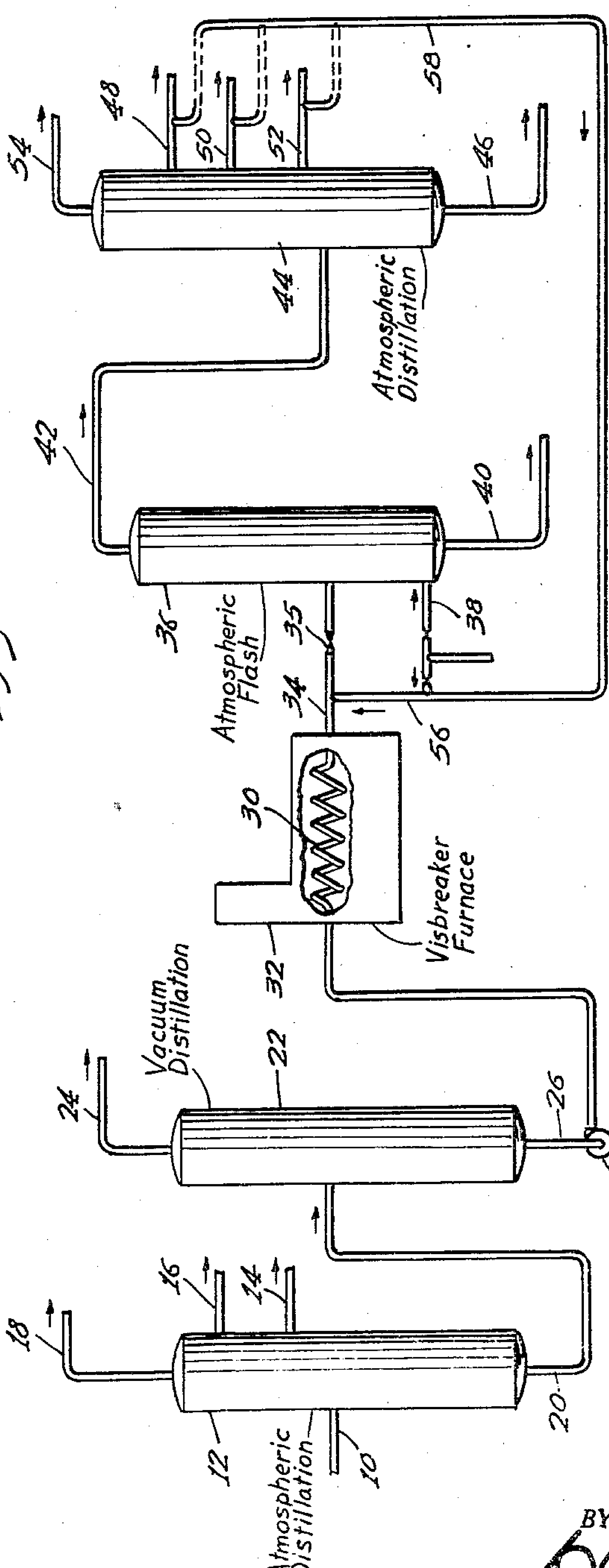
Sept. 2, 1958 H. BEUTHER ET AL 2,850,436

METHOD FOR THE PREPARATION OF SOLID PETROLEUM PITCH

Filed March 16, 1954 2 Sheets-Sheet 1

Fig. 1.



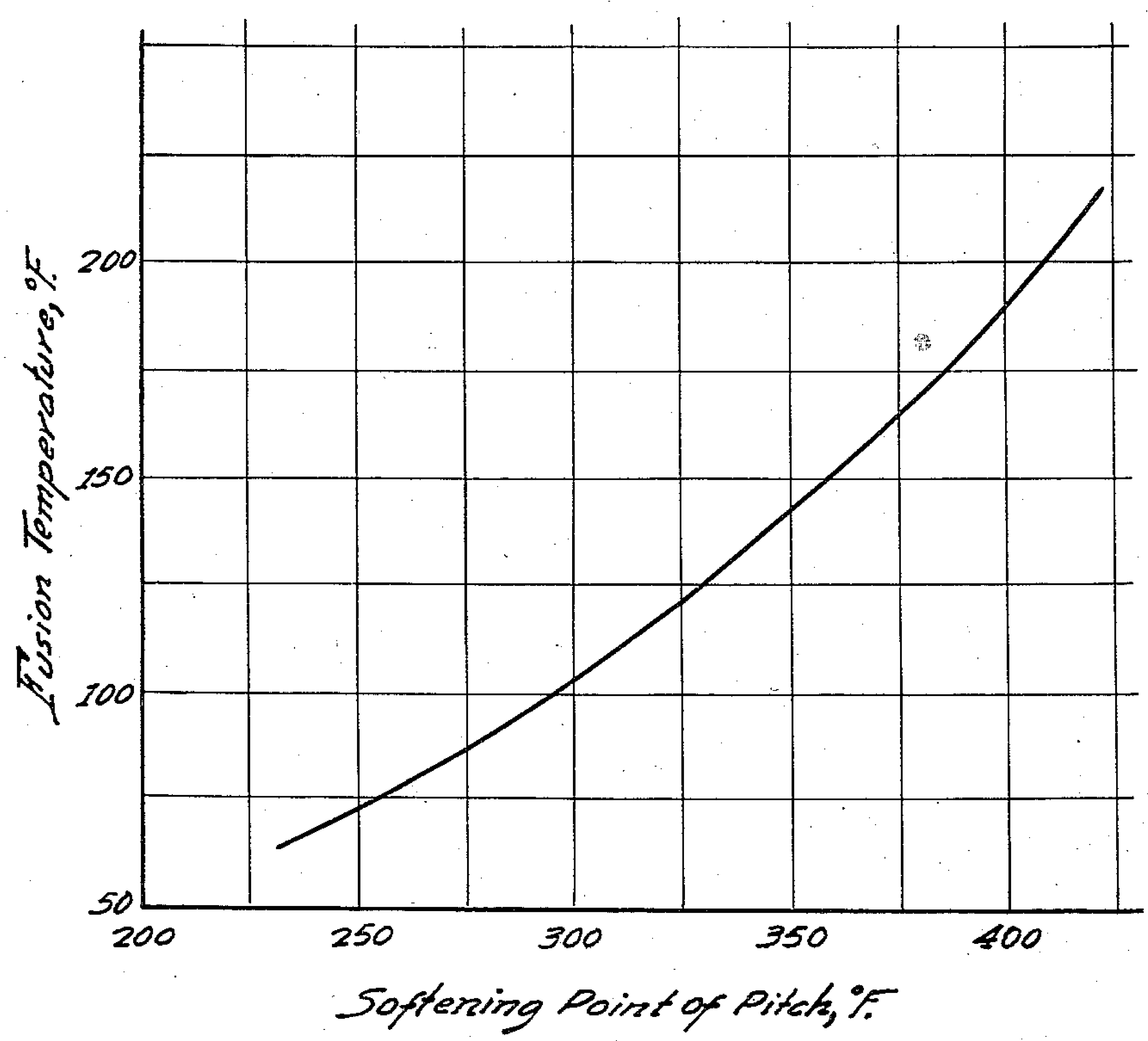
INVENTORS.
Harold Beuther and
Richard G. Goldthwait.
BY
Horace B. Cooke
ATTORNEY.

Sept. 2, 1958 H. BEUTHER ET AL 2,850,436

METHOD FOR THE PREPARATION OF SOLID PETROLEUM PITCH

Filed March 16, 1954 2 Sheets-Sheet 2

Fig. 2.



INVENTORS.
Harold Beuther and
Richard G. Goldthwait.
BY Horace B. Cooke
ATTORNEY.

United States Patent Office

2,850,436

Patented Sept. 2, 1958

2,850,436

METHOD FOR THE PREPARATION OF SOLID PETROLEUM PITCH

Harold Beuther and Richard G. Goldthwait, Penn Township, Allegheny County, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

Application March 16, 1954, Serial No. 416,634

8 Claims. (Cl. 196—50)

This invention relates to a process for the preparation of solid pitches from petroleum crude oils and more particularly to a process of excellent operability for the preparation of solid petroleum pitches having very high softening points and especially suitable for use as solid fuels.

The demand for distillate products from petroleum, notably for gasoline and domestic fuel oils, has increased tremendously during recent years and has made it necessary to refine increased quantities of crude oils. There has not, however, been a corresponding increase in the demand for heavy residual fuel oils. As a result of this unbalanced demand, the disposal of residual fuel oils at a profit has become increasingly difficult. At the present time, residual fuel oils, commonly designated as No. 6 fuel oil, are generally sold at a lower price than the crude oil from which they are derived.

Several methods have been employed to increase the percentage of distillate oils obtained from the crude oils. Deeper and deeper cuts have been made into the crude by vacuum distillation to increase the amount of distillate oil available for use as a catalytic cracking charge stock. The increase in distillate oils obtained by this method is limited. If still deeper cuts in the crude oil are attempted, in many instances the distillate is contaminated with metals and has a high carbon residue which makes it unsuitable for use as a catalytic cracking charge stock. In addition, the residual oil obtained from many deeper vacuum reductions is of such a high viscosity that it must be cut with a lighter oil, commonly designated as a cutter oil to produce a salable No. 6 fuel oil. The cutter oil, which is usually a catalytic furnace oil, in most instances could be used in a domestic furnace oil and its blending with the highly viscous residual oils seriously reduces its value.

Another process that has been employed to eliminate the unbalanced demand for distillate and residual oils is the delayed coking process in which no residual oil is produced. This process requires multiple coking drums, expensive controls and piping, and coke removal equipment. Since it is necessary to place one of the coking drums offstream periodically to remove coke, the process is expensive to operate. Moreover, the distillate oils obtained in the delayed coking process are cracked oils which are not as good charge stocks for catalytic cracking operations as virgin distillate oils or distillate oils which have only been lightly cracked.

Another possible method of increasing the ratio of distillate oils to residual oils produced in a refinery is to produce solid petroleum pitches from some of the residual oils. These pitches, unlike petroleum coke, are liquid at the operating temperatures employed and are therefore removed from the unit as a liquid. This eliminates the need of multiple reactors, as in delayed coking, which must be periodically shut down to remove coke. While the pitches are solid materials, they will flow and fuse

or cake when subjected to continued pressure, even at temperatures well below their melting point.

Since extremely large amounts of pitches would be produced if a substantial part of the residual oils were converted to the production of pitches, it is probable that the most important use of the pitches would be as a solid fuel. It is essential, therefore, that the pitches be capable of withstanding the pressures and temperatures likely to be encountered when stored in large piles without caking. It has been found that pitches having softening points, as determined by the ring and ball test method (ASTM D36), above about 350° F. may be stored without danger of caking in piles of heights ordinarily used for storing solid fuels at temperatures normally encountered. On the other hand, pitches having softening points below about 325° F. will cake or fuse when stored in high piles at temperatures of approximately 100° to 130° F., which are likely to be encountered.

The preparation of petroleum pitches of low softening point, for example softening points below about 300° F., has offered no serious difficulties. In general, such low softening point pitches may be prepared from any crude oil by processes having satisfactory operability characteristics. However, petroleum pitches having softening points below about 300° F. are not satisfactory for use as solid fuels in many instances because of their poor storage characteristics. The preparation of pitches having softening points above about 350° F. is far more difficult. Processes employing extremely deep vacuum reductions are costly because of the very large steam requirements. Processes employing severe visbreaking or deep atmospheric flashing with steam generally have poor operability characteristics.

The term "operability" is used to designate the ability of a process to continue operation for long periods without shut-downs for cleaning fouled equipment. An indication of the operability of a process in which high boiling residual products are formed is the amount of insoluble carbonaceous sediment in the residual product. If the sediment is high, operating difficulties resulting from fouling of the process equipment may be expected. Usually, the operability of a process may be improved by reducing the severity of high temperature operations, such as cracking or flashing, in the process, and particularly the time the hydrocarbons are subjected to high temperatures.

This invention resides in the preparation of petroleum pitches having softening points of approximately 350° F. or higher by visbreaking a residue containing at least about thirty percent asphaltenes and having a softening point of 160° F. or higher. The visbroken residue is then flashed at a temperature which is sufficiently low to avoid cracking in the flash tower to produce a pitch of the desired softening point as a bottoms product.

Figure 1 is a diagrammatic flow sheet of the process for the preparation of petroleum pitches according to this invention.

Figure 2 is a plot showing the relationship of the fusion temperature of the petroleum pitches under simulated storage conditions to the ring and ball softening point of the pitches.

The data from which Figure 2 of the drawings was prepared were obtained by subjecting pitch of the indicated softening point to a pressure corresponding to the pressure exerted by a pile of the pitch forty feet high for a period of twenty-four hours. The fusion temperature is the temperature at which the pitch caked when stored under pressure for the test period. The data set forth in Figure 2 of the drawings were obtained for a petroleum pitch prepared from a Baxterville (Mississippi) crude. The fusion temperature for pitches prepared from other crudes may vary slightly from the fusion temperature of the Baxterville pitch of corresponding softening point. However, in most cases, it will be within about 10° F. of the fusion temperature of the pitches of corresponding softening point prepared from the Baxterville crudes.

Referring to Figure 2 of the drawings, it will be noted that a petroleum pitch having a softening point of approximately 350° F. fuses at a temperature slightly above 140° F. In addition to their good storing qualities, petroleum pitches having softening points in excess of about 350° F. are brittle and easily pulverized to form a powdered fuel. On the other hand, if the softening point of the pitch is approximately 300° F., it will fuse under the test conditions at a temperature of approximately 100° F. Temperatures higher than 100° F. and up to about 130° F. may frequently exist in storage piles either because of heat from the direct sunlight and the surrounding atmosphere, or because of the pitch being warm when piled.

The petroleum pitches of approximately 350° F. and higher, and not less than 325° F., softening point are prepared according to this invention from residues of certain crude oils. The crude oils providing suitable sources of the residues are any crudes from which residues having softening points, as determined by the ring and ball method, above 160° F. and an asphaltene content above thirty percent may be derived. In general, the preferred crudes are those usually described as asphaltic base crudes, such as those from Baxterville, Merey, and Eastern Venezuela fields. Other preferred crudes are those designated as heavy Mara, heavy Western Venezuela, and heavy Eastern Venezuela crudes. The designation "heavy" ordinarily indicates that the crude has a gravity of about 20° API or lower; however, gravity alone does not determine whether or not a crude oil is a satisfactory charge stock for the preparation of the pitches. The composition of the highest boiling point fractions of the crude oil rather than the composition of the entire crude determines whether or not the crude will be a satisfactory charge stock.

The crude oils are passed through an atmospheric distillation unit in which gases, gasoline, and light gas oil are separated from the bottoms which are passed to a vacuum distillation unit. The atmospheric distillation is a conventional operation in which the fractions separated as separate streams will be determined by the crude oil processed and the requirements of the refinery. The vacuum distillation is a deep reduction of the bottoms from the atmospheric distillation, but presents no serious operational difficulties. For example, a vacuum distillation at a flash temperature of 1030° F., corrected to 760 mm. of mercury pressure, may be employed. The vacuum reduction of the crude oil removes heavy oils from the residue. Those heavy oils are virgin distillates which are desirable as charge stock for catalytic cracking. The vacuum reduction must be sufficiently deep to provide a residue having a ring and ball softening point above 160° F. and an asphaltene content above about thirty percent for use as a charge stock to subsequent operations. The asphaltene content may be determined by dissolving a known weight of the residue in approximately ten times its volume of pentane, separating the soluble and insoluble material, washing the insoluble material with additional pentane until a residue of substantially constant weight is obtained, removing pentane from the residue, and weighing the residue. The asphaltene content is expressed in terms of the percentage of the original sample that the residue constitutes.

The residue from the vacuum distillation is passed through a visbreaking operation at a temperature of about 900° to 950° F. and at a suitable pressure, preferably between approximately 50 and 1000 pounds per square inch gauge, for example, a pressure of 200 pounds per square inch. The visbreaking is a short-time, once-through coil cracking operation and about fifteen percent or less of the charge to the visbreaking operation is converted to gasoline of 400° F. end point. The time of cracking is indicated by a coil volume of approximately 0.012 to 0.050 cubic foot above 750° F. per barrel throughput per day. In some instances, it is desirable to quench the products discharged from the cracking operation with steam, naphtha, gasoline, light gas oil, etc. to reduce and control the temperature to prevent further cracking.

The visbroken residue is then flashed in a tower, operated preferably at substantially atmospheric pressure and at temperatures sufficiently low to prevent further cracking of the heavy oils, to produce a pitch of the desired softening point. The total conversion to 400° F. end point and lighter products is not a complete indication of the operability of the process. If the temperature of the atmospheric flash tower is sufficiently high for cracking to occur therein, the relatively long residence periods of liquids and vaporized heavy oils in the tower will result in excessive coke formation and fouling of the tower. Excessive coke formation in the flash tower is prevented by maintaining the tower at a temperature not exceeding 810° F. In some instances it is desirable to add steam to the flash tower to aid in stripping high boiling point oils from the pitch. The amount of steam added will depend upon many factors among which are the crude being processed, the cracking severity in the visbreaking coil, the temperature of the flash chamber, the stripping efficiency of the apparatus and the desired softening point of the pitch. The amount of steam employed may range from 0 to 80 pounds per barrel of charge to the visbreaking furnace. Steam, gases, gasoline, and gas oil are delivered overhead from the atmospheric flash tower and a petroleum pitch of the desired softening point is withdrawn as a bottoms product.

The pitch produced by this invention in addition to having a finite ring and ball softening point of about 350° F. and higher has a specific gravity usually ranging from 1.050 to 1.175 and not exceeding about 1.200. The specific gravity of the pitch is an indication in part of the amount of cracking of the residue. Specific gravities in excess of 1.200 are an indication that the pitch has been severely cracked either in the visbreaking furnace or the subsequent flash distillation. The pitch is characterized by being substantially completely soluble in trichloroethylene or carbon disulfide, having a penetration below 5 at 210° F./100 grams/5 seconds and a heat of combustion of about 17,000 B. t. u.'s per pound.

An embodiment of apparatus suitable for the preparation of petroleum pitch according to this invention is illustrated diagrammatically in Figure 1. A petroleum crude oil of the type described above is introduced through line **10** into an atmospheric distillation tower **12**. Light gas oil and more volatile fractions are withdrawn from tower **12** as distillate products or through suitable side draw-off lines, such as lines **14** and **16**, and an overhead product line **18**. A heavy bottoms product is withdrawn from the bottom of the atmospheric distillation tower **12** through line **20** and discharged into a vacuum distillation tower **22**. A heavy gas oil suitable for charge stock to a catalytic cracking operation is distilled from the top of tower **22** through line **24** and a heavy residual oil suitable for the preparation of petroleum pitches according to this invention is withdrawn from the bottom of vacuum tower **22** through a line **26**.

The atmospheric distillation tower **12** and vacuum tower **22** are conventional apparatus for the processing of petroleum oils and other suitable apparatus may be substituted for those towers. It is essential to this invention, however, that the residual oil withdrawn through line **26** have a ring and ball softening point higher than 160° F. and contain at least about thirty percent asphaltenes.

A pump **28** increases the pressure on the residual oil in line 26 to a pressure suitable for visbreaking and pumps the residual oil through heating coils 30 in a visbreaking furnace 32. The temperature of the residual oil is increased to a temperature of 900° to 950° F. in the furnace 32. Visbreaking furnace 32 is operated to crack the residual oil in a short-time operation at relatively high temperature. The conversion to 400° F. end point gasoline does not exceed approximately fifteen percent of the residual oil.

The effluent from the visbreaking furnace is delivered through a line 34 and a pressure reducing valve 35 into an atmospheric flash tower 36 in which cracked heavy gas oil and lighter fractions are distilled overhead. Vaporization of the overhead products from the flash tower 36 may be aided by the introduction of steam through a line 38. The petroleum pitches of this invention are withdrawn from the bottom of the tower 36 and delivered to storage through a line 40.

The distillate from atmospheric flash tower 36 is delivered overhead through a line 42 to an atmospheric distillation tower 44. Distillation tower 44 is of conventional design and operation for the separation of the lower boiling fractions from a heavy bottoms oil, ordinarily used in No. 6 fuel oil, which is withdrawn from the tower 44 through the line 46. In the distillation tower 44 illustrated in the drawings, side streams of gasoline, naphtha and gas oil are withdrawn through lines 48, 50, and 52, respectively, and gas is taken off overhead through a line 54.

In order to control the temperature of the material discharged from the visbreaking furnace 32 to prevent further cracking, a quench stream may be introduced into line 34 through line 56. The quench stream may be of steam, naphtha, gasoline, or gas oil. In the flow sheet illustrated in Figure 1 of the drawings, a recycle line 58 is provided to return a quench stream from the distillation tower 44 to line 56 and then into line 34.

Petroleum pitches were prepared according to this invention from the residues of several crudes. The results of the runs for the production of petroleum pitches are set forth in the following table.

following the visbreaking, even though the residue constitutes a long cut of the crude.

The softening point of the residue charged to the visbreaker is of extreme importance in determining the softening point of the pitch obtained. A comparison of run No. 2 and run No. 5 shows that an increase in the softening point of the residue of an Eastern Venezuela crude from 166° to 180° F. results in an increase in the softening point of the resultant petroleum pitch even though the steam introduced into the atmospheric distillation tower was reduced from 79.9 to 43.7 pounds per barrel of charge. Both residues were visbroken at the same temperature prior to the flash distillation. The softening point of the residue charged to the visbreaker is additionally important to the operability of the process. If lower softening point residues are charged to the visbreaker, the amount of heavy oil introduced into the atmospheric flash tower is increased. A pitch of the desired softening point can then be obtained either by markedly increasing the temperature of the atmospheric flash distillation which results in the formation of coke in the flash tower or by increasing the steam rate which may be limited by the design of the equipment.

The softening point of the pitch also depends upon the severity of the visbreaking. For example, it will be noted from run No. 2 and run No. 3 that increasing the visbreaking temperature of an Eastern Venezuela residue having a softening point of 180° F. from 925° to 940° F. allows a reduction in the steam required in the flash tower from 44 pounds per barrel of charge to 0 without appreciably reducing the softening point of the pitch.

The softening point of the pitch is also determined by the temperature and steam rate employed in the atmospheric flash distillation of the visbroken residue. In the examples set forth in the table, the temperature in the flash tower was substantially constant in all runs with the exception of the run in which residues from Baxterville and Merey crudes were the charge stocks. The steam introduced into the flash tower is then a measure of the effect of increased severity of flash conditions. As shown by runs Nos. 3 and 4, an increase in the steam

TABLE I

Production of pitch by visbreaking of vacuum reduced crudes

	Crude oil source										
	Eastern Venezuela					West. Ven., hvy.	East. Ven., hvy.	Mara, hvy.	Bax-ter-ville	Ku-wait*	Merey
Run No.	1	2	3	4	5	6	7	8	9	10	11
Charge stock, percent of crude	9.7	11.6	11.6	11.6	12.6	46.2	37.2	48.8	33.3	14.4	26.1
Gravity, ° API	3.8	5.2	5.2	5.2	5.2	3.6	3.0	2.9	−0.8	2.4	0.4
Softening point, ° F	218	180	180	180	166	162	182	195	280	165	245
Asphaltene content, weight percent	38.9	32.4	32.4	32.4	29.8	27.2	33.7	38.7	64.4	28.8	48.6
Operating conditions:											
Furnace temp, ° F	925	925	940	940	925	940	925	925	925	960	925
Furnace pressure, p. s. i. g	200	200	200	200	200	200	200	200	200	200	200
Furnace coil vol. above 750 F., cu. ft./bbl./day	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020
Flash temp., ° F	806	800	809	806	803	795	800	800	775	800	775
Stripping steam, lb./bbl. of charge	0.0	43.7	0.0	17.9	79.9	20.8	37.1	31.9	0.0	53.8	0.0
Pitch properties:											
Specific gravity solid state, 77° F./77° F	1.120	1.154	1.143	1.178	1.095	1.213	1.161	1.167	1.065	1.212	1.1
Softening point, ° F	347	364	360	380	345	361	357	334	392	356	350

* Propane asphalt.

It will be noted from the data presented in the above table that the softening point of the pitch will depend to an important extent upon the crude oil from which the charge stock to the visbreaking operation was derived. For example, pitches having softening points above 350° F. may be prepared from Baxterville and Merey crudes with visbreaking temperatures of 925° F. without the addition of steam in the atmospheric flash distillation

introduced into the flash tower from 0 to 17.9 pounds per barrel of charge resulted in an increase of 20° F. in the softening point of the pitch, even though the residue charged to the visbreaker and the visbreaking conditions were the same in both instances.

This invention has been described for the preparation of pitches by visbreaking residues obtained by distillation of certain crudes. Residues obtained by other processes such as those using selective solvents to separate heavy asphaltic residues from the remainder of the crude may also be used. An example of a suitable process for the preparation of the charge stock to the visbreaker is propane deasphalting. Residues prepared by propane deasphalting, like those prepared by distillation methods, must have a softening point above 160° F. and an asphaltene content above about thirty percent, to allow the preparation of pitches of the desired softening point in a process of satisfactory operability.

Data for an experimental run on a residue obtained by propane deasphalting a Kuwait crude are presented under run No. 10 of the table. In that run, the asphaltene content of the residue was slightly below thirty percent which made it necessary to employ very severe visbreaking conditions, as indicated by the high furnace temperature and the high specific gravity of the pitch, to obtain a pitch of the desired softening point. The conditions of run No. 10 are near the borderline of satisfactory conditions. It is probable that a process employing the visbreaking conditions of run No. 10 and using the residue of that run for charge stock to the visbreaking would not be satisfactory for continuous operation and it would be desirable to prepare a residue of higher asphaltene content for use as a charge stock to the visbreaker.

The visbreaking of high softening point residues of selected crude oils and subsequent flash distillation of the visbroken residuum according to the method herein described produces a petroleum pitch of a very high softening point. Because of the very high softening point of the pitch, it may be stored under the pressure and at the temperatures commonly encountered in the storage of solid fuels without fusing. Moreover, the process of this invention avoids conditions encouraging the formation of coke, and as a result has excellent operability characteristics.

We claim:

1. A process for the preparation of a petroleum pitch having a ring and ball softening point above about 350° F., a specific gravity below about 1.200 and substantially complete solubility in trichloroethylene and carbon disulfide comprising reducing an asphaltic base petroleum crude oil to form a residue having an asphaltene content above about thirty percent and a softening point above about 160° F., severely visbreaking the residue in a once-through short-time coil operation at a temperature of 900° to 950° F., quenching the visbroken material as it is discharged from the visbreaking coil, and flashing the visbroken residue at substantially atmospheric pressure at a temperature not exceeding 810° F. to from the petroleum pitch as a bottoms product.

2. A process for the preparation of petroleum pitches having ring and ball softening points above about 350° F., consisting essentially of distilling an asphaltic base petroleum crude oil in an atmospheric distillation to produce a bottoms fraction, deeply vacuum distilling the bottoms fraction to produce a residue having a ring and ball softening point above about 160° F. and an asphaltene content of at least about 30 percent, thermally cracking the residue in a once-through, coil-only operation at a temperature of about 900° to 950° F. to convert about 15 percent of the residue to 400° F. end point gasoline and lighter fractions, and flashing the visbroken residue at substantially atmospheric pressure and a temperature below 810° F. to produce the pitch as a bottoms product.

3. A process for the preparation of solid petroleum pitches having ring and ball softening points above about 350° F. consisting essentially of separating a residue having a ring and ball softening point above 160° F. and an asphaltene content in excess of about 30 percent from an asphaltic base petroleum crude oil, severely visbreaking the residue in a once-through, coil-only thermal cracking operation at a temperature of about 900° to 950° F., and flashing the visbroken residue at substantially atmospheric pressure and a temperature below 810° F. to produce the pitch as a bottoms product.

4. A process as set forth in claim 3 in which steam is added during flashing of the visbroken residue.

5. A process as set forth in claim 3 in which the visbroken residue is quenched prior to flashing at substantially atmospheric pressure.

6. A process for the preparation of petroleum pitches having ring and ball softening points above about 350° F. comprising distilling an asphaltic base petroleum crude oil in an atmospheric distillation to produce a bottoms fraction, vacuum distilling the bottoms fraction to produce a residue having a ring and ball softening point above about 160° F. and an asphaltene content of at least about 30 percent, severely visbreaking the residue in a coil-only thermal cracking operation at a temperature of about 900° to 950° F. in which the coil volume above 750° F. is approximately 0.012 to 0.05 cubic foot per barrel of throughput per day to yield about 15% 400° F. end point gasoline and lighter fractions based on the residue, and flashing the visbroken residue at substantially atmospheric pressure and a temperature below 810° F. to produce the pitch as a bottoms product.

7. A process for the preparation of petroleum pitches having ring and ball softening points above about 350° F. comprising distilling an asphaltic base petroleum crude oil in an atmospheric distillation to produce a bottoms fraction, extracting the bottoms fraction with a selective solvent to produce a residue having a ring and ball softening point above about 160° F. and an asphaltene content of at least about 30 percent, severely visbreaking the residue in a coil-only, once-through thermal cracking operation at a temperature of about 900° to 950° F. in which cracking to 400° F. end point gasolines is limited to about 15 percent, and flashing the visbroken residue at substantially atmospheric pressure and a temperature below 810° F. to produce the pitch as a bottoms product.

8. A process for the preparation of a petroleum pitch substantially completely soluble in trichloroethylene and having a ring and ball softening point above about 350° F. and a specific gravity below about 1.200, comprising distilling an asphaltic base petroleum crude oil in an atmospheric distillation to produce a bottoms fraction, vacuum distilling the bottoms fraction at conditions of temperature and pressure adapted to produce a residue having a ring and ball softening point above about 160° F. and an asphaltene content above about 30 percent, severely visbreaking the residue in a coil thermal cracking operation at a temperature of about 900° F. to 950° F. to form about 15%, based on the residue, 400° F. end point gasoline and lighter fractions, and flashing the thermally cracked product in the presence of added steam and at substantially atmospheric pressure and a tempreature below 810° F. to produce the pitch as a bottoms product.

References Cited in the file of this patent

UNITED STATES PATENTS

2,305,440	Noel	Dec. 15, 1942
2,633,449	Cheney	Mar. 31, 1953
2,651,601	Taff et al.	Sept. 8, 1953
2,662,051	Pelzer	Dec. 8, 1953
2,733,192	Sage	Jan. 31, 1956
2,762,754	Offutt et al.	Sept. 11, 1956