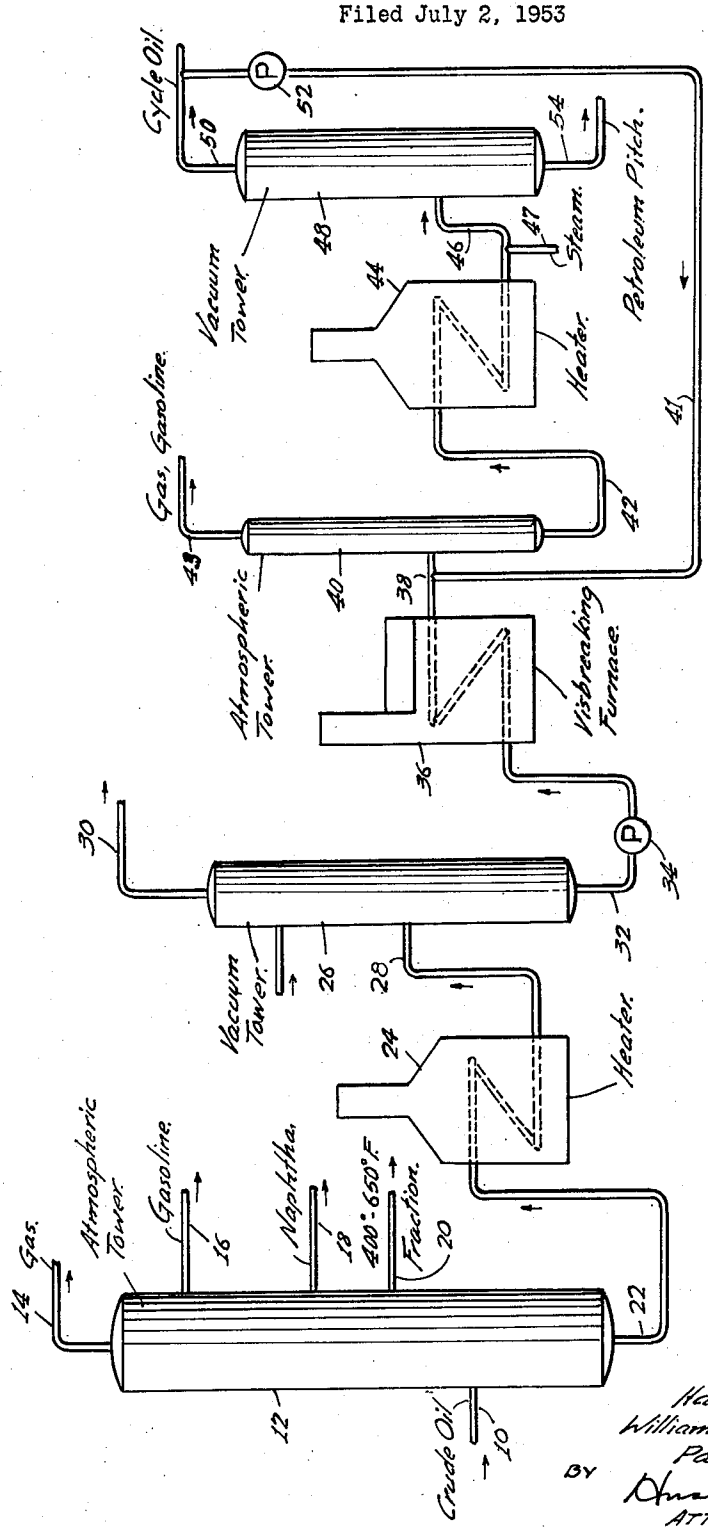
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PETROLEUM PITCH AND PROCESS FOR ITS MANUFACTURE

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PETROLEUM PITCH AND PROCESS FOR ITS MANUFACTURE

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3 Claims. (Cl. 196—50)

This invention relates to petroleum pitches, and more particularly to petroleum pitches having very high softening points, and a process for their preparation.

Crude petroleum oil as received at the refinery is processed into marketable products which differ in many of their properties and uses, but are separated from one another principally by their different boiling ranges. Usually, the more volatile, distillate products, namely gasoline, kerosene, diesel fuel, and domestic heating oil, may be sold at relatively high prices and, thus, bring the highest return on the crude oil. The market price of heavy residual fuel oils, commonly identified as No. 6 fuel oil, is much lower than the price of the distillates, and generally is even lower than the price of the crude oil. Moreover, in order for the No. 6 fuel oil to meet the usual specifications, particularly in regard to viscosity, it is necessary to blend the residual products with a light oil of low viscosity, commonly a cycle oil from catalytic or thermal cracking operation, usually referred to as a cutter oil. Thus, catalytic cycle oil used as a cutter is degraded from a product of relatively high value, such as a domestic heating oil, to the low-priced No. 6 fuel oil.

Several refining techniques have been employed in an effort to reduce the amount of No. 6 fuel oil obtained from crude oil. A commonly used process is to subject the residual oil obtained from the atmospheric distillation of the crude to a mild cracking operation known as visbreaking. The viscosity of the residual oil is reduced by the visbreaking which also provides small amounts of cracked distillates. The degree of cracking in the usual visbreaking process is limited by the serious coke formation of residual stocks containing heavy oils when severely cracked.

Another process which has been used to reduce the amount of No. 6 fuel oil is the vacuum distillation of the crude oil to form a relatively small amount of a very heavy virgin residue. The virgin residue is then blended with a cycle oil to a specification viscosity. While this process does provide added quantities of a distillate which may be used as a cracking charge stock, the amount of cutter oil required to blend with the heavy residue is relatively large.

A process in which the production of a No. 6 fuel oil is completely eliminated is a coking operation. In that process, the residual product from the initial distillation of the crude is cracked in a drum or chamber under long-period, low-severity operating conditions to form a cracked distillate and coke. The coking operation is an expensive process in which considerable difficulty and high labor and utility costs are encountered in removing the coke from the drums in which it is formed and collected.

In our application Serial No. 262,566, entitled "Thermal Conversion of Reduced Crudes," filed December 20, 1951, now U. S. Patent No. 2,762,754, a process is described and claimed in which a crude oil is subjected to a very deep vacuum reduction to produce a virgin residual stock having an initial boiling point generally in the range of 900° and 950° F. The residual stocks have a Conradson carbon residue number of at least 18, an API gravity of below 10, and a viscosity, SUS at 210° F. of at least 6000. It has been found that a residual stock of that type may be visbroken at unexpectedly high severities for short periods without excessive coke formation. While the more severe visbreaking conditions made possible by the extremely deep vacuum reduction of the crude markedly reduce the amount and the viscosity of the bottoms from the visbreaking operation, it is still necessary to blend some relatively high-priced catalytic cycle stock with the bottoms to produce a No. 6 fuel oil having an acceptable viscosity.

According to this invention, the value of the products from certain crude petroleum oils is markedly increased by the preparation of a novel, high-softening point petroleum pitch in place of the No. 6 fuel oil. The pitch is prepared by a deep vacuum reduction of a paraffinic or mixed base crude oil followed by the visbreaking of the bottoms thus produced at conditions of high severity. The visbroken material is then subjected to a second vacuum distillation at extremely high distillation temperatures, such as approximately 1100° F. (corrected to 760 millimeters of mercury) to produce a high-softening point petroleum pitch as a residue.

The single figure of the drawings is a diagrammatic flow sheet of a process for producing the petroleum pitch of this invention.

The novel petroleum pitches of this invention are characterized by a very high softening point, as determined by the ring and ball A. S. T. M. test No. D–36–26, above about 350° F. In most instances the softening point will fall within the range of 350° F. to 450° F. The softening point will depend upon the characteristics of the charge stock as well as the severity of the visbreaking conditions and the distillation temperature employed in the distillation following the visbreaking. Increasing the severity of the visbreaking and increasing the temperature of the final vacuum distillation each tend to increase the softening temperature of the pitch. Pitches having softening points above 450° F. may readily be prepared by a suitable selection of charge stock and visbreaking and distillation temperatures. Throughout the specification and claims of this application the term "softening point" of a pitch shall refer to the softening point as determined by A. S. T. M. test No. D–36–26 and the term distillation temperature shall mean distillation temperature corrected to a pressure of 760 mm. of Hg, absolute, unless otherwise indicated.

The pitches may be liquefied at temperatures of 650° F. to 750° F. and cast in any desired shape. The petroleum pitches have a low penetration and are brittle. Their penetration, which is of the order of 0 to 5 as determined in accordance with A. S. T. M. test No. D–5–49 at 210° F., 100 grams, and 5 seconds, has a low variation with changes in temperature, as indicated by a susceptibility factor generally ranging from about 15 to 25.

Chemically, the petroleum pitches are unlike coal tar pitches or petroleum coke. The pitches are practically completely soluble in benzene, carbon disulfide or trichloroethylene, which indicates the absence of free carbon or coke-like constituents. For example, the solubility of the pitches in trichloroethylene is of the order of 99+%. However, the Conradson carbon residue of the pitches, as determined by A. S. T. M. test No. D–189–46 is above about 40%. The tar-insoluble material, as measured by dissolving in a refined grade of creosote (Kolineum), is less than about 0.4%. The acetone-insoluble material in the petroleum pitches varies within the range of approximately 80 to 95%.

The properties of the petroleum pitches are such that they may be used as a substitute for gilsonite in the compounding of paints and rubber. They have low specific gravities, generally below about 1.200, for example from about 1.050 to 1.200, but preferably from 1.100 to 1.200, probably resulting from the absence of synthetic asphalt formation in their preparation. The definite softening point and the possibility of liquefying the petroleum pitches allows their use as a binder. The brittleness of the pitches allows them to be readily ground and used as a powdered fuel.

The process for the preparation of petroleum pitches according to this application is particularly suitable for use on paraffinic and mixed base crude oils. Typical crude oils which may be successfully and economically treated according to this invention are those from Kuwait, Mid-Continent and West Texas fields. High softening point petroleum pitches may also be prepared from more naphthenic crudes by the process herein described but those crudes may also be processed by a more simple, economical and direct process to prepare solid petroleum pitches.

Referring to the single figure of the drawings in which a flow sheet of the process used in the preparation of the petroleum pitches is illustrated diagrammatically, a crude oil is introduced through line **10** into an atmospheric distillation tower **12**. The crude oil is heated in any conventional manner prior to introduction into the atmospheric tower **12** to supply the heat necessary for the vaporization of the volatile fractions. Gas is taken from the top of the tower through a line **14** and the usual side streams such as one of gasoline, naphtha, and a heavy fraction, for example a 400° to 650° F. fraction, may be removed as side streams through lines **16**, **18**, and **20**, respectively. The atmospheric distillation tower **12** and its operation are conventional and clearly other arrangements of fractionating equipment for the separation of the various fractions may be made without departing from this invention.

The bottoms from atmospheric tower **12** are withdrawn through a line **22** and delivered to a heater **24**. The heater **24** heats the bottoms sufficiently to allow a very deep vacuum reduction of the bottoms in the vacuum tower **26**. The upper temperature limit to which the bottoms from the atmospheric tower may be heated in heater **24** will depend upon the maximum temperature which may be employed without excessive thermal conversion of the bottoms. The temperature of the bottoms discharged from the heater **24** will generally be from 700° F. to 800° F.

The hot bottoms are delivered from heater **24** through line **28** into the vacuum tower **26** in which a very deep cut is made to form a heavy residue. The conditions of vacuum and temperature in the vacuum tower are such that a distillation temperature, corrected to a pressure of 760 mm. of Hg, of approximately 1000° F. is obtained. A heavy gas oil, suitable as a catalytic cracking charge stock, is removed from the top of vacuum tower **26** through a line **30**. The residue from the vacuum tower is taken therefrom through line **32** at the bottom of the tower **26** and delivered by means of a pump **34** to a visbreaking furnace **36**.

The vacuum distillation in tower **26** is such that the residue from the vacuum tower **24** will have an initial boiling point of approximately 900° to 950° F., a Conradson carbon residue in excess of 18, a gravity less than 10° API, and an SUS viscosity at 210° F. greater than 6,000. In highly paraffinic crudes, the residue from the vacuum tower **26** may be as low as 5 percent of the total volume of the crude. In other crude oils which may be processed according to this invention to produce the novel petroleum pitches, such as a Kuwait crude, the residue from the vacuum tower may constitute as much as approximately 20 percent of the crude. Residues having the properties set forth above may be visbroken at unexpectedly severe conditions without the formation of excessive coke, as described in our United States Letters Patent No. 2,762,754.

The residue from the vacuum tower is heated in the coil of visbreaking furnace **36** to temperatures in the range of 900° to 1000° F., preferably 920° F. to 980° F., to subject the residue to a short-period, high-severity visbreaking process. Pressure has relatively little effect on the severity of the visbreaking, and may range from 50 to 1000 p. s. i. gauge. The time of cracking is indicated by a coil volume of approximately 0.020 to 0.035 cubic foot above 750° F. per barrel of throughput per day. The severity of cracking at these conditions is such that the yield of 400° F. end point gasoline is in the range of 8 to 20 percent. The severe cracking conditions employed in visbreaking furnace **36** will result in the formation of excessive amounts of coke if charge stocks employed in the conventional visbreaking operations are subjected to them.

The cracked products from the furnace **36** are quenched with cycle oil to a temperature below that at which cracking occurs and are delivered through line **38** to an atmospheric distillation tower **40**. A suitable stock for quenching is the cycle stock recovered in the manner hereinafter described and introduced into line **38** through line **41**. Gas and gasoline are withdrawn from the top of the tower **40** through line **43**, and a bottom stream is taken from the tower through line **42**. The bottom stream is heated in a heater **44**, then delivered from the outlet of the heater through line **46** to a vacuum tower **48**. Vacuum tower **48** is operated at a very high temperature and vacuum to permit a very deep reduction of the visbroken charge to that tower. In addition, steam is preferably introduced into the charge to the tower **48** through a line **47** to reduce the partial pressure of the hydrocarbons further. A distillation temperature of the order of 1100° F., for example above 1075° F., corrected to 760 mm., is employed in the tower **48**. A heavy cycle oil is withdrawn overhead from vacuum tower **48** through line **50**. Part of the cycle oil may be returned, after cooling in a condenser **52**, through line **41** for quenching the visbroken product discharged from the furnace **36**. The bottoms from the tower **48**, constituting the petroleum pitch of this invention, are withdrawn through line **54**.

The distillation temperature in tower **48** will vary with the desired softening point of the pitch, the crude oil employed as a charge stock, the degree of the first vacuum reduction and the severity of the visbreaking step. For example, the distillation temperature required in vacuum tower **48** for the production of pitches of different softening points from Kuwait crude which has been visbroken at different temperatures is illustrated in Table I.

TABLE I

[Distillation temperatures required to produce petroleum pitch from visbroken Kuwait crude.]

	Distillation Temperature, ° F. (Corrected to 760 Mm. Hg)		
Visbreaking Temperature, ° F.	900	930	950
Softening Point of Pitch (R. & B.), ° F.:			
350	1,180	1,140	1,095
400	1,205	1,180	1,145
450			1,180

Example 1

A Kuwait crude oil having a gravity of 31.5° API is reduced by atmospheric distillation and then by vacuum distillation at a temperature of 1030° F., corrected to 760 mm. The bottoms from the vacuum distillation, constituting 17.7% of the crude oil, have a gravity of

5.4° API, a Conradson carbon residue of 22.0, and an SUS viscosity at 210° F. of 16,200. The residue is visbroken at a temperature of 950° F. and pressure of 200 pounds per square inch to produce approximately 15% gasoline. The visbroken products are stripped in an atmospheric distillation and then vacuum distilled at a temperature of 1150° F., corrected to 760 mm., to produce a pitch as a residue, and an overhead catalytic cracking charge stock. The pitch has a specific gravity of 1.196, a softening point, ring and ball ASTM D–36–26, of 415° F., and a Conradson carbon residue of approximately 63. The pitch is practically completely soluble in trichloroethylene, benzene, and carbon disulfide.

The deep vacuum reduction following the visbreaking of heavily reduced crudes entirely eliminates the production of No. 6 fuel oil and the necessity of blending cycle oil with bottoms to produce a fuel oil of acceptable viscosity. Moreover, the very deep vacuum reduction of the visbroken bottoms increases the amount of cracking charge stock obtained.

We claim:

1. A process for the preparation of a petroleum pitch substantially completely soluble in benzene and having a softening point above 350° F. comprising distilling a reduced crude petroleum oil selected from the group consisting of paraffinic and mixed base crude oils under a vacuum to produce a residual stock having a Conradson carbon number of at least 18, an API gravity below 10, and a viscosity, SUS at 210° F., of at least 6000, heating the residual stock to a temperature of 900° to about 1000° F. and quickly thereafter quenching the heated residual stock to visbreak the residual stock in a high severity, short-period visbreaking operation, said visbreaking operation yielding about 15% gasoline and lighter hydrocarbons, flashing low boiling fractions from the visbroken products to leave a visbroken bottoms product, heating the visbroken bottoms, and vacuum distilling the thus heated bottoms at a distillation temperature above 1075° F., corrected to 760 mm. of mercury absolute pressure, in the presence of steam to form the petroleum pitch as a residual product.

2. A process for the preparation of a petroleum pitch substantially completely soluble in benzene and having a softening point above 350° F. comprising distilling a petroleum crude oil selected from the group consisting of paraffinic and mixed base crude oils under vacuum to produce a residual stock having a Conradson carbon number of at least 18, an API gravity below 10° and a viscosity, SUS at 210° F., of at least 6000, heating the residual stock to a temperature of 900° to 1000° F. in a coil having a volume above 750° F. of 0.02 to 0.035 cubic foot per barrel of residual stock per day to thermally crack the residual stock to yield about 8 to 20 percent 400° F. end point gasoline, and vacuum distilling the thermally cracked residual stock at a distillation temperature above 1075° F., corrected to 760 mm. of mercury absolute pressure, to form the petroleum pitch as a bottoms product.

3. A process for the preparation of a petroleum pitch substantially completely soluble in benzene and having a softening point above about 350° F. comprising thermally cracking a residual stock consisting essentially of a virgin residue of a petroleum crude oil selected from the group consisting essentially of paraffinic and mixed base crude oils, said residual stock having a Conradson carbon number of at least 18, an API gravity below 10° and a viscosity, SUS at 210° F. of at least 6000 at a temperature of 900° to 1000° F., in a coil having a volume above 750° F. of 0.02 to 0.035 cubic foot per barrel of residue per day to thermally crack the residue to yield 8 to 20 percent 400° F. end point gasoline, stripping gasoline and lighter fractions from the thermally cracked residual stock in a once-through operation, and vacuum distilling the stripped thermally cracked residue at a distillation temperature above 1075° F., corrected to 760 mm. mercury absolute pressure, to form the petroleum pitch as a bottoms product.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,847,359 August 12, 1958

Harold Beuther et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 44, for "softening point above 350° F." read -- softening point above about 350° F. --.

Signed and sealed this 28th day of October 1958.

(SEAL)

Attest:

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