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PROCESS FOR THE PRODUCTION OF PITCH FROM PETROLEUM RESIDUES

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2 Sheets-Sheet 1

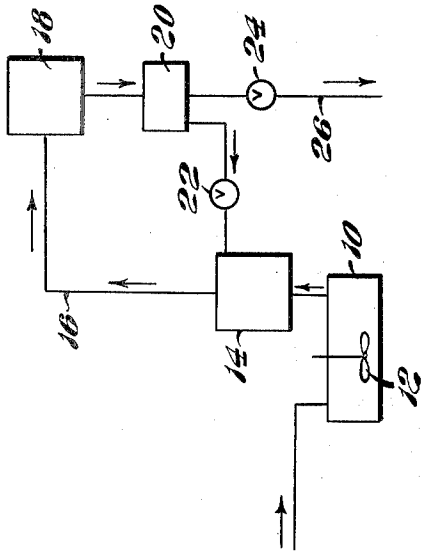
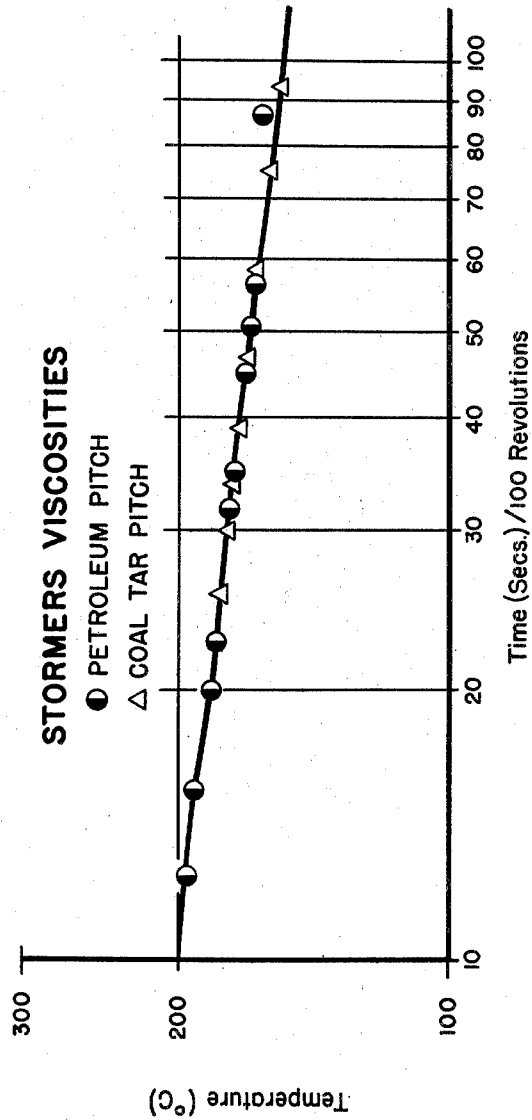


Fig. 3.

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C_I Vs DISTILLATE SEPARATION RATE

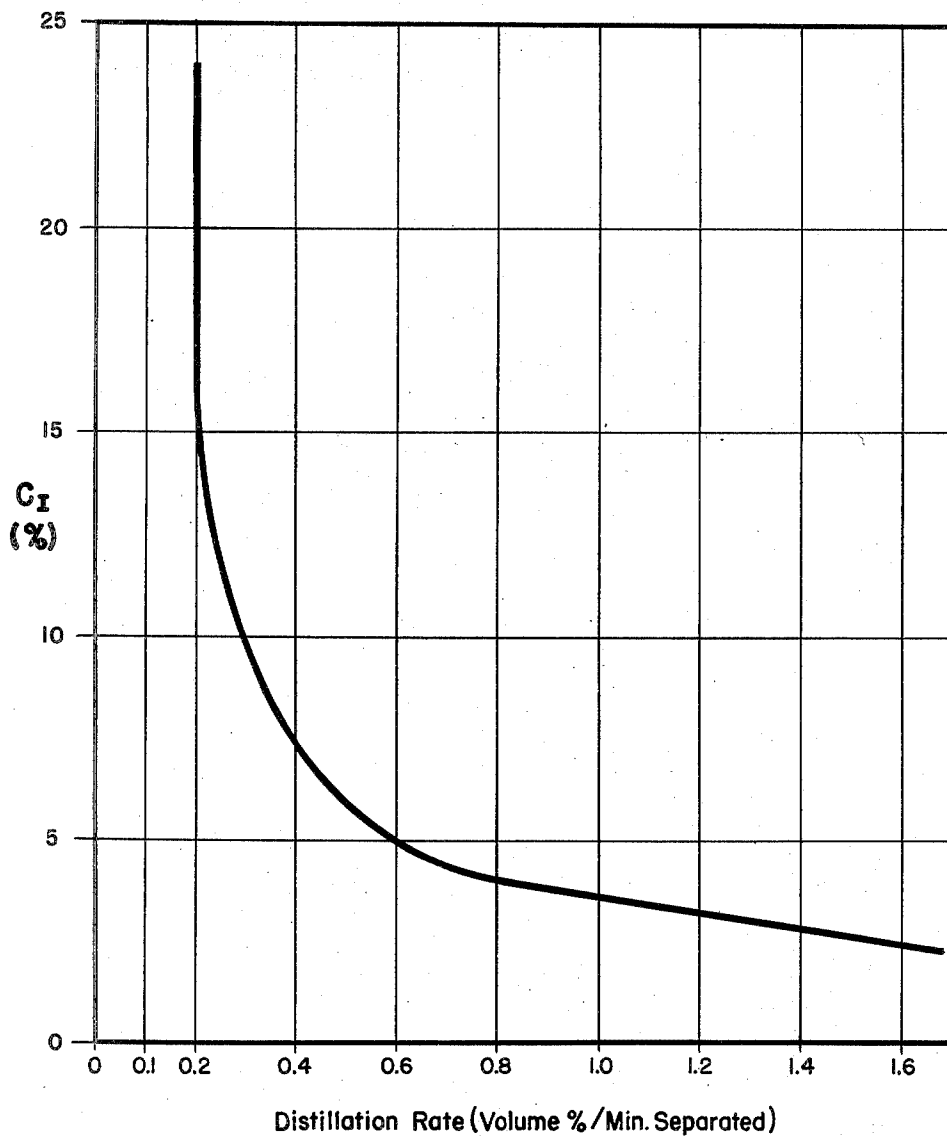


Fig. 2

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1

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PROCESS FOR THE PRODUCTION OF PITCH FROM PETROLEUM RESIDUES

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4 Claims. (Cl. 196—76)

This invention relates to the production from petroleum residues of pitch having particular utility as a binder for carbon electrodes.

Most carbon electrodes are manufactured from a suitable hard carbonaceous material, usually calcined coke. As the coke has no natural adhesiveness it must be bound together in suitable shapes with a compatible material. In making electrodes, the coke is ground, mixed with the binder, molded and baked to carbonize the binder. Several hundred thousand tons of binder are used annually in electrodes.

In the art of electrode manufacture it has been learned from experience that the nature and quality of the binder used is extremely critical. Petroleum tars and pitches have not heretofore proved to be generally useful as binders because of their high contaminant contents and poor coke yields and particularly because of their migration during baking of the electrode which leaves areas of unbonded carbon in the finished article. In this condition the electrode is of uneven mechanical strength and is variable in conductivity. Consequently, petroleum pitches have not heretofore been used to any extent as binders for electrodes and coal tar pitch has had a virtual monopoly for such usage.

We have discovered that pitches fully the equal of coal tar pitches as electrode binders may be produced by the novel process of our invention from certain petroleum residues which are in themselves quite unsuitable for the purpose. This process is characterized by the steps of distilling a petroleum residue of critical specifications, withdrawing overhead a critical amount of distillate per unit time until a critical amount of the original charge remains and recovering this remaining material as product.

More specifically, the process of this invention is carried out by heating a measured charge of a petroleum residue having a hydrogen/carbon (H/C) ratio of 1 to 1.15 and a mean molecular weight (cryoscopic determination) of 300 to 400, such materials being commercially available as residues from thermally cracking a catalytically cracked petroleum. As distillation, which may be conducted under atmospheric or superatmospheric pressure, commences, the bulk of the distillate is refluxed to the original charge and a small and critical amount, averaging between 0.2% and 0.4% per min. of the distillate based on the volume of the original charge, is separated from the system. The heat applied to the charge is continuously increased as necessary to continue distillation and the removal of distillate is continued at the specified rate until 50 to 40% of the volume of the original charge remains. This remaining material is the pitch product of our invention. This may be drawn off in molten condition and used in that condition or it may be allowed to harden and then reheated for subsequent use.

Pitches suitable for binders for electrodes must fall within a fairly narrow range of specifications as follows:

Softening point----- Not above 120° C.
C_I----- Not below about 8% by weight.
C_{II}----- Not below about 20% by weight.
Coking value----- Above 30%.

2

Of these specifications C_I is the hydrocarbon fraction which is insoluble in nitrobenzene and C_{II} is the hydrocarbon fraction which is soluble in nitrobenzene but insoluble in acetone. Coking value is the percentage of material remaining after heating a sample of pitch for 7 minutes at 950° C. in a dry atmosphere.

The pitch produced by the process of our invention falls within the above specifications and may be used interchangeably with coal tar pitch as an electrode binder. Petroleum do not meet these specifications and are not good binders.

It is the principal object of this invention to provide a process for producing an electrode binder from petroleum.

It is the further object of this invention to provide a commercially practicable and efficient process for converting certain petroleum residues to a valuable pitch product.

It is another object of this invention to provide a novel petroleum pitch which can be used instead of coal tar pitch in all electrode binding applications.

Our invention will best be understood and appreciated from the following description of the process taken in connection with the accompanying drawings in which:

Fig. 1 is a flow sheet of the process, and

Fig. 2 is a graphical representation of percentage of C_I content as a factor of distillate withdrawal rate for products constituting 40 to 50% of the original charge and having softening points below 120° C. and coking values above 30%.

Fig. 3 is a graphical representation of viscosities of representative products of the process of this invention and of electrode binder coal tars of the same melting point.

Referring first to Fig. 1, petroleum residue as above defined is charged in a measured amount to a still pot 10 heated by conventional means. A stirrer 12 is provided to agitate and maintain uniformity of mixture of the charged material. The charge is heated to 600°–650° F. and as distillation commences the vapors pass upwardly through scrubber 14. The higher boiling vapors condense in the scrubber and fall back into the still pot 10.

The distillate vapors uncondensed in the scrubber 14 flow through conduit 16 into a condenser 18 and from there the condensed liquids flow into reflux tank 20. A pipe line having a valve 22 leads from the tank 20 back to the scrubber 14. By suitable adjustment of the valves 22 and a valve 24 in the discharge line a portion of the distillate is returned as scrubbing fluid to scrubber 14 and the critical 0.2 to 0.4% per minute on the average of the distillate is removed from the system through conduit 26. As the distillation process continues the temperature of the charge is increased to 800–900° F.

The importance of maintaining the critical rate of distillate separation is illustrated by the graph of Fig. 2. Fig. 2 illustrates the dependency of C_I content upon rate of removal of distillate. It will be noted that as removal increases above an average of about 0.4 volume per cent per minute, the C_I content drops off rapidly below the minimum requirement of 8%. The graph further illustrates that the optimum distillate removal rate is about 0.2% per minute.

Fig. 3 compares viscosities of the product of this invention with those of a standard coal tar pitch, the product of this invention taken as representative being a pitch having a C_I content of 9.7, a C_{II} content of 35.4 and a melting point of 101.

In the following example are set forth representative runs which illustrate the interrelation between the critical process conditions and the nature of the product.

Example 1

Run No.	Rate vol. percent distillate removal/min.	Vol. percent distillate total removal	Percent C _I content	Percent C _{II} content	Softening pt. (° C.)	Coking value, percent
20	0.37	55	12.8	33.5	113.7	34.9
21	0.25	50	8.1	32.4	94.9	36.3
24	0.20	55	9.7	35.4	101	37.9
26	0.20	58	11.7	43.7	111.5	39.5
27	0.20	55	8.0	39.1	85.2	35.4
29	0.20	57	9.0	42.4	118	40.2
30	0.20	56	9.3	36.8	93.4	33.8
Coal Tar 1			15.9	24.9	95	41
Coal Tar 2			16.5	21.3	72	39.1
Coal Tar 3			18.9	21.4	116.8	46.7

In the following examples are compared three pitches, pitch A being a typical pitch of our invention, pitch B being a typical coal tar pitch and pitch C being the residue from the bottom of a refinery vacuum still. The performance of these pitches in electrodes is likewise shown in the example.

Example 2

	Pitch		
	A	B	C
Softening point.....	112	110	110
C _I content.....	12	16	6
C _{II} content.....	36	32	17
Coking value.....	39.5	44	37
Percent ash.....	.05	.08	.05
Specific gravity.....	1.28	1.30	1.20

	Electrode		
	A	B	C
Apparent density (green).....	1.55	1.56	1.45
Apparent density (baked).....	1.42	1.48	1.35
Electrical resistivity (ohm inches).....	0.00322	0.00283	0.010
Compression failure test (lbs. per sq. in.).....	3,700	4,000	2,800

It will be apparent that by our novel process we are able to produce from petroleum residues, themselves lacking in the necessary qualities, pitches having the very desirable properties above discussed. Just why these results can be achieved is not fully understood since the fractions labeled C_I and C_{II} have never been fully analyzed. We reason from observation that during the distillation and refluxing of the major proportion of the distillate the petroleum undergoes extensive polymerization so that a portion of the charge is converted to C_I and C_{II} components while

noncontributing fractions are slowly removed. It is clear to us that the removal rate of the distillate is exceedingly critical and that the percentage of total distillate removed is likewise critical. Also we have found that the process can be successfully carried out only when starting with a raw material falling within the defined specifications.

Having thus disclosed our invention and described in detail an illustrative procedure for carrying it out, we claim as new and desire to secure by Letters Patent:

1. A process for the production of pitch from petroleum residues, which comprises the steps of distilling a measured charge of petroleum residue while agitating the charge, withdrawing distillate at the average rate of about 0.2 to 0.4% per minute of the volume of the original charge and continuously refluxing the remainder of the distillate to the charge, continuing distillation until 40% to 50% of the volume of the original charge remains, and drawing off the remaining material as the pitch product with a content not below 8% of hydrocarbons insoluble in nitrobenzene and a content not below about 20% of hydrocarbons soluble in nitrobenzene but insoluble in acetone.

2. The process of claim 1 in which the petroleum residue charge has a hydrogen/carbon ratio in the range 1 to 1.15 and a mean molecular weight in the range 300 to 400.

3. A process for the production of pitch having a content of at least about 8% of hydrocarbons insoluble in nitrobenzene and a content of at least 20% of hydrocarbons soluble in nitrobenzene but insoluble in acetone and a softening point below 120° C. from petroleum, which comprises the steps of heating a charge of a petroleum residue having an H/C ratio in the range 1 to 1.15 and a mean molecular weight in the range 300 to 400 to distillation temperatures, distilling the charge, withdrawing distillate at the average rate of 0.2 to 0.4% per minute of the volume of the original charge and continuously refluxing the remainder of the distillate to the charge, continuing distillation until about 40 to 50% of the original charge remains, and removing the remaining material as the pitch product of the process.

4. The process of claim 3 in which the distillate is withdrawn at the average rate of about 0.20% of the volume of the original charge.

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