with propane wherein the asphalt-containing oil is stripped of some of its oily constituents in such a manner that the asphalt does not adhere as a hard mass to the fractionation equipment. Still other objects and advantages of my invention will be obvious to thise skilled in the art upon reading the following disclosure, which, taken with the attached drawing, forms a part of this specification.

In preparing to apply the above mentioned unique properties of liquid propane to actual commercial separation of certain grades of lubricating oil from residual stocks a hitherto unrecognized problem was encountered. Upon treating some Mid-Continent reduced crude oil stocks with liquid propane in a countercurrent contacting tower at a propane to oil volume ratio of about 7:1 with temperatures ranging from about 195° F. at the top to about 175° F. at the bottom of the tower an SAE 40 oil was separated in the overhead product. On the other hand, when a very similar Mid-Continent reduced crude oil stock was charged to the process under the same operating conditions a similar fraction of lubricating oil was initially obtained but the column rapidly filled with hard asphaltic material in the stripping section, thereby making continuous operation impossible. In this second case, the formation of a third phase, that is, a semi-fluid asphaltic phase was produced along with a propane-rich light oil fraction and an oil-rich solution of propane in heavy oil. Upon contacting the charge oil with liquid propane this third phase when first formed was sufficiently fluid to flow nearly to the bottom of the column before the ascending propane had washed it sufficiently to cause it to set to a hard cake. Upon continued operation this asphalt cake builds up in the column until complete closure of the column occurs. Why one low asphalt-containing oil should deposit its asphalt while another low asphalt-containing oil does not when the two oils contain similar amounts of asphalt is not definitely understood.

In a study of three well known Mid-Continent reduced crude oils which have been long recognized as excellent sources of lubricating oil stocks hard deposits were formed when treating two of

these stocks with liquid propane while the third was fractionated with propane continuously and without difficulty. It has also been found that some West Texas reduced crude oils can be fractionated with propane while others cannot on account of asphalt deposition. It is therefore to be realized that propane fractionation cannot be universally applied to all so-called low asphalt content reduced crude lubricating oil stocks.

Pilot plant propane fractionation studies of a Mid-Continent reduced crude lubricating oil of known asphalt depositing tendency has demonstrated that a propane fractionation operation in which just a very small amount of asphalt is deposited is not sufficient to solve the problem since such a stock when fractionated with propane under conditions to prepare an SAE 50 lubricating oil stock rapidly forms a plug in the fractionating column, thus indicating an equilibrium three-phase condition peculiar to the particular stock involved.

On the other hand, by increasing the concentration of oil in the stripping section of the fractionator decreases the potential stripping power of the propane and thereby prevents over extraction of the oil-rich phase and the phase relationships existing in the stripping section of the tower are so altered that a hard asphalt deposit is not formed.

Broadly speaking, my invention consists of a fractionation operation in which a lubricating oil stock can be fractionated by liquid propane at a relatively high temperature to produce an overhead fraction having a definite viscosity while heavier oils and asphaltic materials are rejected as a separate relatively heavy oil phase and this phase settles to the bottom of the vessel to accumulate as an oil rich phase.

The figure shows diagrammatically, partly in section and partly in elevation, one form of apparatus in which the process of my invention may be practiced.

The apparatus consists essentially of an elongated fractionating tower which is provided with several inlet and outlet pipes. A pipe 2 is intended for introduction of feed stock to the vessel while a pipe 3 near the bottom provides for introduction of propane. An overhead pipe 7 is for withdrawal of overhead product while bottoms product may be withdrawn through a pipe 8, as shown. Two side connections are pipes 9 and 11. Through pipe 9 material can be withdrawn from the vessel, passed through a heat exchanger 13 and pumped by a pump 10 through the line 11 into a lower section of the vessel. A heating coil 12 is provided in the upper portion of the tower through which may pass a heat exchange fluid for providing reflux to the top of the vessel. A baffle plate 14 is provided as shown as attached to the side wall of the vessel in such a manner that some settling space is provided before liquid material is withdrawn through the pipe 9.

Reference numeral 4 refers to a liquid propane phase containing some dissolved oil. This propane-rich phase and the oil-rich phase 5 meet at a common interface 6 which is maintained at a relatively low point in the column. The propane inlet line 3 is also positioned at a point in the column sufficiently low that the propane feed may pass through the oil-rich phase in the bottom of the column before emerging as the propane phase 4.

At about the mid-section of the tower, specifically at the point of introduction of the charge stock to the vessel, oils which are soluble in propane dissolve therein while the asphaltic material and the heavier oil fraction including naphthenic and aromatic constituents and any other material not soluble in propane remain with the asphalt as a heavy oil phase. This heavy oil phase settles as a disperse phase toward the bottom of the vessel while the dissolved oil in solution in propane flows upward toward the top of the column. Temperature gradient ranging from about 170°–180° F. at the bottom to about 195°–210° F. at the top of the column is maintained for fractionation purposes. The temperature at the feed point of this zone is maintained between the approximate limits of 180° and 190° F. A peculiar property of liquid propane, which, however, is known to the art, is that the solubility of oil in propane decreases with rise of temperature at temperatures approaching the critical temperature of propane. Also the solubility of asphalt in propane at these temperatures is very low while the solubility of the naphthenic and aromatic hydrocarbons is somewhat greater. The solubility of the paraffinic or high viscosity index oils is greatest of any of these components. Thus, by maintaining the top of the tower at the highest temperature a precipitation of the naphthenic and aromatic constituents occurs as these materials rise from the feed point toward the top of the tower.

According to my process for the production of an SAE 50 oil stock at the temperature stated liquid propane equal in volume to about eight times the volume of the oil feed stock is introduced through the propane inlet line 3. This large volume of propane possesses rather marked dissolving action on the disperse oil phase settling from the oil inlet line 2 so that under conventional operation conditions so much of the oil is dissolved from this settling disperse phase that the asphalt constituents are precipitated as relatively hard and adhesive asphalt and during the precipitating action the asphaltic material becomes deposited upon the inner walls and upon any contacting elements within the vessel. Upon continued operation for even a short time under these conditions the entire cross section of the vessel frequently becomes plugged with this deposit of asphalt. To prevent the deposition of such a hard and difficultly removable asphalt deposit, I withdraw through the line 9 some propane solution rich in dissolved oils and inject this withdrawn solution into the lower part of the propane phase and at least below the feed inlet, preferably at a point just above the interface between the liquid propane and the oil-rich phase. In this manner, the propane introduced through line 3, upon reaching the interface 6, very quickly acquires an appreciable oil content from the propane solution introduced through the line 11. In this manner, the dissolving power of the newly added propane is reduced to such an extent that overstripping of the oily constituents from the material settling through this stripping section of the tower is markedly reduced and the asphalt material does not separate as a hard and adhesive material but actually accumulates as a liquid oil-rich phase in the bottom section of the vessel. This oil-rich phase is sufficiently fluid that it may be withdrawn through the line 8 and pumped to subsequent treating apparatus or to storage or other disposal as desired. In case it is desired to cool the propane solution which is withdrawn through line 9 to a temperature existing in the lower section of the tower the heat exchanger 13 is operated as a cooler. The proportion of pro-

pane solution cycled from the upper-section into the lower section of the tower may range from 10 to 50 per cent of the solution passing from the feed point 2 toward the top of the tower. In case the recycle amounts to only 10 to 15 per cent, for example, the cooler 13 may not be necessary but, in case as large a proportion as 40 to 50 per cent is recycled the temperature gradient to the tower may be interfered with and it may be preferable to cool the material in cooler 13 to a temperature of approximately 175° F. prior to its introduction through line 11. In this manner a definite and desirable temperature gradient may be maintained through the length of the fractionator.

Specific example

In a specific embodiment of the present invention a selected reduced crude oil stock is subjected to vacuum distillation to remove substantially all of the SAE 10 and 20 grades of oil. This reduced crude oil then containing only SAE 30 and higher viscosity grades of oil and asphalt is pumped to the propane fractionator 1 through the line 2. The propane column 1 is maintained at a pressure of 640 pounds per square inch gauge with the feed point inlet located approximately mid-way between the top and bottom of the column. The temperature at the feed plate and of the incoming charge oil is held at about 185° F. Propane at about 175° F. is pumped into the column through the line 3 at a rate such that the volume ratio of propane to the oil feed is about 8:1. It might be mentioned that the pressure of 640 pounds per square inch gauge is approximately 50 pounds higher than the vapor pressure of propane at 195° F. This latter temperature is maintained in the vicinity of the heating coil 12 at the top of the tower.

The ascending propane stream serves to strip the downflowing oil of hydrocarbons not dissolved by the propane solution at the feed plate while in the upper and fractionating section above the feed plate the heavier and more aromatic components are precipitated from the propane oil solution by virtue of the temperature gradient ranging from about 185° F. at the feed plate to about 195° F. at the top of the column.

In order to prevent overstripping of the oil phase in the lower section of the column I withdraw a portion of the propane-oil solution at a point slightly above the feed plate through line 9 and cool this liquid to about 175° F. and inject it into the column at a point slightly above the interface 6. The propane-oil stream which is withdrawn through line 9 is substantially saturated with oil at the conditions maintained at the level of withdrawal. Upon cooling the oil to a slightly lower temperature before injection into the bottom of the column changes the solubility relationships in such a manner that the solution is no longer saturated but the composition of the solution is not changed and upon introduction of this solution into the propane phase just above the interface 6 increases the concentration of oils in the stripping column. In this manner the stripping power of the ascending propane is markedly reduced and overstripping of the settling asphaltic material is not accomplished and as mentioned hereinbefore, the asphaltic material reaches the oil rich phase 5 in a liquid condition without separating as a third (liquid or solid) phase.

By providing the baffle 14, the more aromatic and naphthenic oils which are precipitated as an oil phase dispersed in propane in the upper section of the column are not recycled to the bottom of the column since such oil should settle through the ascending column of propane for stripping purposes since high viscosity index oil may be carried downward with this aromatic and naphthenic oil and such stripping tends to increase the yield of high viscosity oil withdrawn in the propane-oil solution from the top of the tower. Baffle 14 may be omitted in certain applications, however.

Any type of liquid-liquid contacting equipment such as slats, baffles or even trays and cap may be provided to promote efficient contacting between the liquid phases. If desired, no packing at all may be used, but liquid-liquid contacting is poor and it is preferable to use contact promoting packings. In the prior art when using packing the asphalt precipitates upon the packing and around the walls of the vessel while when no packing is used the asphalt deposits upon the walls of the tower and ultimately will plug the entire cross section. Hence, the use of efficient contacting or packing material is highly desirable and especially so when using the process of my invention which permits use of packing and at the same time prevents deposition of asphalt.

This fractionator tower may be provided with packing or contacting material as desired and may be constructed of materials readily available commercially. In the propane treating of oils corrosion problems are not critical and less expensive materials of construction may be used. However, such a vessel and its auxiliary equipment will need to be constructed to withstand the relatively high operating pressures. Such auxiliary equipment as valves, temperature and pressure indicating and recording devices, and pumps, and flow control apparatus are not shown nor described for purposes of simplicity. The use of such auxiliary equipment is well known by those skilled in the art. It will be realized that those skilled in this art may vary the operating conditions and other variable of apparatus and process without departing from the intended spirit and scope of my invention.

Having disclosed my invention, I claim:

1. In the propane fractionation of lubricating oil constituents from low asphalt-content reduced crude lubricating oil stocks with liquid propane wherein solid asphaltic material precipitates upon initial contact with the propane and adheres to and plugs the fractionating apparatus in the region adjacent and below the raw feed entry point, a process for continuously carrying out this fractionation operation without precipitating said asphalt and plugging said apparatus comprising maintaining a body of liquid propane containing oil in solution in a contacting zone, introducing said oil stock into said body of propane at midpoint thereof, maintaining a body of an oil-rich phase below said body of propane in said zone, said body of propane and said body of oil-rich phase meeting at a common interface, introducing liquid propane into said body of oil-rich phase, removing propane containing oil in solution from a point above the feed stock introduction point of said zone, introducing said removed propane containing oil in solution into said zone at a point near the bottom of said zone but above and adjacent said interface, withdrawing propane containing oil in solution from the top and withdrawing oil-rich phase from the bottom of said zone as products of the process.

2. The process of claim 1 wherein the oil-rich

phase in the bottom of said zone is maintained at a temperature between the limits of 170° and 180° F., the temperature at the feed point of said zone is maintained between the limits of 180° and 190° F., and the temperature at the top of said zone is maintained between the limits of 195° and 210° F., and said zone is maintained under a pressure greater than the vapor pressure of propane at 210° F.

3. The process of claim 1 wherein the ratio of the volume of propane to the volume of the low asphalt-content reduced crude lubricating oil charge stock is eight to one.

4. The process of claim 1 wherein a temperature gradient ranging from 175° F. at the bottom of said zone to 195° F. at the top of said zone is maintained, said zone is maintained at a pressure greater than the vapor pressure of propane at 195° F., and the volume ratio of propane to low asphalt-content reduced crude lubricating oil charge stock introduced to said zone is eight to one.

5. The process of claim 1 wherein the amount of propane containing oil in solution removed from a point above the feed point and introduced at a point adjacent said interface of said zone is within the limits of 10% to 50% of the propane solution ascending in the zone at the point of solution removal.

6. In the fractionation and recovery of lubricating oil constituents from asphalt-containing lubricating oil stocks with propane wherein a hard deposit of asphalt is formed and adheres to and plugs the oil fractionating apparatus, a process for continuously carrying out said fractionating operation without plugging of said apparatus by deposited asphalt comprising maintaining a body of liquid propane containing oil in solution in a vertically disposed, elongated contacting zone, introducing said oil charge stock into said body of propane containing oil in solution at an intermediate point thereof, maintaining a body of an oil-rich phase below said body of propane containing oil in solution in said zone, said body of propane and oil in solution and said body of oil rich phase meeting at a common interface at a point near the bottom of said zone, introducing liquid propane into said body of oil-rich phase, removing propane containing oil in solution from said zone at a point above the charge oil inlet point, introducing said removed propane containing oil in solution into said zone at a point near but above said interface, withdrawing propane containing oil in solution from the top of said zone and withdrawing oil-rich phase from the bottom of said zone as the two products of the process.

7. In the process of claim 6, cooling the removal propane containing oil in solution to the temperature of the oil-rich phase in said zone.

8. The process of claim 7 wherein a temperature gradient between 15° F. and 30° F. is maintained throughout said zone with a minimum temperature at the bottom of the zone of 170° F., and the temperature at the top of said zone is higher than at the bottom thereof, said zone is maintained under a pressure greater than the vapor pressure of propane at 195° F., the volume ratio of propane to lubricating oil charge stock introduced to said zone is eight to one and the volume of propane containing oil in solution removed from said zone at a point above the charge stock inlet point and reintroduced into said zone at a point near but above said interface is within the limits of 10% to 50% of the propane solution of oil ascending in the zone at the point of solution removal.

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Certificate of Correction

Patent No. 2,558,809 July 3, 1951

BRUCE C. BENEDICT

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 14, for "thise" read *those*; column 8, lines 14 and 15, for "removal" read *removed*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 6th day of November, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.