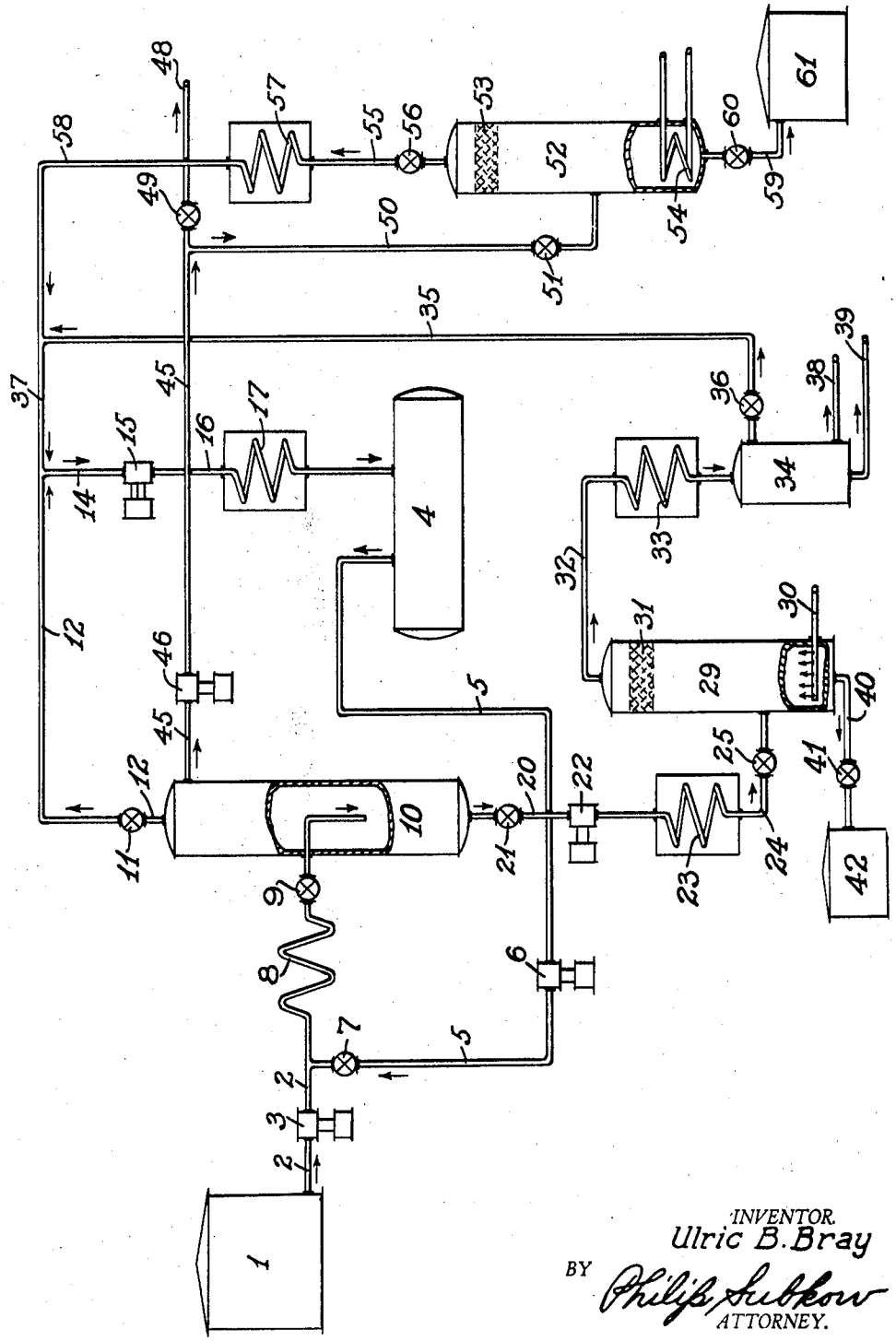
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METHOD FOR TREATING OILS

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METHOD FOR TREATING OILS

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The present invention relates to a method for separating asphalt from oil. More specifically, it relates to a method for separating asphalt from asphaltic oils substantially free from wax by means of solvents and low temperatures. This invention is a continuation, in part, of my co-pending application Serial No. 610,130, filed May 9th, 1932.

In the aforementioned co-pending application, I disclosed a process for the co-precipitation of asphalt and wax by means of a liquefied normally gaseous hydrocarbon solvent, in particular, liquid propane, wherein the asphalt and wax containing oil was commingled with said solvent under pressure sufficient to maintain the solvent in a liquid state. This caused the asphalt to be thrown out of solution. Then a portion of the liquid propane was allowed to vaporize under reduced pressure to chill the mixture of oil, solvent, wax and asphalt to a sufficiently low temperature to cause precipitation of the wax. The ebullition or boiling which accompanies the vaporization of the liquid propane caused a violent agitation of the mass and the precipitated asphalt acted as nuclear or gathering bodies for the agglomeration of the wax as it was precipitated at the lower temperatures attained. The agglomerated particles of asphalt and wax were then separated from the oil solvent solution and the solvent was removed from the oil. This oil was a lubricating oil substantially free from asphalt and wax.

In the present discussion of my invention, by the term "propane", I intend to include such hydrocarbons as are normally vaporous at ordinary temperature and pressure. Such hydrocarbons include methane, ethane, propane, butane, iso-butane and mixtures thereof. These volatile solvents may be obtained by rectification of casing head gasoline by the so-called "stabilizing" method, now conventional in the natural gasoline industry. They are the overhead obtained. They are liquefied by compression and cooling in the conventional manner and are drawn off into pressure chambers where they are maintained in a liquid state until used. A typical analysis of such a fraction is 6.72% ethane, 72.20% propane, 19.91% iso-butane and 1.17% normal butane. Such a fraction may be maintained in a liquid state at a pressure of 125 lbs. per square inch at a temperature of about 75° F. The predominating hydrocarbon member in this mixture is propane and hereafter when I use the term "propane" or "liquid propane", I am referring to such a fraction.

In the foregoing process, I have observed that the lubricating oil produced is also substantially free from the heaviest viscous oil fractions and has a lower Conradson carbon value. It is my belief that the presence of these heavy viscous oil fractions in lubricating oils are largely responsible for the high Conradson carbon values of the oil. In the foregoing process of my co-pending application, the heaviest viscous oil fractions were removed by chilling the oil containing both asphalt and wax. In other words, I have discovered that chilling an oil to precipitate wax will also effect precipitation of the heavy viscous oil fractions which, when separated from the oil, will produce a lubricating oil of lower Conradson carbon value.

I have now discovered that substantially all asphaltic oils contain such heavy viscous oil fractions irrespective of whether they contain wax. It will be observed that all asphaltic oils contain more or less wax; some contain large quantities of wax while others are substantially free but nevertheless contain a small quantity. Thus, such California crude oils as McKittrick, Poso Creek, Coalinga, Summerland and Sunset are typical asphaltic crudes containing very little wax, while other crudes as Montebello, Kettleman Hills, Santa Fe Springs, Elwood, Torrance and Santa Barbara are classed as mixed base crudes, that is, containing large quantities of wax as well as asphalt. However, as stated, substantially all of these oils contain high molecular weight bodies which are responsible for the high Conradson carbon value of lubricating oils containing the same. In treating oils substantially free of wax, it is customary to maintain the temperatures for separation of asphalt at approximately atmospheric temperature, i. e. about 80° F. At such temperature, the heavy viscous oil fractions will not separate from the oil. My present invention is directed towards removal of such fractions from asphaltic oils substantially free from wax.

I have, therefore, discovered that on asphaltic oils substantially free from wax, temperature influences the recovery and character of oil and asphalt separated from petroleum oils by means of solvents. At room temperatures, i. e. about 80° F. and with the use of equal volumetric ratios of liquid propane to residuum and on identical oil stocks, the percent of oil recovered will be greater and, therefore, the amount of asphalt will be less than when the separation is carried out at lower temperatures. In other words, the reduction of temperature on the mixture of propane and residuum lowers the solubility of asphalt in

the propane oil solution so that it is possible to recover a greater amount of asphalt at the lower temperature than at a more elevated temperature. Conversely, the yield of oil recovered becomes correspondingly lower with reduction of temperatures. However, the character of the oil produced is better, that is, it is clearer and has a lower Conradson carbon value. This may be attributed to the fact that the heavy viscous oil fractions normally present in the asphaltic oil which cause the increase of the Conradson carbon value of the oil are soluble in the solution of oil and propane at more elevated temperatures but are insoluble at lower temperatures and, therefore, are precipitated together with the asphalt which thus lowers the yield of oil recovered.

It will be observed that by the term "asphalt", I intend to include such fractions which will separate or precipitate from asphaltic oils substantially free from wax when such oils are commingled with liquid propane or other solvents. Thus, the mixture of heavy viscous oil fractions and the asphalt or bitumen content of the oil when separated therefrom by means of solvents at low temperatures will be considered an asphalt.

I have also discovered that I may obtain a greater yield of asphalt from asphaltic oils by using a lower volumetric ratio of propane to residuum at the lower temperature than may be obtained by using higher volumetric ratios at more elevated temperatures. Thus, for example, on a Poso Creek residuum topped to an on-stream viscosity of 67 seconds Saybolt Universal at 100° F., I have recovered smaller quantities of oil and correspondingly greater amounts of asphalts by using a volumetric ratio of 2.5 to 1 at a temperature of −20° F. than by employing a volumetric ratio of 5 to 1 at 80° F. In the former case, the amount of oil recovered was about 74.5%, whereas when a volumetric ratio of 5 to 1 was employed at 80° F. the percent of oil recovered amounted to 79%. This amount may be lessened, that is, more asphalt may be precipitated from solution by increasing the volumetric ratio of propane to residuum. For example, by using volumetric ratios of 15 to 1 and 20 to 1, the percent of oil recovered will approximate 76.5% indicating that more asphalt is thrown out of solution. The oil recovered by using lower volumetric ratios and lower temperatures had a better color and a lower Conradson carbon value than any of the oils extracted at 80° F. irrespective of the volumetric ratio. This indicates that the heavy viscous oil fractions in the oil will not precipitate from solution except that when the temperature is sufficiently lowered to throw these out of solution. Such low temperatures may be obtained by mixing the residuum with a higher initial volumetric ratio and then evaporating a portion of the propane by release of pressure until the desired final volumetric ratio and low temperature is obtained. In the above example, I commingled 4.2 parts of liquid propane to one part of Poso Creek residuum under pressure sufficient to maintain the solvent liquid and then reduced the pressure to evaporate propane until approximately 2.5 parts of propane to one of residuum remained and the temperature was lowered to −20° F.

With the above discussion in mind, it will be perceived that it is an object of my invention to separate asphalt from an asphalt containing oil by means of a solvent at low temperatures, i. e. approximately 0 to −40° F.

It is a further object to separate heavy viscous oil fractions from asphaltic oils substantially free from wax as well as the asphalt content of the oil.

Another object of my invention resides in commingling asphalt containing oil with a liquefied normally gaseous hydrocarbon solvent under pressure sufficient to maintain the solvent liquid and then reducing the temperature of the mixture by releasing the pressure to evaporate a portion of the solvent and thus precipitate asphalt and heavy viscous oil fractions from the mixture, removing the precipitated asphalt and heavy viscous oil fractions under pressure from the oil solvent solution and separating the solvent from the oil.

Other objects and advantages of my invention will be apparent from the following description of my invention taken from the drawing which represents a schematic arrangement of apparatus for carrying out my invention:

Referring to the drawing, an asphalt containing oil substantially free from wax is taken from tank 1 and is passed into line 2 via pump 3 where it meets liquid propane taken from storage tank 4 via line 5 and pump 6 which forces the propane through valve 7 into line 2. The amount of propane introduced into line 2 will depend upon the character of the oil and the temperatures desired in decanter 10. For example, operating on a Poso Creek residuum topped to an on-stream viscosity of 67 seconds Saybolt Universal at 100° F., it is desirable to mix 4.2 parts of liquid propane to 1 part of the residuum so that in the subsequent vaporization of propane in decanter 10 approximately 2.5 parts of propane will remain and the temperature will be lowered to approximately −20° F. The mixture of liquid propane and residuum is passed through turbulence coil or mixing coil 8 and then through pressure reduction valve 9 into decanter or asphalt precipitator 10. In decanter 10 sufficient propane vaporizes to reduce the temperature of the remaining material to a sufficiently low temperature which causes the asphalt and heavy viscous oil fractions to precipitate from solution. The desired low temperature is obtained by controlling the pressure in decanter 10 by the proper operation of valve 11 on line 12 and compressor 15 which is connected to the decanter by lines 14 and 12. The pressure to be maintained in the decanter 10 will generally be about 0 to 25 lbs. gauge which corresponds to a temperature of approximately between −40° F. to 0° F. As the propane solution passes through valve 9, its pressure is reduced so that a portion of the propane evaporates in the decanter 10 and the vapors pass out of the top through line 12 controlled by valve 11 and then into line 14 to compressor 15 where the vapors are compressed, passed through line 16, liquefied in cooler 17 and passed to propane storage tank 4.

The asphalt precipitated in decanter 10 settles to the bottom of the decanter and is removed by line 20 controlled by valve 21 and pump 22 as a mixture of asphalt, heavy viscous oil fractions and propane. Pump 22 forces this mixture under pressure through heating coil 23 where it is heated to a sufficiently high temperature to melt the asphalt and vaporize the residual propane. The heated mixture is then flashed through pressure reduction valve 25 on line 24 into evaporator 29 which operates at a lower pressure. Superheated steam is introduced into evaporator 29 through perforated pipe 30 to supply additional heat and to reduce the asphalt to the proper specification, generally only as regards flash and fire points. The overhead from evaporator 29 passing through

mist extractor 31 is sent through line 32 to cooler 33 and then to separator 34. The uncondensed propane from separator 34 is sent through line 35 controlled by valve 36 to line 37 and line 14 to suction of compressor 15 where its pressure is raised to that in the high pressure system and is then sent to cooler 17 where it liquefies and runs down into propane storage tank 4. Any condensed light oil in separator 34 is withdrawn through line 38 and condensed water through line 39. The asphalt is taken from the bottom of evaporator 29 and sent through line 40 controlled by valve 41 to storage tank 42.

The overflow from decanter 10 consisting of propane and oil free from asphalt and heavy viscous oil fractions and also wax is sent through line 45 by pump 46 and then through line 48 controlled by valve 49 to acid treatment and neutralization with alkali, valve 51 on line 50 being closed. If desired, valve 49 on line 48 may be closed and valve 51 opened so that the overflow from decanter 10 may pass into line 50 and then into evaporator or heater 52 provided with mist extractor 53 where the propane present is vaporized by the aid of steam circulated through the closed steam coil 54. The vaporized propane passes out of the heater through line 55 controlled by valve 56 and then passes through cooler 57 into lines 58, 37 and 14 to compressor 15, cooler 17 into storage tank 4. The propane-free oil passes from heater 52 by means of line 59 controlled by valve 60 into tank 61. This oil will comprise a lubricating oil of low Conradson carbon content and free from heavy viscous oil fractions, wax and asphalt. The oil may be acid and alkali treated prior to its use or may be treated by other methods now conventional.

It is to be understood that the above is merely illustrative of preferred embodiments of my invention of which many variations may be made by those skilled in the art without departing from the spirit thereof.

I claim:

1. A method for separating asphalt from oil which comprises commingling an asphalt containing oil substantially free from wax with a liquefied normally gaseous hydrocarbon solvent to precipitate asphalt, reducing the temperature during said precipitation, congealing and precipitating heavy viscous oil fractions which are responsible for high Conradson carbon values of oils together with said asphalt, separating said precipitated heavy viscous oil fractions and asphalt from the oil solvent solution and separating residual solvent from the oil solvent solution to produce a lubricating oil of low Conradson carbon value.

2. A method for separating asphalt from oil which comprises commingling an asphalt containing oil substantially free from wax with a liquefied normally gaseous hydrocarbon solvent under pressure sufficient to maintain said solvent in the liquid state, precipitating asphalt, reducing the temperature of said mixture by releasing the pressure to vaporize a portion of the solvent to thus chill the oil, congealing heavy viscous oil fractions which are responsible for high Conradson carbon values of oils in said oil, separating said precipitated asphalt and congealed heavy viscous oil fractions from the oil solvent solution and separating the residual solvent from the oil whereby a lubricating oil is produced having a low Conradson carbon value.

3. A method for separating asphalt from oil which comprises commingling an asphalt containing oil substantially free from wax with a liquefied normally gaseous hydrocarbon solvent and precipitating asphalt, chilling said mixture to a temperature between 0 and —40° F. and congealing heavy viscous oil fractions which are responsible for high Conradson carbon values of oils in said oil, separating said precipitated asphalt and congealed heavy viscous oil fractions from the oil solvent solution and separating residual solvent from the oil.

4. A method for producing an asphalt containing heavy viscous oil fractions normally present in oils which comprises mixing an asphalt containing oil substantially free from wax with a liquefied normally gaseous hydrocarbon solvent and precipitating asphalt, chilling said mixture and congealing and precipitating heavy viscous oil fractions which are responsible for high Conradson carbon values of oils, separating said congealed heavy viscous oil fractions and said precipitated asphalt from the oil solvent solution and separating the residual solvent from said separated congealed viscous oil fractions and asphalt.

5. A method as in claim 1 in which the liquefied normally gaseous hydrocarbon comprises propane.

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