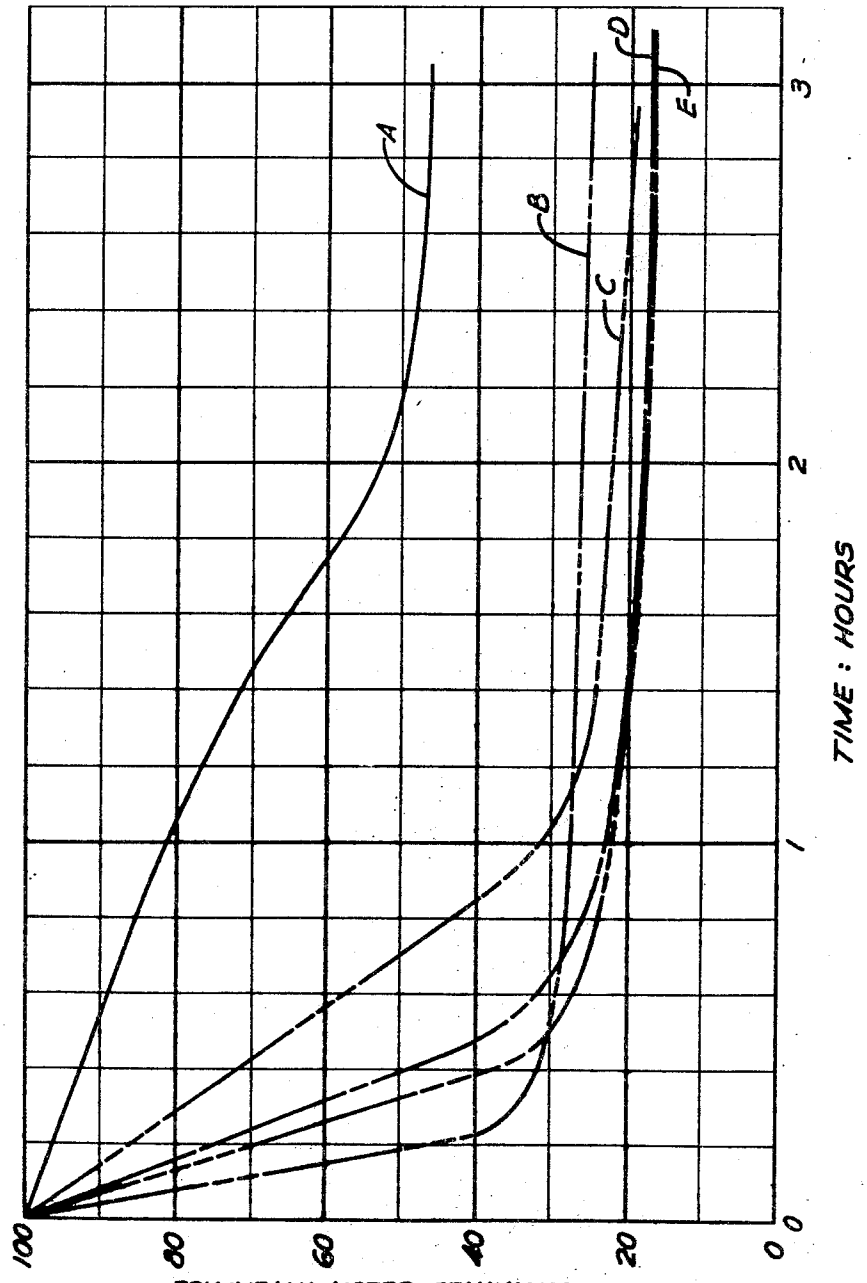
Sept. 11, 1962 H. BEUTHER ET AL 3,053,750

TREATMENT OF PETROLEUM FRACTIONS FOR THE SEPARATION OF ASPHALTIC MATERIAL

Filed May 9, 1960



INVENTORS
HAROLD BEUTHER
RICHARD A. FLINN
OLAF A. LARSON

BY

ATTORNEY

United States Patent Office 3,053,750 Patented Sept. 11, 1962

3,053,750

TREATMENT OF PETROLEUM FRACTIONS FOR THE SEPARATION OF ASPHALTIC MATERIAL

Harold Beuther, Gibsonia, Richard A. Flinn, Pittsburgh, and Olaf A. Larson, Oakmont, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

Filed May 9, 1960, Ser. No. 27,955
3 Claims. (Cl. 208—45)

This invention relates to the improvement of residual petroleum fractions which contain asphaltic materials and in particular relates to an improved process for separation of asphaltic materials from such residual petroleum fractions.

It is of course well known to deasphalt residual petroleum fractions by adding a deasphalting solvent thereto. Such a solvent is one in which the asphaltic materials are relatively insoluble but which is miscible with the hydrocarbon components of the residual fraction. A typical deasphalting process of this type involves utilization of liquified propane as a deasphalting solvent. The liquid propane is mixed with the residual stock usually at a temperature below the critical temperature of the propane. The asphaltic materials are precipitated and are separated from the hydrocarbon-solvent mixture. Deasphalting solvents such as pentane have been mentioned as possible solvents for partial replacement of liquified propane. These deasphalting procedures have been unsatisfactory in certain respects. Thus low boiling solvents remove large amounts of useful hydrocarbons with the asphalt. One the other hand utilization of other solvents exacerbates the problem of rapidly settling the asphaltic materials.

This invention has for its object to provide improved procedure for treatment of residual stocks. An additional object is to provide improved procedure for deasphalting residual petroleum fractions. A still further object is to provide improved procedure for removal of asphaltic materials from residual stocks whereby the settling of the asphaltic materials can be markedly improved. A further object is to provide improved procedure for removing asphalitic materials from residual stocks using higher boiling hydrocarbons as deasphalting solvents. Other objects will appear hereinafter.

These and other objects of our invention are accomplished by visbreaking a residual stock. The visbroken residual stock is then intermixed with a deasphalting solvent in an amount sufficient to cause some initial precipitation of asphaltic material. This mixture is heated to an elevated temperature, which temperature is below the softening point of the asphaltic material. This temperature is also below the boiling point of the deasphalting solvent under the conditions of use. Thereafter an additional amount of deasphalting solvent is added to the heated mixture. This additional deasphalting solvent is at a lower temperature than the heated mixture to which it is added. This has a quenching effect on the heated mixture so that it is rapidly cooled to a lower temperature. The precipitated asphaltic material is then separated from the hydrocarbon components of the visbroken residual fraction. This procedure results in more rapid settling of asphaltic material and also results in other advantages described below.

The charge stock to our process may be any residual petroleum fraction which contains asphaltic materials and which has an API gravity of below about 20. In most cases the residual fraction will be obtained by subjecting a crude petroleum which contains asphaltic material to either atmospheric distillation or vacuum distillation to obtain a residual fraction having a low gravity.

On the other hand there are certain crudes which have a gravity of below about 20 API and with such crudes it is satisfactory to directly charge them to the process of our invention. The expression "residual petroleum stock" as used herein and in the appended claims is to be understood to include not only these residual fractions produced by distillation and containing asphaltic materials but also heavy crudes having a gravity below about 20° API and containing asphaltic materials.

The residual petroleum stock may be subjected to any type of visbreaking operation known in the prior art. Ordinarily visbreaking is not carried out under severe enough conditions to result in formation of more than about 10 percent gasoline. However the severity for the purposes of our invention may be such as to result in the formation of between about 4 and 20 percent by volume of gasoline. The severity of the visbreaking operation is regulated by the temperature of heating, the time of heating and the pressure. We have found that visbreaking of a mild degree, i.e. as low as 4 percent gasoline, results in a marked improvement. We prefer to visbreak to a gasoline yield of about 8 to 12 percent. In general a temperature of between about 850° and 975° F., a heating time of between about 250 and 1000 seconds and a pressure of between about 50 and 600 p.s.i.g. is employed for the visbreaking step. Procedures for visbreaking are well known in the prior art and reference is made thereto for further details. See for instance Sachanen, Conversion of Petroleum, Second edition, Reinhold Publishing Corporation, 1948, pages 252–254.

The lower boiling products such as gasoline formed during the visbreaking operation have a harmful effect on the subsequent deasphalting operation. This is due to the fact that the gasoline so formed contains olefins and aromatics which tend to keep the asphaltic materials in solution. Therefore it is preferable, but not necessary, to remove this gasoline prior to deasphalting. The higher boiling components formed during the visbreaking operation such as furnace oil also contain aromatic hydrocarbons which exert a slight solubilizing effect on the asphaltic materials. However due to the fact that these aromatic hydrocarbons are of higher molecular weight, this reduction in the rate of asphaltic material precipitation is not as great as it is with the lower molecular weight gasoline fraction. Ordinarily we prefer to leave the furnace oil fraction or the components boiling above gasoline and formed during the visbreaking operation in the visbroken material and have them present during the deasphalting step. The reason we prefer to have these higher boiling components present is that they reduce the viscosity of the visbroken residue and this beneficial effect usually offsets the slight disadvantage involved.

In the deasphalting step a portion of the deasphalting solvent is added to the visbroken residue and this mixture is heated to an elevated temperature which is below the softening point of the asphaltic materials which are to be precipitated. The amount of deasphalting solvent which is initially added can vary widely. However there should be at least enough added to cause precipitation of a small proportion of asphaltic materials. This incipient precipitation forms particles on which additional asphalt may form, thus increasing the rate of deasphalting and improving the nature of the asphaltic particles. We prefer to use sufficient solvent to cause initial precipitation of between about 25 and 75 percent of the asphaltic material present. The mixture of visbroken residue partially precipitated asphalts and solvent is then heated to an elevated temperature of above about 180° F. but below the softening point of the asphaltic material in question. Ordinarily we prefer to heat to a temperature which is

about 50°–75° F. below the softening point of the asphaltic material in question. With most asphaltic materials we find that a temperature of about 275°–300° F. is satisfactory for forming a hard granular asphaltic precipitate which can be rapidly settled and filtered. The longer the mixture of visbroken asphaltic material and solvent is held at the elevated temperature, the better the subsequent filtration or separation will be. A heating time of between about 1 and 60 minutes is generally satisfactory. Simply heating to the desired temperature and immediately quenching gives satisfactory results. After heating to or at the desired temperature, the balance of the deasphalting solvent is added. This additional solvent is at a substantially lower temperature so that the heated mixture is rapidly quenched to a lower temperature. Ordinarily we prefer to quench to a temperature below about 150° F.

The deasphalting solvent may be of any of those conventionally employed for this purpose such as propane. However we prefer to employ a paraffinic hydrocarbon having 5 to 18 carbon atoms in the molecule. Thus we have found that hydrocarbons such as heptane or cetane will cause improved precipitation and settling of the asphaltic material and will also result in less entrainment of hydrocarbons in the asphaltic layer. The total amount of solvent used may be the same as that conventionally used in deasphalting operations, i.e. between about 0.1 and 10 parts by volume of solvent to 1 of visbroken residue and preferably 0.5 to 4.0 volumes of solvent to 1 of visbroken residue. If desired deasphalting may be carried out under pressure to keep the solvent in liquid phase. Reference is made to the prior art on solvent deasphalting for further details on deasphalting procedure. See for instance Kalichevsky, Petroleum Refining With Chemicals, Elsevier Publishing Company, 1956, pages 388–396.

It will be apparent from the foregoing that an outstanding advantage of our invention is that it increases the rate at which asphaltic material settles from the solvent mixture. Therefore in the preferred embodiment of our invention we subject this mixture to settling to permit the asphaltic material to separate from most of the hydrocarbon-solvent mixture. In accordance with this preferred embodiment the hydrocarbon layer is then removed by decanting or in any other desired manner. We prefer to then filter the asphaltic layer to separate the asphaltic materials from the entrained hydrocarbons and to wash the asphaltic material with a solvent to remove any further hydrocarbons or the asphaltic granules. Our procedure results in granulated asphaltic material which can be easily and rapidly filtered and washed with hydrocarbon solvents such as pentane or with the solvent used for deasphalting. The hydrocarbon layer separated after the quenching step, preferably after addition of the hydrocarbons removed by filtering and washing, is subjected to distillation to remove the deasphalting solvent. The resultant product is a high-grade deasphalted oil which can be used for a variety of purposes. For instance, it can be used as a catalytic cracking feed stock. The product is not only relatively free of asphaltic materials but also of the metalliferous substances which are frequently present in residual stocks. Therefore the deactivating effect these metalliferous substances exhibit in connection with cracking catalysts is minimized or avoided.

EXAMPLE

A 19 percent Kuwait residue prepared by vacuum distillation of a Kuwait crude was subjected to visbreaking by heating to 915° F. for a period of about 400 seconds at a pressure of 278 p.s.i.g. The product was subjected to distillation to remove 10 percent gasoline formed during the visbreaking. The gasoline-free residue from this visbreaking and distillation operation had the properties given in Table I.

Table I

Gravity, ° API	7.4
Viscosity, SUV @ 210° F.	334
Pour point, ° F.	40
Carbon Residue, percent by wt.	22.86
Vanadium, p.p.m.	104
Nickel, p.p.m.	29.8

A part of the visbroken residue described in Table I was divided into five portions. One portion was deasphalted by mixing with 6 volumes of heptane to 1 of the visbroken residue. This mixture (A) was settled at 80° F. Another portion (B) of visbroken residue was mixed with 2 parts heptane to 1 part residue and heated to 200° F. This heated mixture was then quenched with an additional amount of heptane amounting to 4 parts heptane to 1 part visbroken residue, the additional amount of heptane being at a temperature such as to cool the heated mixture to 80° F. at which temperature the quenched mixture was settled. The third portion (C) of the visbroken residue was mixed with 6 parts heptane to 1 part residue and settled at a temperature of 135° F. The fourth portion (D) of visbroken residue was mixed with heptane in a ratio of 6 parts heptane to 1 residue and heated to 200° F. and then settled at 135° F. The fifth portion (E) was mixed with 2 parts heptane to 1 part residue and heated to 200° F. This heated mixture was then quenched with an additional amount of heptane amounting to 4 parts to 1 part visbroken residue, the additional amount of heptane being at a temperature such as to cool the heated mixture to 135° F. at which temperature the quenched mixture was settled.

The rate of settling of the five mixtures described above was determined by introducing them into a settling chamber in which the level of the asphaltic components could be regularly observed. This level was periodically recorded. After settling the asphaltic material was removed, dried and its volume determined. The density was also determined and the difference between the volume of the asphalt, as thus determined, and the volume of the asphaltic layer was taken to be the actual volume of the hydrocarbons entrained in the asphaltic layer. The results of these determinations are given in Table II.

Table II

Mixture	Weight of Asphaltenes Below Interface @ 0 hrs.	Volume of Maltenes Below Interface @ 0 hrs.	Weight of Asphaltenes Below Interface @ 3 hrs.	Volume of Maltenes Below Interface @ 3 hrs.	Average slope of curve 0–0.2 hr., percent Maltenes/hr.
A	27.5	1,092	27.5	508	17.5
B	29.8	1,092	29.8	273	260
C	29.9	1,092	29.9	208	70
D	29.6	1,092	29.6	186	125
E	30.1	1,092	30.1	181	170

In the accompanying drawing we have graphically presented the data given in the above example. It will be noted from the drawing that the quenching operation of the invention (curve B) resulted in a much more rapid settling and in a lower amount of entrainment of hydrocarbons in the asphaltic layer. While curves C and D indicate a lower amount of hydrocarbons entrained after a period of ¾ to 1¼ hours than does curve B, this is due to the fact that curves C and D used a settling temperature of 135° F. whereas curve B was settled at 80° F. The higher temperature results in a more compact asphaltic layer. Referring to curve E, it will be noted that in connection with this operation quenching to 135° F. gives a somewhat larger entrainment during the early portions of the settling period than was obtained in curve B, but a smaller amount of entrainment during longer settling periods. An advantageous mode of operation would be a combination of the operations illustrated in curves B and E., i.e., a quenching to a rela-

tively low temperature such as about room temperature or 80° F., followed by heating to a somewhat higher temperature of about 135° F. and settling at this temperature.

We claim:

1. The process which comprises in combination visbreaking a residual petroleum fraction, removing hydrocarbons boiling below about 400° F. from the visbroken residual fraction, intermixing the visbroken residual fraction with a deasphalting solvent in an amount sufficient to cause precipitation of between about 25 and 75 percent of the asphaltic material present, heating the mixture to an elevated temperature which is above about 180° F. but which is below the softening point of the asphaltic material and which is below the boiling point of the deasphalting solvent under the conditions of use, adding additional deasphalting solvent to the heated mixture, said additional solvent being at a lower temperature than that to which the visbroken residual fraction and solvent mixture is heated, whereby the heated mixture is quenched to a temperature below about 150° F., and separating the precipitated asphaltic material from the hydrocarbon components of the residual fraction.

2. The process which comprises in combination visbreaking a residual petroleum fraction to form between about 4 and 20 percent of liquid hydrocarbons boiling up to about 400° F., removing hydrocarbons boiling below about 400° F. from the visbroken residual fraction, intermixing the visbroken residual fraction with a deasphalting solvent in an amount sufficient to cause precipitation of between about 25 and 75 percent of the asphaltic material present, heating the mixture to a temperature above about 180° F., which is below the softening point of the asphaltic material and which is below the boiling point of the deasphalting solvent under the conditions employed, adding additional deasphalting solvent to the heated mixture, said additional solvent being at a lower temperature than that to which the visbroken residual fraction and solvent mixture is heated, whereby the heated mixture is quenched to a temperature below about 150° F., and separating the precipitated asphaltic material from the hydrocarbon components of the residual fraction.

3. The process which comprises in combination intermixing a visbroken residual petroleum fraction which is substantially free of hydrocarbons boiling below about 400° F. with a deasphalting solvent which contains between about 5 and 18 carbon atoms in the molecule in an amount sufficient to cause precipitation of between about 25 and 75 percent of the asphaltic material present, heating the mixture to a temperature above about 180° F., which temperature is below the softening point of the asphaltic material and which is below the boiling point of the deasphalting solvent under the conditions employed, adding additional deasphalting solvent to the heated mixture, said additional solvent being at a lower temperature sufficient to cool the heated mixture to about 80° F., thereafter heating the cooled mixture to a temperature of about 135° F., settling the precipitated asphaltic material from the hydrocarbon components of the residual fraction and removing the settled asphaltic material from the hydrocarbon components of the residual fraction.

References Cited in the file of this patent

UNITED STATES PATENTS

2,943,050 Beavon ---------- June 28, 1960