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## TREATMENT OF HYDROCARBON OILS

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The present invention relates to the separation of hydrocarbon oils into fractions and relates more particularly to the separation, in the presence of a solvent, of hydrocarbon constituents having relatively high critical temperatures from those of lower critical temperature.

A principal object of this invention is the separation of hydrocarbon oils, and particularly viscous hydrocarbon oils derived from petroleum, into a plurality of fractions by means of a solvent at or above the critical temperature thereof.

A further object of this invention is the separation of a hydrocarbon oil, and particularly a wax-bearing hydrocarbon oil, into a plurality of fractions at least one of which contains substantially less wax than the initial oil, such separation being accomplished by means of a solvent at or above the critical temperature thereof.

A further object of this invention is the separation of a hydrocarbon oil into a plurality of fractions by means of a solvent and the refining of at least one of said fractions in the presence of solvent at or above the critical temperature thereof.

In the production of lubricating oils, particularly from crude oils or crude oil residuums, the separation of desirable high boiling oil fractions, substantially free from asphaltic or tarry materials and wax, has been a difficult and expensive procedure. Due to the tendency of these high boiling fractions to crack or decompose at high distillation temperatures, it has been necessary to devise methods for separating the high boiling hydrocarbons possessing desirable lubricating qualities from the heavy asphaltic or tarry materials under such conditions that substantial decomposition is eliminated, or at least reduced to a minimum. Among the methods heretofore employed may be mentioned (1) vacuum distillation, which involves expensive equipment having a large volume capacity and requiring relatively high temperature to produce high viscosity oils free from asphaltic or tarry materials, and (2) treatment of hydrocarbon oils, and particularly crude residuums, at normal temperatures with a precipitating agent such as liquid propane whereby the hydrocarbon oil is freed of asphaltic matter. The latter method requires the employment of large volumes of precipitating agent with the accompanying expense of removal by distillation and the resulting deasphaltized oil has substantially the same wax content as the initial oil.

I have found that hydrocarbon oils may be separated into fractions at temperatures such that decomposition of desirable oils is avoided and the heat requirements in the process are reduced to a minimum. When, for example, two liquids having different critical constants are brought above the critical temperature of the more volatile one, while the system is maintained at an elevated pressure which may be of the order of the critical pressure of the more volatile component, the latter vaporizes and all or a portion of the less volatile component is caused to pass into solution in the vapor phase, the extent to which solution of the less volatile component occurs being dependent upon the temperature and pressure employed. Under these conditions, for a given temperature above the critical temperature of the more volatile component, an increase of pressure causes increased solution of the less volatile component in the vapors of the more volatile component.

In accordance wth the present invention, hydrocarbon oils may be separated into a plurality of fractions by admixing the oil with a solvent having a relatively low critical temperature, for example, within the range of from about 0° C. to about 250° C., and heating the admixture or solution at least to and preferably above the critical temperature of the solvent and under an elevated pressure, which may or may not be in excess of the critical pressure, whereby the solvent and at least a portion of the oil passes into vapor phase. The liquid and vapor phases may then be separated by suitable means. Under certain conditions, the treatment may be effected in such a manner as to obtain two liquid phases and a vapor phase.

In one aspect of my invention, hydrocarbon oil is mixed with a solvent which at ordinary temperature and pressure may be gaseous, for example, carbon dioxide, freon, ethane, propane, butane and the like, or with a normally liquid sovent such as pentane, petroleum ether or naphtha, gasoline and diethyl ether. The mixture or solution is then brought to a temperature preferably above the critical temperature of the solvent, whereupon the latter passes into the vapor phase and at the same time a portion of the oil passes into solution in the dense solvent vapors, upon increasing the pressure on the system preferably to the order of the critical pressure of the solvent. The solvent vapors containing oil in solution therein are separated from the unvaporized oil, for example, by conventional means such as a separating tank or evaporator, or a fractionating column, or by centrifugal action. Upon cooling the vapor, under pressure, to a temperature slightly below the critical temper-

ature of the solvent, two liquid phases may be formed, one of which consists primarily of that portion of the oil previously dissolved in the solvent vapors and containing some of the solvent, while the other liquid phase is solvent practically free from oil. The oil and solvent phases are then separated, for example, by decantation, and the solvent may be returned to the system as a liquid for reuse in the treatment of additional quantities of oil. Any solvent contained in the separated oil phase may be recovered therefrom, for example, by vaporization.

In another aspect of my invention, hydrocarbon oil is admixed with one or more of the solvents previously mentioned and the admixture is brought to a temperature in excess of the critical temperature of the solvent and under a substantial superatmospheric pressure, whereupon the solvent and a portion of the oil pass into the vapor phase. The solvent vapors containing oil, above the critical temperatures of the solvent and under substantial pressure, are withdrawn from contact with the liquid residual oil and passed into contact with a refining agent, such as, for example, sulfuric acid, fuller's earth or similar refining agents. In this manner, the oil may be purified in the vapor phase in the presence of the solvent at a temperature above the critical temperature thereof. The purified oil is separated from the refining agent, and the solvent may be recovered as a liquid by cooling the oil-solvent vapors to a temperature slightly below the critical temperature of the solvent, while maintaining a substantial pressure thereon. Or, the solvent may be separated from the treated oil by merely releasing the pressure thereon, and applying additional heat, if necessary, to vaporize the solvent from the oil.

I have found that a petroleum naphtha of 59° A. P. I. gravity, when admixed with a crude oil residuum having an A. P. I. gravity of 16.2° and a Saybolt universal viscosity of 560 seconds at 210° F., in the ratio of 9 parts of naphtha to 1 part of residuum by weight, and heated to about 575° F. under superatmospheric pressure, a heavy asphaltic or tarry material is thrown out of solution. Upon further heating the solution to about 590° F., the major portion of the naphtha passes into the vapor phase, leaving substantially all of the oil in the liquid phase. At a temperature of about 600° F. a considerable portion of the oil in the liquid phase passes into solution in the dense naphtha vapors, as is evidenced by a marked darkening of the vapors and a decrease in the volume of the oil in the liquid phase.

Similarly, a petroleum naphtha of 88° A. P. I. gravity, when admixed with the same residuum in about the same proportions as above, and the resulting solution heated to about 425° F. under a substantial superatmospheric pressure, a heavy tar is thrown out of solution. Upon heating the solution to about 435° F., the major portion of the naphtha passes into the vapor phase, leaving substantially all of the oil in the liquid phase. Further heating under increasing pressure causes vaporization of the oil, and at a temperature of about 500° F. a considerable portion of the oil passes into solution in the naphtha vapors, leaving only a very viscous tar in the liquid phase. At 575° F. essentially all of the oil has passed into the naphtha in the vapor phase.

Butane, when employed in the treatment of the same crude residuum, effects a separation of asphaltic material at a temperature of about 320° F. and under elevated pressure. Vaporization or solution of the oil in the dense butane vapors is appreciable at 400° F. and proceeds with increasing temperature and pressure.

Ethane, propane, carbon dioxide and freon, when admixed with a high molecular weight oil such as the crude residuum above mentioned, and heated to or above their respective critical temperatures, require relatively high pressures to cause substantial vaporization or solution of the oil in the solvent vapors. However, petroleum oils of lower molecular weight, for example, paraffine distillate, may be separated into fractions, in accordance with my invention, at reasonable temperatures and pressures by solvents such as ethane, propane, freon and the like.

The separation of a hydrocarbon oil, for example, a long residuum having an A. P. I. gravity of 21.5° and a Saybolt universal viscosity of 150 seconds at 210° F., into fractions, at least one of which contains the bulk of the asphaltic material, may be satisfactorily accomplished when employing ethane, propane or butane, preferably above the critical temperature thereof and under superatmospheric pressure, the choice of solvents depending upon the quantity of light oils contained in the residuum. The use of butane in this treatment requires temperatures of the order of 350° to 500° F. and pressures within the range of from 1000 to 2000 lbs./sq. in. Separations utilizing propane involve temperatures of the order of from about 250° F. to about 400° F., while ethane may be employed at temperatures from about 100° F. to about 250° F., and under pressures of the order of from 2000 to 5000 lbs./sq. in. In all cases, the temperatures, pressures and ratio of solvent to oil will vary, depending upon the character of the oil and the degree of separation or fractionation desired.

My invention may be further illustrated by the following example:

A hydrocarbon oil having an A. P. I. gravity of 16.2°, a Saybolt universal viscosity of 562 seconds at 210° F., an O. D. color of 27,700 and a viscosity-gravity constant of 0.872, was admixed with 88° A. P. I. petroleum naphtha to give a solution containing 71.5% by weight of naphtha. This solution was passed continuously into a pressure vessel and heated to a temperature of from about 470° F. to 490° F., under a pressure of the order of from 750 to 780 lbs./sq. in. Naphtha vapor containing heavy oil in solution was continuously withdrawn from the pressure vessel, cooled, and the naphtha was thereafter removed from the oil fraction by vaporization. The resulting oil fraction, substantially free from asphaltic or tarry material, amounted to about 28.9% by weight of the initial stock charged and had an A. P. I. gravity of 19.8°, a Saybolt universal viscosity of 185 seconds at 210° F., an O. D. color of 2860 and a viscosity-gravity constant of 0.857. The asphalt-free overhead oil fraction contained less wax than the initial stock, thus indicating that at least a partial dewaxing of the oil was accomplished during the vapor phase separation.

It will be seen, that in accordance with my invention, I am able to separate desirable oil fractions from hydrocarbon oils, and more particularly from hydrocarbon residual oils, such fractions being substantially free of asphaltic materials and containing less wax than the initial oil undergoing treatment.

In the appended claims, the term "solvent" is to be understood to comprehend compounds of the type which are substantially miscible with

hydrocarbon oil at ordinary temperatures, such as ethane, propane, butane, pentane, petroleum ether or naphtha, diethyl ether, dichloro-difluoromethane (freon), carbon dioxide, and which are capable of separating a hydrocarbon oil, at elevated temperatures and pressures into a plurality of fractions differing in one or more important or critical characteristics such as viscosity, gravity, color, boiling range, viscosity-gravity constant, wax content, or the like.

What I claim is:

1. The method of separating a viscous hydrocarbon oil into fractions having different physical properties, which comprises admixing said hydrocarbon oil with from about 2 to about 9 parts by weight of a solvent, bringing the admixture to a temperature and pressure above the critical temperature and pressure of said solvent, the relation of said temperature to said pressure being so controlled as to effect formation of a vapor phase comprising solvent and lower boiling components of said viscous oil dissolved therein, and a liquid phase comprising higher boiling components of said viscous oil, separating the vapor phase from the liquid phase so formed at a temperature and pressure above the critical temperature and pressure of said solvent, and removing solvent from said phases to produce oil fractions differing in physical properties.

2. The method according to claim 1, wherein the solvent employed is of the group consisting of ethane, propane, butane, pentane and low boiling petroleum naphtha.

3. The method according to claim 1, wherein the vapor phase comprising solvent containing lower boiling components of the viscous oil is separated from the liquid phase and contacted with a refining agent at a temperature and pressure above the critical temperature and pressure of the solvent.

4. The method of separating a petroleum residuum into fractions having different physical properties, which comprises admixing said residuum with from about 2 to about 9 parts by weight of a relatively low boiling hydrocarbon solvent, bringing the admixture to a temperature and pressure above the critical temperature and pressure of said solvent, the relation of said temperature to said pressure being so controlled as to effect formation of a vapor phase comprising solvent and lower boiling components of said residuum dissolved therein, and a liquid phase comprising higher boiling components of said residuum, separating the vapor phase from the liquid phase so formed at a temperature and pressure above the critical temperature of said solvent, and removing solvent from said phase to produce oil fractions differing in physical properties.

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