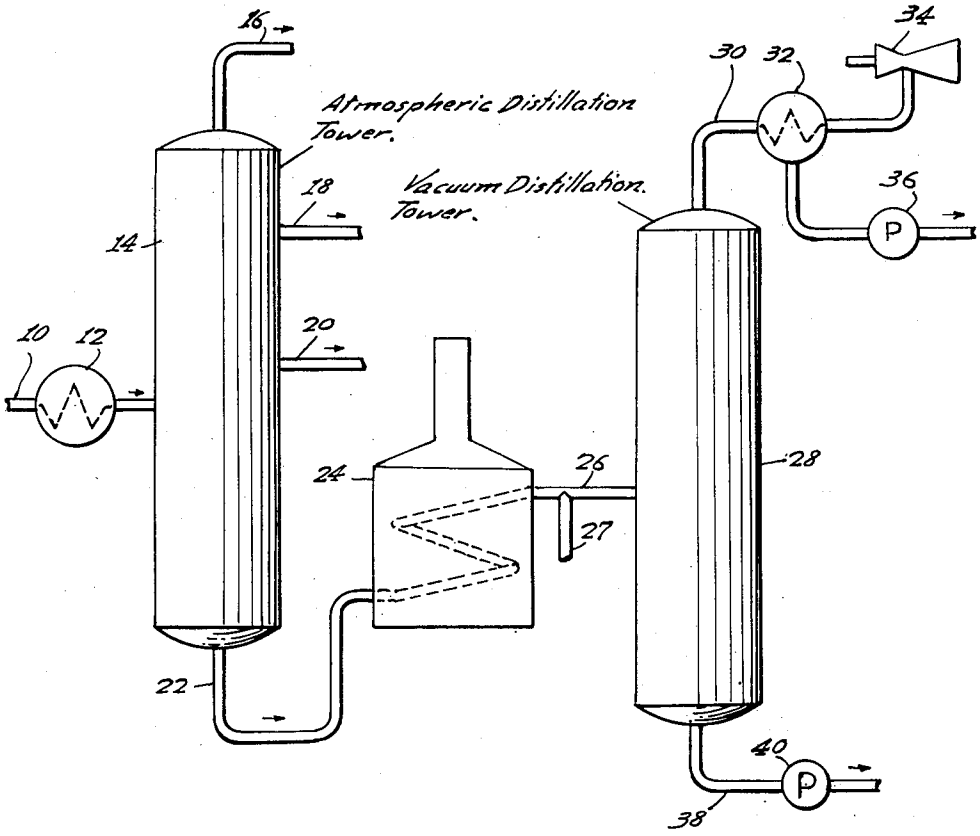
June 18, 1957 H. BEUTHER ET AL 2,796,388

PREPARATION OF PETROLEUM PITCH

Filed July 2, 1953



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BY
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United States Patent Office

2,796,388

Patented June 18, 1957

2,796,388

PREPARATION OF PETROLEUM PITCH

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Application July 2, 1953, Serial No. 365,582

2 Claims. (Cl. 196—76)

This invention relates to a petroleum pitch, and more particularly to a solid petroleum pitch and a process for its preparation from asphaltic or naphthenic crudes.

In a conventional process for the refining of petroleum crudes, the crude is fractionated in an atmospheric distillation tower to separate the distillates from the heavy non-volatile residue. The residue is then passed through a visbreaking operation in which it is thermally cracked at mild cracking conditions to reduce its viscosity. Gas oil or other distillates produced in the visbreaking operation are then ordinarily recycled through other cracking operations at increased severity to produce gasoline having improved anti-knock and other characteristics. The visbroken bottoms are blended with a relatively light oil, for example a virgin distillate or a cycle stock from a cracking process, designated as a cutter oil, to yield a fuel oil, ordinarily identified as No. 6 fuel oil, having an acceptable viscosity. Since insufficient light oil to blend with the bottoms and cut their viscosity to the desired range is produced in the refining of certain heavy crudes, it is sometimes necessary to obtain cutter oil from an outside source. The price of No. 6 fuel oil is frequently lower than the price of the crude, and is considerably lower than the price of distillate products such as domestic heating oils, in which the light oils used as cutter oils ordinarily are employed. For this reason, a process for refining petroleum crudes which will result in a minimum degradation of cutter oils to No. 6 fuel oil is desirable.

The processes for the catalytic cracking of gas oils have frequently caused refiners to alter their refining processes by the substitution of vacuum distillation for thermal cracking or other treatment of the bottoms from the atmospheric distillation. In this manner, the amounts of virgin stock for charging to catalytic cracking operations is increased. However, the bottoms from the vacuum reduction are highly viscous and must be blended with a cutter oil to produce a fuel oil having an acceptable viscosity. The vacuum reduction, therefore, increases the amount of virgin catalytic cracking charge stock obtained from the crude, but still has the disadvantage of requiring blending of cycle stock with bottoms to form No. 6 fuel oil.

One process that is used to reduce the amount of No. 6 fuel oil produced from a crude is the coking operation. In that process, the bottoms from a distillation tower or from other cracking processes are discharged from a cracking furnace into a coking drum in which they are held for a sufficient period of time to convert the heavy material to coke. Ordinarily, no No. 6 fuel oil is produced in a coking operation; hence, it is not necessary to degrade any cutter oil to fuel oil. However, the coking operation is expensive because of high labor and utility costs resulting from the difficulty in removing coke from the coking drum.

According to this invention, certain heavy asphaltic or naphthenic crudes of low hydrogen to carbon ratio are extremely deeply reduced in a continuous vacuum flash distillation. The residue from the vacuum reduction is a solid petroleum pitch having a very high softening point making it suitable for use as a solid fuel, or, in some instances, as a binder. By the production of the solid petroleum pitch in this manner, the hydrogen to carbon ratio of the distillates is increased by removal of a high proportion of the carbon of the crude oil in the pitch. In addition, an increased amount of virgin distillate suitable as a charge stock for catalytic cracking operations is obtained as a result of the very deep cut made into the crude.

The single figure of the drawings is a diagrammatic flow sheet of a process for the preparation of the solid petroleum pitches of this invention.

Referring to the drawings, the heavy crude feed passes through line 10 to a pre-heater 12 in which it is heated to a temperature sufficient to volatilize a portion of the distillable fractions of the crude. Pre-heater 12 may be of any suitable type such as a heat exchanger or a fired heater. The heated crude is discharged from the pre-heater 12 into an atmospheric distillation tower 14 in which gases and low-boiling fractions of the crude are vaporized and discharged overhead through a line 16. Typical conditions at the inlet to the tower are a temperature of approximately 700° F. and a pressure of 20 p. s. i. gauge. In the usual operation, a gasoline fraction will be withdrawn through a side drawoff 18 and a gas oil through the side drawoff 20. Atmospheric distillation tower 14 may be of any conventional design and the distillate products withdrawn from the tower will depend primarily upon the design of the tower, the requirements of the particular refinery, and the characteristics of the feed stock.

The bottoms from atmospheric distillation tower 14 are withdrawn through a line 22 and passed through a heater 24 in which they are heated to a temperature sufficiently high to permit an extremely deep vacuum reduction of the bottoms. In the preparation of the high-softening point petroleum pitches of this invention, the formation of coke should be avoided; hence, the maximum temperature in heater 24 will be limited by the cracking of the bottoms to form coke and will be dependent upon the characteristics of the bottoms and the heating curve of the furnace 24. Ordinarily, the temperature in heater 24 will range from approximately 650° F. to a maximum of approximately 850° F. The temperature actually employed will be governed, in part, upon the rate at which the bottoms are passed through the furnace, the pressure employed in the vacuum distillation, and the amount of steam added to the bottoms to aid in the distillation.

The hot bottoms from heater 24 are passed through line 26 into a continuous flash vacuum distillation tower 28. Steam is preferably added to the bottoms, as through line 27, to reduce the vacuum required for the distillation. The temperature and pressure in tower 28 must be such as to cause a very deep reduction of the crudes to form the petroleum pitch of this invention as a residue. The minimum distillation temperature that may be employed in tower 28 will depend in part upon the particular crude being treated, and in general the heavier and more naphthenic the crude, the lower the distillation temperature required. In general, the distillation temperature in tower range 28, corrected to 760 millimeters of mercury will range from a minimum of 1050° F. for very heavy crudes such as Baxterville crudes to a maximum in the range of approximately 1200° F. Distillation temperatures higher than 1200° F. might be employed if the heating characteristics of the heater 24, and other conditions, permitted heating to higher temperatures without excessive coking.

The distillation temperature in tower 28 is directly de-

pendent upon the desired softening point of the petroleum pitch prepared according to this invention. For example, with a Baxterville, Mississippi, crude which has been reduced to 95.2% bottoms in the atmospheric distillation tower, a pitch having a softening point, determined by ASTM D36–26 ring and ball test, of 360° F. may be obtained by vacuum distillation in tower **28** at a flash temperature of approximately 1070° F. (corrected to 760 millimeters of mercury). On the other hand, if a pitch having a softening point of 472° F. is desired, a temperature of approximately 1200° F. (corrected to 760 millimeters of mercury) in the vacuum distillation tower is required.

It is necessary in the preparation of petroleum pitches to make an extremely deep cut into the heavy asphaltic crudes without substantial formation of coke. Continuous flash vaporization at high vacuum is particularly suitable. Volatile components remaining in the reduced crude, together with steam which is generally added, aid in the vaporization of extremely heavy oils in a continuous flash vacuum distillation tower to facilitate their removal from the pitch without employing excessively high temperatures. Batch distillation processes are not satisfactory because of the very high temperatures required to distill the heavy oils, and the long periods at which the residue is at a high temperature.

A gas oil is withdrawn overhead from vacuum distillation tower **28** through line **30** and passed to a condenser **32**. Non-condensable gas is withdrawn from the system by a steam ejector or other vacuum pump **34** to maintain a vacuum on the tower **28**. The gas oil condensed in condenser **32** is suitable for use as a furnace oil or catalytic cracking charge stock, and is delivered from the system by a pump **36**. The residue from the bottom of vacuum distillation tower **28** constitutes the novel petroleum pitch of this invention, and is withdrawn as a liquid through line **38** by means of a pump **40** and delivered to any suitable cooling and solidification equipment.

The petroleum pitches of this invention are characterized by a high but finite softening point above 350° as determined by the ring and ball ASTM test D36–26. The specific gravity of the pitch is in the range of 1.050 to approximately 1.20 and in most instances in the range of 1.10 to 1.20.

The petroleum pitches are brittle, dark and resemble gilsonite rather than petroleum coke in their characteristics. In addition to having a finite softening point, the petroleum pitches are substantially completely soluble in carbon disulfide, benzene, and trichloroethylene. The petroleum pitches contain less than 0.4% material insoluble in refined creosote solvents (Kolineum). The acetone insoluble materials in the pitches will range from approximately 80 to 95%, and the Conradson carbon residue (ASTM test D189–46) is above about 40%. The petroleum pitches of this invention have a low penetration of the order of about 0 to 5 at 210° F./100 grams/5 seconds as determined in accordance with ASTM test D5–49, and are characterized by a susceptibility factor of about 15 to 25. The susceptibility factor may be calculated from the following formula:

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$$\left(\frac{\text{Penetration @ } 150°/100 \text{ g./5 sec.}}{\text{@ } 114°/200 \text{ g./5 sec.}} + \frac{\text{Penetration @ } 185°/\ 50 \text{ g./5 sec.}}{\text{@ } 150°/100 \text{ g./5 sec.}}\right)$$

The crude oils from which the petroleum pitches of this invention may be prepared by the process described are heavy crude oils which have a high carbon to hydrogen ratio. They may be either of asphaltic or naphthenic base. A typical United States crude fitting this description is a Baxterville, Mississippi, crude oil having a gravity of about 15.3° API. Heavy Western Venezuela, Eastern Venezuela, Coastal, and California crude oils are also suitable for the preparation of petroleum pitches by the method herein described.

Whether or not a crude oil is a satisfactory charge stock from which high softening point pitches may be prepared according to this invention may be determined by the following test procedure. Furnace oil is distilled from the crude oil and the bottoms from that distillation are cut at a 1030° F. flash temperature, corrected to 760 millimeters of mercury absolute pressure, and the asphaltene content of the resulting bottoms determined in accordance with the pentane precipitation technique of ASTM test D893–50T. The asphaltene content of the bottoms form a 1030° F. flash temperature of furnace oil-free crude oils suitable for the preparation of pitches according to this invention is above about 30%.

Example 1

A Baxterville, Mississippi, crude having a gravity of approximately 15.3° API was reduced to 95.2% bottoms in an atmospheric distillation. The bottoms were then vacuum reduced in a continuous flash distillation at a flash temperature of approximately 700° and an absolute pressure of 4½ millimeters of mercury. Steam was added to the reduced crude at the rate of 26.1 pounds per barrel of charge. The flash temperature, corrected to 760 millimeters of mercury, was 1068° F. The distillate taken overhead from the vacuum distillation constituted approximately 69.4% of the crude by volume and had a gravity of 22.4° API. The petroleum pitch from the vacuum distillation upon solidification had a specific gravity of 1.099 and a softening point, by the ring and ball test, ASTM D36–26, of 360° F. The penetration of the pitch at 210° F./100 grams/5 seconds was 4. The Conradson carbon residue of the pitch was 43½% and the percent of the pitch insoluble in trichloroethylene was 0.08.

Example 2

The reduced crude from the atmospheric distillation described in Example 1 was vacuum distilled at a flash temperature of 775° F., a flash pressure of 5.9 millimeters of mercury, and a steam addition rate of 28.1 pounds per barrel of charge. The flash temperature, corrected to 760 millimeters of mercury, was 1160° F. The pitch recovered as bottoms from the vacuum distillation constituted 20.8% of the crude by volume and had a softening point by the ring and ball test method of 390° F. The Conradson carbon residue of the pitch was 48½ percent and the percent of the pitch insoluble in trichloroethylene was 0.11. The penetration of the pitch at 210° F./100 grams/5 seconds by ASTM test D5–49 was 0.

Example 3

The reduced crude from the atmospheric distillation described in Example 1 was flashed at a temperature of 799° F., a pressure of 7.4 millimeters of mercury, and a steam addition rate of 31.8 pounds per barrel of charge. The flash temperature, corrected to 760 millimeters of mercury, was 1201° F. The pitch recovered as bottoms from the vacuum distillation constituted 17.9 percent of the crude and had a softening point of 441° F. as determined by the ring and ball test method. The penetration of the pitch as determined by ASTM test D5–49 at 210° F./100 grams/5 seconds was 2. The pitch contained 0.11 percent material insolubles in trichloroethylene and had a Conradson carbon residue of 55.2%.

Example 4

An Eastern Venezuela crude oil having a gravity of 33.2° API was distilled in an atmospheric distillation tower to yield 46.8 percent bottoms. The bottoms were then vacuum distilled at a flash temperature of 788° F., an absolute pressure of 8.6 mm. of mercury and a steam addition rate of 22.3 pounds per barrel of charge. The flash temperature, corrected to 760 mm. of mercury, was

1138° F. The pitch recovered as bottoms from the vacuum distillation had a specific gravity, in the solid state, of 1.124, a ring and ball softening point of 426° F., a Conradson carbon residue of 53.7 percent and contained 0.13 percent material insoluble in trichloroethylene.

Example 5

An Eastern Venezuela tar oil having a gravity of 14.8° API was distilled in an atmospheric distillation tower to yield 98.0 percent bottoms. The bottoms were then flashed in a vacuum distillation tower at a flash temperature of 761° F., absolute pressure of 6.6 mm. of mercury and a steam addition rate of 36.8 pounds per barrel of charge. The flash temperature corrected to 760 mm. of mercury was 1170. The pitch recovered as bottoms from the vacuum distillation had a specific gravity of 1.123, a ring and ball softening point of 369° F., a penetration at 77° F., 100 grams, in 5 seconds of 1. The Conradson carbon residue was 46.4 percent and the pitch contained 0.25 percent material insoluble in trichloroethylene.

Example 6

A mixture of Western Venezuela crudes having a gravity of 12.5° API was distilled in an atmospheric distillation tower to yield 96 percent bottoms. The bottoms were then vacuum distilled at a flash temperature of 785° F., a pressure of 8.7 mm. of mercury absolute and steam added at the rate of 31.7 pounds per barrel of charge. The flash temperature of the vacuum distillation corrected to 760 mm. of mercury was 1180° F. The petroleum pitch recovered as bottoms had a specific gravity of 1.118, a softening point of 356° F. and a penetration of 0 at 77° F., 100 grams and 5 seconds. The Conradson carbon residue was 46.7 percent and the pitch contained 0.24 percent material insoluble in trichloroethylene.

Example 7

A Mara tar oil having a gravity of 15.0° API was distilled in an atmospheric distillation tower to yield 81.8 percent bottoms. The bottoms were vacuum distilled at a flash temperature of 776° F., a pressure of 9.6 mm. of mercury absolute and a steam addition rate of 33.0 pounds per barrel of charge. The flash temperature corrected to 760 mm. of mercury was 1170. The petroleum pitch recovered as bottoms from the vacuum distillation had a ring and ball softening point of 388 and a specific gravity of 1.139. The penetration of the pitch at 77° F., 100 grams and 5 seconds was 1. The Conradson carbon residue of the pitch was 43.7 percent and the pitch contained 0.51 percent material insoluble in trichloroethylene.

We claim:

1. A process for the preparation of a petroleum pitch having a softening point above about 350° F. and substantially complete solubility in benzene consisting essentially of distilling in an atmospheric distillation a petroleum crude oil selected from the group consisting of naphthenic base crude oils, asphaltic base crude oils and mixtures thereof, said petroleum crude oils having at least 30 percent asphaltenes in the residue from a flash distillation at a temperature of 1030° F., corrected to 760 millimeters of mercury absolute pressure, of the furnace oil-free bottoms of the crude oil, heating the bottoms from the atmospheric distillation under conditions of temperature and residence time substantially to avoid cracking of the bottoms, adding steam to the heated bottoms, and vacuum distilling the mixture of bottoms and steam at an actual temperature in the range of 700° to 800° F., the actual temperature and the amount of steam and the absolute pressure in the vacuum distillation being correlated to provide a flash temperature of 1050° F. to about 1200° F., corrected to 760 millimeters of mercury absolute pressure, to form the pitch as a residual product of the vacuum distillation.

2. A process for the preparation of a solid petroleum pitch having a ring and ball softening point above about 350° F. and characterized by substantially complete solubility in benzene consisting essentially of continuously vacuum distilling virgin bottoms of a crude oil having at least 30% asphaltenes in the residue from a flash distillation at a temperature of 1030° F., corrected to 760 mm. of mercury absolute pressure, of the furnace oil-free bottoms of the crude oil, injecting steam into the vacuum distillation, the actual flash temperature being in the range of about 700° to 800° F. and correlated with the absolute pressure and the rate of steam addition to provide a distillation temperature, corrected to 760 mm. of mercury absolute pressure, in the range of 1050° F. to about 1200° F., the rate of heating to the flash temperature being such as substantially to avoid cracking of the virgin bottoms, and cooling the residual product from the vacuum distillation to produce a solid pitch.

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