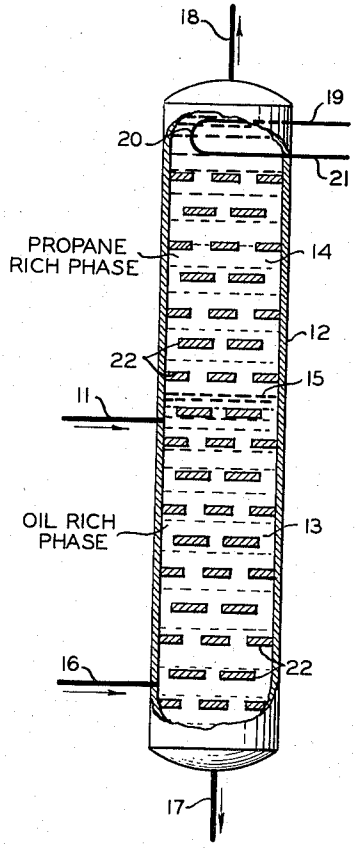
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PROPANE FRACTIONATION OF REDUCED CRUDE OIL

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PROPANE 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 the 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 asphaltic constituents are not precipitated and caked in the oil 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 temperature 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 oils may be fractionated continuously by liquid propane under high pressure and at a relatively high temperature, while other such crude oil stocks can be fractionated only for very short periods of time. In this latter case it has been found that the fractionating equipment became plugged with a deposit of asphaltic material. This asphaltic material has apparently been precipitated from the oil upon contact with the high temperature liquid propane. It should be mentioned that the oils in question were low asphalt-containing oils and did not differ significantly from each other in total asphalt content, as conventionally determined. Why some caused plugging trouble and others did not is not clearly understood.

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An object of my invention is to devise a process in which a low asphalt-containing reduced crude lubricating oil stock is fractionated for the separation and recovery of lubricating oil constituents. Another object of my invention is to devise a method for the separation and recovery of lubricating oil fractions from such low-asphalt content crude lubricating oil stocks by fractionation with liquid propane without the formation of hard asphaltic deposits in the oil fractionation apparatus. Still another object of my invention is to devise a continuous process for the removal and production of lubricating oil fractions by fractionation with propane from low-asphalt containing reduced crude oil stocks suitable for the manufacture of lubricating oils, wherein the asphaltic constituents are maintained in such a form that they do not adhere as a hard mass to the fractionation equipment. Still other objects and advantages of my invention will be obvious to those 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 fractionation of certain grades of lubricating oils from residual stocks, a hitherto unrecognized problem was encountered. Upon fractionating 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 to 1 at a pressure of about 640 pounds per square inch gage, 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 lubricating 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 a hard asphaltic material in the stripping section thereby making continuous operation impossible. In this second case, a third phase, that is, a semi-fluid asphaltic phase was apparently 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 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 known.

In a study of three well known Mid-Continent crude oils which have long been 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 low asphalt content reduced crude oils can be continuously fractionated with propane while others cannot. It is therefore realized that propane fractionation cannot be universally applied to all so-called low-asphalt content reduced crude lubricating oil stocks, as conventionally practiced.

I have discovered a method for operation of fractionating columns wherein low-asphalt content reduced crude lubricating oil stocks may be continuously fractionated with propane for the separation and recovery of lubricating oil fractions.

The figure shows diagrammatically a fractionating column, partly in elevation and partly in section, suitable for the practice of my invention.

Referring now to the drawing, the apparatus consists of a more or less conventional propane fractionating column **12** having several inlet and outlet connections. A pipe **11** at about a midpoint in the column is for introduction of the feed stock into the column. A pipe **16** near the bottom of the column serves for the introduction of liquid propane. Bottoms material may be withdrawn through a line **17** while overhead material may be withdrawn through a line **18**. A heating coil **20** is provided in the top of the column for heating the contents for the maintenance of a temperature gradient through the column. The pipe **19** serves to conduct a heating fluid, such as, for example, steam from a source not shown to the coil **20**, while pipe **21** serves to conduct steam and/or condensate away from the coil. Liquid phase conditions should be maintained.

In the operation of propane fractionation columns, it is common practice to maintain the interface between the lower oil-rich phase and the upper propane-rich phase at a point well below the charge oil inlet point. In fact the crude oil charge line is usually positioned in the upper portion of the tower so that reduced crude oil entering the tower may have sufficient time for intimate and efficient contacting with the propane before it reaches the bottom of the tower.

It is while operating under these conditions, i. e., addition of charge stock to the propane-rich phase, that I have found asphalt deposits within the tower. In most commercial towers are positioned packing or contact promoting apparatus of some type. This contacting apparatus may be in the form of slats, baffles or vanes, or filling material of some type which is adapted to promote contacting between the propane and the oil being treated. It is obvious that the more of this contacting equipment positioned in the treating tower, the greater is the surface upon which the asphalt from these certain crude oils may deposit. A tower may be operated without any slats or contact promoting equipment, but in such cases contacting between the crude oil and the propane is less efficient. To promote efficiency of operation, contacting apparatus is nearly always used in treating towers. I have now discovered that asphalt-containing reduced crude oils can be

propane fractionated to yield overhead products of lubricating oils and bottoms products containing the asphalt, lower molecular weight naphthenic, and aromatic material, in a sufficiently fluid condition that the asphaltic constituents do not adhere to the internal packing material in the contacting tower and that they can be easily withdrawn from the tower. This operation requires that the interface between the propane-rich phase and the oil-rich phase be carried at a point above the charge stock inlet point and at about the center of the column. When the charge oil is introduced into a phase in which it is soluble the oil becomes easily dispersed through the cross-section of the vessel near the point of entry of the charge stock. Liquid propane entering the vessel through a line **16** on passing upwardly through this oil-rich phase then has ample opportunity to strip propane soluble materials from the propane insoluble materials. The degree of this stripping will, of course, be dependent upon structural and operating conditions, for example, a longer oil stripping section will, of course, promote more efficient stripping. By the time the rising propane reaches the interface **15**, it is saturated or substantially saturated with propane soluble material and the propane-rich solution above the interface **15** is propane saturated with oil at the existing temperature and pressure.

The maintenance of a lower temperature in this section **13** of the tower below interface **15** will promote stripping of a greater fraction of the charge oil while maintenance of a higher temperature in this section will promote dissolving of less material by the liquid propane. In like manner, the pressure maintained within the column quite markedly affects this stripping operation. When the liquid propane, with its acquired oil charge, reaches the upper surface **15** of this oil phase in lower section **13** it accumulates there as a separate and distinct phase floating in the upper section **14** upon the surface **15** of the oil-rich phase. Since propane is continuously added to the tower through line **16**, the propane is continuously rising as a discontinuous phase through the oil-rich phase and then the propane-rich phase rises through the upper section of the tower as a continuous propane-rich phase. If heat is added to this propane-rich phase from coil **20**, the heavier oily material, along with aromatic material, will be precipitated at the higher temperature in the vicinity of this coil. The precipitated oil, as droplets, is, of course, heavier specifically than the propane-rich phase and it settles or sinks through the slowly rising propane-rich phase. During the descent through this propane-rich phase these oil droplets are washed with propane for removal of whatever materials are soluble in propane under the existing conditions.

At the bottom of the propane-rich phase, this settled material then enters the oil-rich phase and due to greater solubility in this latter phase the aromatic and heavier oily material becomes dissolved therein and the asphaltic material remains at least in a fluid condition. However, this asphaltic material may remain entirely dispersed in this rich oil phase or it may remain substantially as particles of precipitate. In any event, the direction of flow of oil in the lower section **13** of the vessel is in a downward direction and, of course, counter-current to the upwardly flowing discontinuous propane phase. By the time this oil-rich material reaches the bottom of the tower the upward rising propane has extracted the lighter lubricating oil constituents or such a frac-

tion of a lubricating oil constituent as desired so that asphaltic material, naphthenic and aromatic materials, and such heavier lubricating oil constituents as desired may be removed through a line 17 for such subsequent treatment as desired.

The material from the top of the tower which survives the precipitating action of the coil 20 through its heating of the contents of the tower may be withdrawn through the overhead line 18 for such subsequent treatment or disposal as desired. Subsequent treatment in this case will at least involve removal of propane from the desired lubricating oil fraction and recycling of the propane into this treating tower. In like manner, one treating step of the bottoms material from line 17 will involve propane recovery.

I have found that by adding the reduced crude charge into this treating vessel at a point below the interface between the two phases, that is, into the oil rich phase the asphaltic material remains in such a condition that it does not adhere to the contacting slats 22 nor to the walls of the vessel in any substantial manner and that this material may be easily removed through the line 17. This operation may be practiced continuously for long periods of time and in fact, indefinitely without undue precipitation of asphalt and plugging up of this apparatus. The exact juxtaposition of the point of feed entry and the interface will depend on several factors such as flow rates and column design. In general it has been found that the reduced crude feed stock should enter the oil-rich phase as far below the interface as is compatible with efficient operation of the stripping section. In most commercial installations the feed entry is located from 2 to 6 feet below the interface.

It is not known definitely why when feed stock is introduced into the tower in the oil-rich phase the asphalt does not precipitate, hence I do not wish to be limited by any theories or explanations as to why my process may be practiced for indefinitely long periods of time without plugging of the fractionation column by deposited asphalt.

I have found that it is advantageous to maintain the temperature of the oil-rich phase constant or substantially constant throughout its portion of the treating tower while a temperature gradient is maintained from about the feed point or specifically from the interface between the two phases to the top of the tower. The actual temperature at the interface 15 between the two phases will be substantially the same as the temperature within the body of the oil-rich phase while the temperature in the vicinity of the heating coil will be the highest of any point in the tower. The precipitating asphaltic materials and oils upon descending from the coil 20 will tend to heat the propane-rich phase. Since these descending particles will become progressively cooler during their descent, then the propane-rich phase will accordingly become progressively warmer as it flows toward the heating coil 20. In this manner, a relatively constant or uniform temperature gradient is maintained in this upper section of the tower. In many operations the temperature difference between the coil 20 and interface 15 may be in the vicinity of 15° to 20° F. or more. In one operation for the production of an SAE 30 to 50 grade of oil the oil-rich phase was maintained at a temperature of about 175° F. and the top of the tower was maintained at about 195° F. When the propane-to-oil volume ratio was about 7 to 1, an SAE 40 grade of oil was recovered through line 18 from the overhead product.

In the operation according to my invention the propane to oil volume ratio is preferably maintained between the limits of 6:1 to 10:1.

Example

As a specific embodiment of the present invention, a selected crude oil stock is topped at atmospheric pressure, then subjected to a vacuum distillation to remove the SAE 10 and 20 viscosity grades of oil. This reduced crude oil is pumped to the propane fractionator 12 through line 11. The propane column is so operated that the continuous phase at the point of feed entry is the oil-rich phase and the oil feed entry is near the mid-point of the column. Liquid propane is introduced through a line 16 at a point near the bottom of the column. The points of oil entry and propane entry are so positioned that the oil-rich phase may be stripped of its light oil content by the propane rising up through the stripping section of the column. The temperature of this oil-rich phase and of the oil feed is maintained at about 175° to 180° F. The top of the tower is maintained at a temperature of about 195° to 200° F., thereby giving a temperature gradient of about 20° F. between interface 15 and the top of the tower. Liquid-phase conditions are maintained at all times with a pressure of about 640 pounds per square inch gauge. Higher pressures may be employed, but corresponding adjustments in temperature must then be made in order to hold the yield and viscosity of the overhead products in the desired range. The yield and viscosity of the overhead product are increased with increasing pressures at a constant temperature gradient while at constant pressure an increase in the top tower temperature or an increase in temperature gradient reduces both yield and viscosity. The overhead product containing the major portion of the propane is removed by way of line 18 to a depropanizing column, not shown. The bottom product containing a minor portion of propane is discharged through line 17 also to a depropanizing column, not shown. The rate of discharge of the oil-rich phase is, of course, so controlled that the interface between the two phases is maintained at a constant level, at least above the oil feed inlet, and preferably from 2 to 6 feet above the feed inlet in most commercial columns.

Materials of construction for use in this apparatus need not be special and may be selected from among those commercially available. A major consideration is, of course, the equipment must be designed and constructed to withstand high pressures, such as the 640 pounds per square inch mentioned above. Corrosion problems may not be pertinent when such inert material as propane is used in treating crude oil bottoms.

Such auxiliary equipment as pressure gauges, valves, pumps, levels and flow controllers, temperature and pressure measuring and controlling devices, etc., have not been shown for purposes of simplicity since the use of this equipment is well understood by those skilled in the art. It will be obvious that many variations and alterations in operating conditions may be made, such as temperature or pressure, or temperature gradient of the propane-rich phase or the exact point of interface between the propane-rich phase and the oil-rich phase may all be varied within a degree and yet remain within 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 and the simultaneous propane fractionation of said lubricating oil constituents wherein solid to semisolid asphaltic material precipitates upon initial contact with the propane under liquid propane fractionation conditions 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 solid to semi-solid asphaltic material and plugging said apparatus with the precipitated asphalt comprising maintaining a body of an oil-rich phase in the lower portion of an elongated and vertically disposed contacting zone, introducing liquid propane into said body of oil-rich phase at a point near the bottom of said zone, maintaining a body of oil dissolved in liquid propane in said zone above and in contact with the first mentioned body of oil-rich phase with a liquid-liquid interface therebetween at a level near the midpoint, vertically, of said zone, introducing said reduced crude lubricating oil stock into said first mentioned body of oil-rich phase at a point below said interface but above the point of introduction of said liquid propane, maintaining substantially the same constant temperature at the oil feed point and throughout said body of oil-rich phase, maintaining said body of oil dissolved in liquid propane under conditions causing propane fractionation of the lubricating oil constituents by maintaining a temperature gradient from the bottom to the top of said body of oil dissolved in liquid propane by the addition of heat to said top of said body of oil dissolved in liquid propane with the bottom being substantially at the temperature of said oil-rich phase and the top being at a higher temperature and at a pressure sufficiently high to maintain the propane in the liquid phase under the aforesaid temperature conditions, removing an oil-in-propane solution from the upper portion of said body of oil dissolved in liquid propane and removing oil-rich phase comprising the asphalt, a residual lubricating oil fraction and some dissolved propane from the lower portion of said first mentioned body of oil-rich phase.

2. In the propane fractionation of lubricating oil constituents from low asphalt-content reduced crude lubricating oil stocks and the simultaneous propane fractionation of said lubricating oil constituents wherein solid to semisolid asphaltic material precipitates upon initial contact with the propane under liquid propane fractionation conditions 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 solid to semi-solid asphaltic material and plugging said apparatus with the precipitated asphalt comprising maintaining a body of an oil-rich phase in the lower portion of an elongated and vertically disposed contacting zone, introducing liquid propane into said body of oil-rich phase at a point near the bottom of said zone, maintaining a body of oil dissolved in liquid propane in said zone above and in contact with the first mentioned body of oil-rich phase with a liquid-liquid interface therebetween at a level near the mid-point, vertically, of said zone, introducing said reduced crude lubricating oil stock into said first mentioned body of oil-rich phase at a point below said interface but above the point of introduction of said liquid propane, maintaining substantially the same constant temperature at the oil feed point and throughout said body of oil-rich phase between 175° F. and 180° F., maintaining said body of oil dissolved in liquid propane under conditions causing propane fractionation of the lubricating oil constituents by maintaining a temperature gradient from the bottom to the top of said body of oil dissolved in liquid propane by the addition of heat to said top of said body of oil dissolved in liquid propane with the bottom being substantially at the temperature of said oil-rich phase of between 175° F. and 180° F. and the top being at a higher temperature of between 195° F. and 200° F. and at a pressure sufficiently high to maintain the propane in the liquid phase under the aforesaid temperature conditions, removing an oil-in-propane solution from the upper portion of said body of oil dissolved in liquid propane and removing oil-rich phase comprising the asphalt, a residual lubricating oil fraction and some dissolved propane from the lower portion of said first mentioned body of oil-rich phase.

3. In the propane fractionation of lubricating oil constituents from low asphalt-content reduced crude lubricating oil stocks and the simultaneous propane fractionation of said lubricating oil constituents wherein solid to semisolid asphaltic material precipitates upon initial contact with the propane under liquid propane fractionation conditions 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 solid to semi-solid asphaltic material and plugging said apparatus with the precipitated asphalt comprising maintaining a body of an oil-rich phase in the lower portion of an elongated and vertically disposed contacting zone, introducing liquid propane into said body of oil-rich phase at a point near the bottom of said zone, maintaining a body of oil dissolved in liquid propane in said zone above and in contact with the first mentioned body of oil-rich phase with a liquid-liquid interface therebetween at a level near the midpoint, vertically, of said zone, introducing said reduced crude lubricating oil stock into said first mentioned body of oil-rich phase at a point below said interface but above the point of introduction of said liquid propane, maintaining substantially the same constant temperature at the oil feed point and throughout said body of oil-rich phase, maintaining said body of oil dissolved in liquid propane under conditions causing propane fractionation of the lubricating oil constituents by maintaining a temperature gradient of at least 15° F. from the bottom to the top of said body of oil dissolved in liquid propane by the addition of heat to said top of said body of oil dissolved in liquid propane with the bottom being substantially at the temperature of said oil-rich phase and the top being at a higher temperature and at a pressure sufficiently high to maintain the propane in the liquid phase under the aforesaid temperature conditions, removing an oil-in-propane solution from the upper portion of said body of oil dissolved in liquid propane and removing oil-rich phase comprising the asphalt, a residual lubricating oil fraction and some dissolved propane from the lower portion of said first mentioned body of oil-rich phase.

4. In the propane fractionation of lubricating oil constituents from low asphalt-content reduced crude lubricating oil stocks and the simultaneous propane fractionation of said lubricating oil con-

stituents wherein solid to semisolid asphaltic material precipitates upon initial contact with the propane under liquid propane fractionation conditions 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 solid to semi-solid asphaltic material and plugging said apparatus with the precipitated asphalt comprising maintaining a body of an oil-rich phase in the lower portion of an elongated and vertically disposed contacting zone, introducing liquid propane into said body of oil-rich phase at a point near the bottom of said zone, maintaining a body of oil dissolved in liquid propane in said zone above and in contact with the first mentioned body of oil-rich phase with a liquid-liquid interface therebetween at a level near the midpoint, vertically, of said zone, introducing said reduced crude lubricating oil stock into said first mentioned body of oil-rich phase at a point below said interface but above the point of introduction of said liquid propane, maintaining the ratio of volume of said liquid propane being introduced to said reduced crude lubricating oil being introduced between the limits of 6:1 to 10:1, maintaining substantially the same constant temperature at the oil feed point and throughout said body of oil-rich phase, maintaining said body of oil dissolved in liquid propane under conditions causing propane fractionation of the lubricating oil constituents by maintaining a temperature gradient of at least 15° F. from the bottom to the top of said body of oil dissolved in liquid propane by the addition of heat to said top of said body of oil dissolved in liquid propane with the bottom being substantially at the temperature of said oil-rich phase and the top being at a higher temperature and at a pressure sufficiently high to maintain the propane in the liquid phase under the aforesaid temperature conditions, removing an oil-in-propane solution from the upper portion of said body of oil dissolved in liquid propane and removing oil-rich phase comprising the asphalt, a residual lubricating oil fraction and some dissolved propane from the lower portion of said first mentioned body of oil-rich phase.

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