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PROCESS FOR FRACTIONATING ASPHALTIC BITUMINOUS MATERIALS UTILIZING AROMATIC HYDROCARBONS OF LESS THAN TEN CARBON ATOMS

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This invention relates to a method for treating bituminous material with the liquid aromatic hydrocarbons having less than 10 carbon atoms to separate asphalt in optimum yields. More particularly, this invention relates to a method of separating asphaltic bituminous materials into its components, i.e. fractions having different softening points. This invention relates also to a new process for manufacturing quality lubricating oils.

The liquid aromatic hydrocarbons are known to be excellent solvents for bituminous materials over a wide temperature range, but some of the earlier art discloses that asphaltenes may be separated at ambient temperature from an aromatic hydrocarbon solution of asphaltic bitumen at a dilution of 100 to 1. Such high dilution requirements preclude the practical use of the aromatic hydrocarbons as fractionation solvents for bitumens. The hydrocarbon solvents which have been used to fractionate asphaltic bituminous materials have been the lower paraffins and olefins, because benzene and the related aromatic hydrocarbons are completely miscible with asphalt in the proportions considered economically feasible.

Therefore, it is a principal object of this invention to provide a method for modifying the miscibility of asphaltic bituminous materials with benzene or the other low molecular weight, liquid aromatic hydrocarbons to permit said aromatic hydrocarbons to be used to separate asphalt or its components from bituminous materials.

A further object of this invention consists in disclosing a novel method for separating asphaltenes as a fluid phase from asphaltic bituminous material using the aromatic hydrocarbons having less than 10 carbon atoms per molecule.

A still further object of this invention is to provide a method for separating bitumen into its component fractions of asphaltenes, resins and oils using the liquid aromatic hydrocarbons having less than 10 carbon atoms per molecule.

Another object of this invention is to disclose a novel method of making quality lubricating oils.

Still other objects of the invention will be apparent in connection with the description of the invention and the claims.

In accordance with the above objects, the invention comprises treating each volume of a bituminous material with at least two volumes of an aromatic hydrocarbon containing from 6 to 9 carbon atoms, inclusive, at an elevated temperature within the paracritical range of the aromatic hydrocarbon, and adjusting the relationship between the pressure and the temperature to obtain a density value for the liquid aromatic hydrocarbon greater than 0.30 g./ml. and less than about 0.50 g./ml. to separate said asphaltic bituminous material into at least two fractions.

Another aspect of this invention relates to the discovery that the bitumens are not miscible with the low molecular weight aromatic hydrocarbons over the entire temperature range from the melting point of said

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low molecular weight aromatic hydrocarbons to their critical temperature. It was further discovered that if the temperature and pressure conditions are controlled to give the solvent a density within a critical range of values, bituminous materials are separated into fractions consisting essentially of pure asphaltenes, resins and oils. A still further aspect of this invention relates to the discovery that by controlling certain critical variables, the low molecular weight aromatic hydrocarbons separate asphalts of varying softening points from steam and/or vacuum reduced crudes and related bituminous materials.

For example, it was discovered that under certain critical temperature and pressure conditions, a solution composed of one volume of bituminous material to at least two volumes of a liquid aromatic hydrocarbon having less than 10 carbon atoms separated into phases to yield a heavy and a light bituminous fraction. Although the phase separation occurred at an aromatic hydrocarbon to bituminous material ratio of 2 to 1, it was observed that the selectivity of the fractionation was poor, and at about four volumes of solvent to each volume of bitumen the selectivity was better. Even though solvent to bitumen ratios as high as 20 to 1 are usable, 4 to 10 volumes of solvent to each volume of bitumen are preferred over the lower or higher solvent to bitumen ratios.

As indicated previously herein, the fractionation of bituminous material only occurs when the temperature exceeds a certain critical value. Therefore, to effect a separation in accordance with the spirit of this invention, the temperature must be at least equal to the paracritical temperature of the solvent. The term "paracritical temperature" is generally considered to be from about 50° F. below to about 50° F. above the critical temperature of the solvent.

The bituminous materials suitable for use in this invention include pyrogenous and native bitumens. The pyrogenous bitumens include reduced crudes of either the steam or vacuum reduced type, shale oils or tars, cracked tars, etc. The native bitumens include gilsonite, grahamite, wurtzilite, native asphalt (Trinidad) etc. The term "asphaltic bituminous material" is used in this specification to indicate bitumens other than those derived from coal.

From Table I, shown hereinafter, it is readily seen that the paracritical temperature of even the lightest aromatic hydrocarbon is very high and the critical temperatures of the aromatic hydrocarbons having more than 9 carbon atoms are well within the range where considerable cracking of bituminous materials is experienced. Therefore, the usefulness of any particular aromatic hydrocarbon in this invention is determined primarily by temperature consideration, and although aromatic hydrocarbons having less than 10 carbon atoms are usable, the preferred ones are those having a critical temperature less than about 650° F.

The preferred aromatic solvents are benzene and toluene, the latter being the first member of the alkyl benzene family.

By controlling the pressure, it is possible to obtain a density value of from 0.30 g./ml. to above 0.50 g./ml. for the solvent when the temperature is within the paracritical range of said solvent. The density of the aromatic hydrocarbons is very sensitive to pressure change when the solvent has a temperature at least as great as the paracritical temperature. For example, the density of benzene at 550° F. and 975 p.s.i.g. is about 0.50 g./ml., but at the same temperature and 700 p.s.i.g., the density of benzene is only about 0.30 g./ml.

Thus, it can be noted that a variation in pressure of 200 p.s.i.g. at the cited temperature is sufficient to change the density of benzene from below to above the opera-

tive density range for my process, and it is apparent that the pressure and temperature must be carefully correlated to obtain a density for the solvent within the operative range, i.e. greater than about 0.30 g./ml. and less than the density at which complete miscibility of the solvent and bituminous material occurs.

The critical constants for benzene, the alkyl benzenes and naphthalene are shown in Table I, to serve as a guide to the selection of the fractionation conditions for each hydrocarbon.

Table I

Hydrocarbon	Critical		
	Temperature, ° F.	Pressure, p.s.i.a.	Density, g./ml.
Benzene	551	714	0.30
Toluene	609	611	0.29
Ethylbenzene	655	590	0.29
o-Xylene	677	542	0.28
p-Xylene	652	514	0.27
m-Xylene	654	526	0.29
n-Propyl benzene	688	460	0.28
i-Propyl benzene	690	475	0.28
1,3,5-trimethyl benzene	693	488	0.28
Naphthalene	890	576	0.28

In accordance with the process, a suitable bitumen such as a reduced crude or gilsonite is dissolved in 10 volumes of a liquid aromatic hydrocarbon having less than 10 carbon atoms, for example, toluene. The aromatic hydrocarbon solution of the bitumen is made in situ in a pressure vessel or is placed in said vessel after its preparation. The temperature is then raised to within the paracritical range for the solvent, and the pressure is adjusted to obtain a density for the solvent of between about 0.30 g./ml. and 0.50 g./ml. Under these conditions, a heavy fraction or phase separates from the aromatic solution of the bitumen and may be drawn off from the pressure vessel in a fluid condition.

The simplest way to obtain the desired pressure-temperature relationship under static operating conditions is by adjusting the percent fill of the vessel. The total amount of bitumen and solvent charged to the vessel is adjusted to vary the amount of vapor space at room temperature in the vessel and thereby control the pressure developed when the contents of the vessel are heated to the paracritical temperature of the solvent.

The above statement is not to be interpreted as a teaching that only static conditions may be used, since the invention may be operated continuously.

It is thus possible to obtain a series of density values for the solvent corresponding to different pressures at the same temperature, and by varying the solvent density over a range of values from about 0.30 to about 0.50 g./ml., it is possible to vary the nature of the separated heavy fraction from essentially pure asphaltenes to a soft asphalt. For instance, when the solvent density is adjusted to a value above 0.40 g./ml. and less than that at which complete miscibility of the solvent and bitumen occurs, the heavy fraction consists of a hard asphaltene, with a softening point in excess of about 250 to 300° F. and a penetration at 77° F. of less than about 5, but when the solvent density is below about 0.40 g./ml., the heavy fraction will be an asphalt. Generally, complete miscibility of the solvent and bitumen occurs at solvent density values above about 0.50 g./ml. The preferred solvent density range for the separation of asphaltenes of 300° F. and higher softening point is about 0.43 to 0.47 g./ml.

When the asphaltenes are removed from the bitumen solution, the material remaining in solution will comprise resins and oils. This mixture of resins and oils will be referred to hereinafter as petrolenes.

If it is so desired, the petrolenes in the aromatic solvent solution may be given an additional treatment to separate the resins as a secondary heavy fraction and leave the oils in solution. For example, the aromatic

solution of petrolenes, remaining in the pressure vessel after the removal of the asphaltenes, may be separated into resins and oils by adjusting the pressure and temperature relationship in the vessel to give a solvent density greater than about 0.30 g./ml. and less than about 0.40 g./ml. The preferred range of density values for separating resins from the petroline solution is about 0.34 to 0.38 g./ml.

The oils remaining dissolved in the benzene after the separation of the resins may be separated from the solvent as a distinct fluid phase by adjusting the temperature-pressure relationship to obtain a solvent density less than about 0.30 g./ml. Under these conditions the solvent demixes from the oil. The solvent may be removed overhead from the vessel, or the oils withdrawn from the bottom of the vessel.

To further illustrate my invention, a propane-precipitated asphalt of 125° F. softening point was charged to a suitable pressure vessel containing benzene. The volume ratio of benzene to asphalt was 10 to 1. The temperature was raised to within the paracritical range for benzene. The pressure on the system was adjusted to give a solvent density of 0.45 g./ml. Under these conditions, a heavy fraction separated as a fluid phase and in excellent yield. This heavy fraction had a softening point in excess of 250° F.

The heavy fraction was removed from the pressure vessel and the temperature and pressure relationship adjusted on the solution of petrolenes to obtain a lower solvent density but one still greater than 0.30 g./ml. Under these conditions another heavy fraction separated. This secondary heavy fraction, a resin fraction, separated as a fluid phase to leave a high quality lubricating oil which was recovered from the benzene solution by distillation.

A reduced crude having a softening point of 110° F. was substituted for the propane-precipitated asphalt in the pressure vessel and the solvent to reduced crude ratio was 10 to 1. The temperature and pressure was adjusted at 550° F. and 975 p.s.i.g., respectively, to give a solvent density slightly in excess of 0.50 g./ml. No heavy phase separated, because this solvent density is in excess of the minimum density value at which complete miscibility of the bitumen and benzene occurs.

The pressure on the system was re-adjusted to about 900 p.s.i.g. at 550° F. to effect a corresponding lowering of the density of the benzene. Under these new conditions, a heavy fraction separated from solution in fair yield.

When the pressure vessel was charged again with 10 volumes of benzene to each volume of a vacuum reduced Oklahoma crude and equilibrium conditions established at 552° F. and 700 p.s.i.g., it was found that the bitumen was completely separated from the benzene.

Thus, although the temperature was within the paracritical range, the pressure was such as to give a benzene density of only 0.30 g./ml. and fractionation was impossible because of the immiscibility of the bitumen and benzene. When the pressure was increased sufficiently to give the solvent a density of 0.49 g./ml., a heavy fraction separated.

It is thus possible to fractionate an asphaltic bituminous material into fractions of varying softening points using the lower molecular weight aromatic hydrocarbon solvents, provided a certain relationship between the temperature and pressure is maintained to give a solvent density which causes the asphaltic bituminous material components to have at least some immiscibility with the solvent.

What is claimed is:

1. A process for separating a heavy fraction from asphaltic bituminous material as a fluid phase, which comprises treating each volume of an asphaltic bituminous material with at least 2 volumes of a liquid aromatic hydrocarbon solvent containing less than 10

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carbon atoms per molecule at elevated temperature and pressure, said temperature being within the paracritical range for said solvent, adjusting the pressure to obtain a solvent density greater than 0.30 g./ml. but less than 0.50 g./ml. and separating the resulting heavy fraction phase from the solution phase.

2. A process for separating a heavy fraction from asphaltic bituminous material as a fluid phase, which comprises treating each volume of an asphaltic bituminous material with at least two volumes of a liquid aromatic hydrocarbon solvent selected from the group consisting of benzene and toluene at elevated temperature and pressure, said temperature being within the paracritical range for said solvent, adjusting the pressure to obtain a solvent density greater than 0.30 g./ml. but less than 0.50 g./ml. and separating the resulting heavy fraction phase from the solution phase.

3. In a process for manufacturing lubricating oils, the improvement comprising treating each volume of an asphaltic bituminous material with at least 2 volumes of a liquid aromatic hydrocarbon solvent containing less than 10 carbon atoms per molecule at elevated temperature and pressure, the temperature being within the para-critical range of the solvent, adjusting the pressure to obtain a solvent density less than about 0.38 g./ml. but greater than 0.30 g./ml., and separating the resulting heavy fraction and lubricating oil phases to obtain the heavy fraction and the lubricating oil.

4. In a process for manufacturing lubricating oils, the improvement comprising treating each volume of an asphaltic bituminous material with at least two volumes of a liquid aromatic hydrocarbon solvent selected from the group consisting of benzene and toluene at elevated temperature and pressure, the temperature being within the paracritical range of the solvent, adjusting the pressure to obtain a solvent density less than about 0.38 g./ml. but greater than 0.30 g./ml., and separating the resulting heavy fraction and lubricating oil phases to obtain the heavy fraction and the lubricating oil.

5. A process for separating asphaltenes from asphaltic bituminous material comprising treating each volume of asphaltic bituminous material with at least 2 volumes of a liquid aromatic hydrocarbon solvent containing less than 10 carbon atoms per molecule at a temperature and pressure within the paracritical range of the solvent, adjusting the temperature-pressure relationship to obtain a solvent density of less than 0.50 g./ml. and greater than 0.40 g./ml. and separating the resulting heavy fraction as a fluid phase.

6. A process for separating asphaltenes from asphaltic bituminous material comprising treating each volume of asphaltic bituminous material with at least two volumes of a liquid aromatic hydrocarbon solvent selected from the group consisting of benzene and toluene at a temperature and pressure within the paracritical range of the solvent, adjusting the temperature-pressure relationship to obtain a solvent density of less than 0.50 g./ml. and greater than 0.40 g./ml. and separating the resulting heavy fraction as a fluid phase.

7. A process for separating asphaltenes from asphaltic bituminous material comprising treating each volume of an asphaltic bituminous material derived from petroleum with at least two volumes of a liquid aromatic hydrocarbon solvent containing less than ten carbon atoms per molecule at a temperature and pressure within the para-critical range of the solvent, adjusting the temperature-pressure relationship to obtain a solvent density of less than 0.50 g./ml. and greater than 0.40 g./ml. and separating the resulting heavy fraction as a fluid phase.

8. A process for separating a heavy fraction from asphaltic bituminous material as a fluid phase, which comprises treating each volume of asphaltic bituminous material with at least 4 volumes of a liquid aromatic hydrocarbon solvent containing less than 10 carbon atoms per molecule at elevated temperature and pressure, said

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temperature being within the paracritical range for said solvent, adjusting the pressure to obtain a solvent density greater than 0.30 g./ml. but less than 0.50 g./ml. and separating the resulting heavy fraction phase from the solution phase.

9. A process for separating a heavy fraction from asphaltic bituminous material as a fluid phase, which comprises treating each volume of asphaltic bituminous material with at least four volumes of a liquid aromatic hydrocarbon solvent selected from the group consisting of benzene and toluene at elevated temperature and pressure, said temperature being within the paracritical range for said solvent, adjusting the pressure to obtain a solvent density greater than 0.30 g./ml. but less than 0.50 g./ml. and separating the resulting heavy fraction phase from the solution phase.

10. In a process for manufacturing lubricating oils, the improvement comprising treating each volume of an asphaltic bituminous material with at least 4 volumes of a liquid aromatic hydrocarbon solvent containing less than 10 carbon atoms per molecule at elevated temperature and pressure, the temperature being within the paracritical range of the solvent, adjusting the pressure to obtain a solvent density less than about 0.38 g./ml. but greater than 0.30 g./ml., and separating the resulting heavy fraction and lubricating oil fraction phases to obtain the heavy fraction and the lubricating oil fraction.

11. In a process for manufacturing lubricating oils, the improvement comprising treating each volume of an asphaltic bituminous material with at least four volumes of a liquid aromatic hydrocarbon solvent selected from the group consisting of benzene and toluene at elevated temperature and pressure, the temperature being within the paracritical range of the solvent, adjusting the pressure to obtain a solvent density less than about 0.38 g./ml. but greater than 0.30 g./ml., and separating the resulting heavy fraction and lubricating oil fraction phases to obtain the heavy fraction and the lubricating oil fraction.

12. In a process for manufacturing lubricating oils, the improvement comprising treating each volume of an asphaltic bituminous material with at least four volumes of a liquid aromatic hydrocarbon solvent selected from the group consisting of benzene and toluene at elevated temperature and pressure, the temperature being within the paracritical range of the solvent, adjusting the pressure to obtain a solvent density less than about 0.38 g./ml. but greater than 0.30 g./ml., separating the resulting heavy fraction and lubricating oil fraction phases to obtain the heavy fraction and the lubricating oil fraction, and recovering solvent from the lubricating oil fraction phase by adjusting the pressure to obtain a solvent density less than 0.30 g./ml. and separating the lubricating oil from the demixed solvent.

55 13. A process for separating asphaltenes from asphaltic bituminous material comprising treating each volume of asphaltic bituminous material with at least 4 volumes of a liquid aromatic hydrocarbon solvent containing less than 10 carbon atoms per molecule at a temperature and
60 pressure within the paracritical range of the solvent to obtain a solvent density of less than 0.50 g./ml. and greater than 0.40 g./ml. and separating the resulting heavy fraction as a fluid phase.

14. A process for separating aliphaticenes from asphaltic bituminous material comprising treating each volume of asphaltic bituminous material with at least four volumes of a liquid aromatic hydrocarbon solvent selected from the group consisting of benzene and toluene at a temperature and pressure within the paracritical range of the solvent to obtain a solvent density of less than 0.50 g./ml. and greater than 0.40 g./ml. and separating the resulting heavy fraction as a fluid phase.

15. A process for separating asphaltenes from asphaltic bituminous material comprising treating each volume of an asphaltic bituminous material derived

from petroleum with at least four volumes of a liquid aromatic hydrocarbon solvent containing less than ten carbon atoms per molecule at a temperature and pressure within the paracritical range of the solvent to obtain a solvent density of less than 0.50 g./ml. and greater than 0.40 g./ml. and separating the resulting heavy fraction as a fluid phase.

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