Oct. 23, 1956 M. E. NASH 2,768,119

PITCHES FROM PETROLEUM AND PROCESS FOR PRODUCING SAME

Filed Dec. 31, 1952

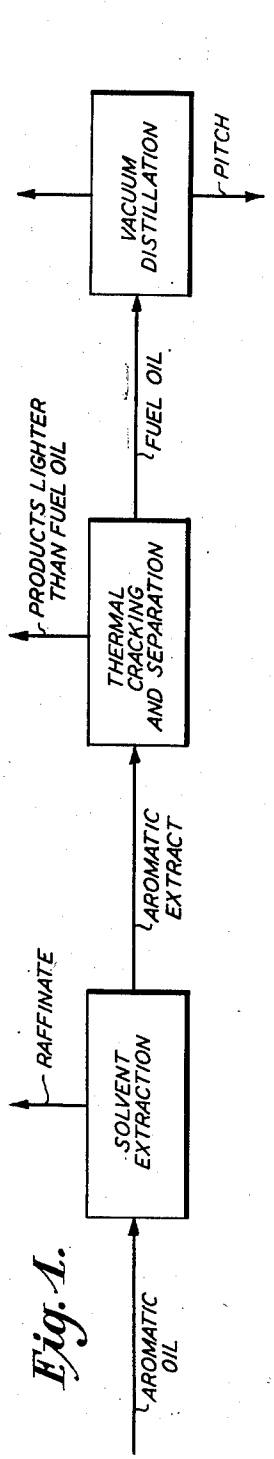


Fig. 1.

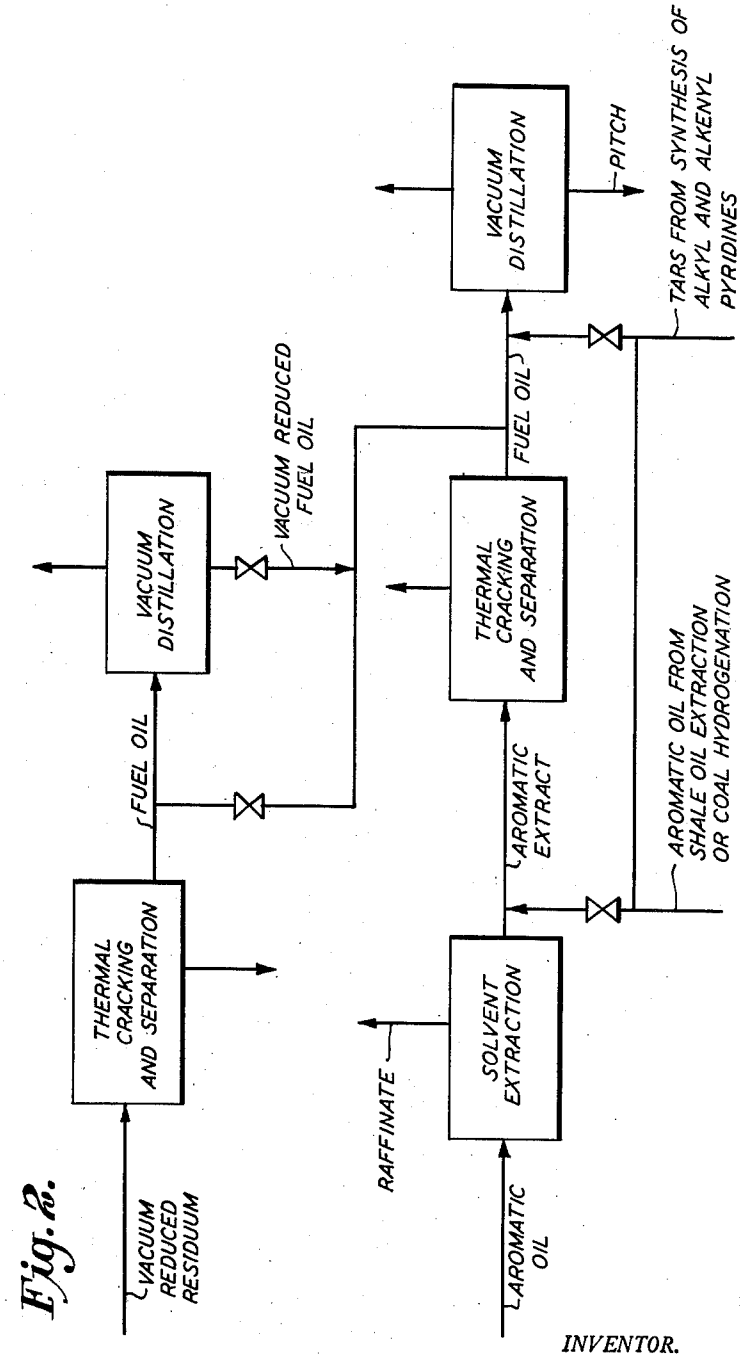


Fig. 2.

INVENTOR.
M. E. Nash

BY
Hudson and Young
ATTORNEYS

United States Patent Office

2,768,119

Patented Oct. 23, 1956

2,768,119

PITCHES FROM PETROLEUM AND PROCESS FOR PRODUCING SAME

Martin E. Nash, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

Application December 31, 1952, Serial No. 328,989

9 Claims. (Cl. 196—14.11)

This invention relates to the production of improved petroleum pitches having properties similar and, in many instances, superior to the properties of coal-tar pitches. In one of its aspects the invention relates to the production of a petroleum pitch from an aromatic oil. In another of its aspects the invention relates to the production of a petroleum pitch from an aromatic oil derived from an oil containing aromatics by solvent extraction of said oil, for example, employing sulfur dioxide as a solvent. In yet another aspect the invention relates to the production of an improved petroleum pitch by thermally treating an aromatic oil, for example, an aromatic extract to produce a fuel oil which is reduced to a suitable pitch product by distillation, preferably vacuum distillation. In still another aspect of the invention there is produced a petroleum pitch by vacuum reduction or distillation of an admixture of a fuel oil derived from a thermally cracked aromatic oil and a fuel oil derived from a thermal cracking of a reduced residuum, for example, a vacuum reduced residuum or fuel oil. In yet another of its manifold aspects the invention relates to the pitch-like products obtained according to a process according to the invention.

It is among the several objects of this invention to produce coal-tar pitch-like product entirely from petroleum, from an aromatic feed stock, alone, or from such a feed stock and a conventional feed stock. Other objects and advantages of a process and a product according to the invention will become apparent from a study of this disclosure, the drawing and the appended claims.

Coal-tar pitch has long been considered superior to petroleum pitch for certain uses, because the former possesses a combination of properties not normally found in the latter. The most important of these properties are low softening point combined with very low penetration at temperatures below and approaching the softening point, i. e., sharp melting point rather than gradual softening with increasing temperature.

I have now found that petroleum pitches having properties equal or superior to those of coal-tar pitch can be produced from certain selected feed stocks by vacuum distillation. The feed stocks must be highly aromatic in nature, and can be prepared by conventional solvent extraction processes with solvents such as SO_2, phenol, Chlorex,[1] furfural and the like, followed by thermal cracking of the solvent-free extract. In certain cases satisfactory feed stocks can be prepared by admixing such highly aromatic oils with fuel oils obtained upon vacuum distillation of the products of thermal or catalytic cracking of other high boiling oils in conventional refinery operations. In some instances, depending upon the character of the fuel oil before it is vacuum distilled, some or all of it can be admixed advantageously with the cracked aromatic extract before it is vacuum distilled.

Thus, according to the invention there are provided new coal-tar pitch-like products produced entirely from petroleum and a process for producing the same which comprises thermally cracking an oil essentially aromatic in character and then vacuum distilling a fuel oil thus obtained to produce a desired product. In a more preferred modification of the invention there is blended with

[1] 2,2'-dichlorodiethyl ether.

the fuel oil, prior to its vacuum distillation, a fuel oil obtained by thermally cracking a residuum oil. The said last fuel oil can be admixed as such or it can be vacuum distilled before it is admixed. In variations of either of the embodiments of the invention which have been disclosed to this point there can be admixed with the feed to the thermal cracking of the essentially aromatic petroleum oil aromatic oils derived from shale oil extraction processes or coal hydrogenation processes. Also, to the fuel oil obtained from the cracking of aromatic oils according to the invention there can be added, prior to the vacuum distillation step, tars produced in the synthesis of alkyl and alkenyl pyridines or such tars can be at least in part blended with the feed to the thermal cracking of the aromatic oil. In some instances it is possible, depending upon the character of the oils derived from shale oil and the other sources here discussed to have these oils constitute the essentially aromatic oil which is cracked thermally to produce the fuel oil which is then treated as above described.

The relative proportions of cracked aromatic oil and cracked vacuum reduced residuum oil, or other oils which are admixed in the process of the present invention, will be different for optimum results for different feed stocks of each type and can be determined by mere routine test by one skilled in the art of producing pitches in possession of the disclosure of the combination of steps of the present invention. As a guide, the cracking of the aromatic oil or extract can be accomplished at a temperature in the range 900° F. to 1050° F.; a pressure in the range 10 p. s. i. g. to 1000 p. s. i. g.; and a time, on a once-through basis, sufficient to produce a fuel oil desirable as a feed stock to the vacuum reduction, for example in the range 30 seconds to 300 seconds; and the fuel oil obtained therefrom by usual fuel oil separation procedures. The conditions for vacuum distilling a fuel oil according to the invention are substantially those which have been employed heretofore in vacuum distilling of other oils. Of course, the pressure is always to be as low as practicable and the temperature as high as practicable. At a pressure of about 1 mm. Hg, a temperature in the range 440° F. to 650° F. has yielded pitch products according to the invention. The distillation or reduction is effected for a time sufficient to obtain the properties desired. Clearly, the essence of the present invention lies in the combination of steps as disclosed and described.

The two embodiments of the invention above discussed are illustrated in the attached drawing. Figure 1 shows the production of pitch from a highly aromatic fuel oil obtained by thermal cracking of the aromatic extract from an SO_2 extraction process. The feed to the SO_2 extraction step is an aromatic gas oil. The final vacuum distillation step can be carried out at a pressure of 1 mm. Hg and a temperature of about 440° F., producing a pitch having the following properties: (Properties of a typical coal-tar pitch of comparable softening point are given for comparison.)

	Pitch prepared from SO_2 extract oil	Coal-tar pitch
Softening point, ° F	188	189.4
Specific gravity	1.1966 (60/60)	1.291 (15.6°C.)
Solubility CS_2	99.72%	
Solubility CCl_4	98.38%	
Solubility n-pentane	37.5%	
Penetrations (100 g., 5 sec.) (standard needle):		
77° F	0	0
100° F	0	0.5
115° F	0	7
130° F	4	36
150° F	48	88

Thus it is apparent that the pitch produced by the process of this invention is superior to the typical coal-tar pitch in having lower penetration values at temperatures approaching the softening point.

The properties of other samples of pitch prepared in like manner, but at higher flash temperatures, are shown in the following tabulation:

	Pitches from Vacuum Reduction of Fuel Oil from Thermal Cracking SO_2 Extract Oil				
Pressure, mm.	1	1	1	1	1
Temperature, ° F.	490	535	-------	565	650
Softening Point, ° F.	210	240	251	277	329
Sp. Gr. at 60/60	1.1970	1.2010	1.2095	1.2029	1.2158
Sol. CS_2	99.68	99.71	99.35	99.69	99.65
Sol. CCl_4	98.13	97.66	96.91	96.62	92.22
Sol. n-pentane	29.9	21.7	-------	13.7	5.5
Penetrations (5 sec., 100 g.):					
77	0	0	0	0	0
100	0	0	0	0	0
115	0	0	0	0	0
130	0	0	0	0	0
150	4	0	0	0	0

The pitches produced according to the invention will have softening points in the approximate range 150° F.–450° F., preferably 185° F.–330° F. as indicated by the tables herein. The specific gravity of such a pitch will be in the approximate range 1.11–1.30 or higher, depending to some extent on the source of the charge stocks.

Figure 2 of the drawing shows an alternative process whereby petroleum pitch may be improved in properties by adding to the conventional petroleum pitch producing feed stock a thermally cracked fuel oil obtained from an aromatic SO_2 extract oil, thereby increasing the aromatic hydrocarbon content of the feed to the final vacuum flash. In the following table are shown (column 1) the properties of a pitch produced in this manner from a 50–50 blend of thermally cracked fuel oil and thermally cracked SO_2 extract oil. In column 2 are shown the properties of a pitch of the same softening point prepared from the conventional feed stock (no aromatic extract oil added).

	1	2
Softening point, °F.	245	245
Specific gravity	1.1369	1.1138
Solubility in CS_2	99.60	99.11
Solubility in CCl_4	93.72	95.11
Penetration (5 sec., 100 g.):		
77° F.	0	0
100° F.	0	0
115° F.	0	1
130° F.	0.5	2
150° F.	1.0	7
77° F. (30 sec., 200 g.)	0.5	1
Volatile Combustible Matter	64.1	67.1
Fixed Carbon	35.8	32.8
Total Sulfur, wt. percent	0.91	1.07

It is at once noted that the pitch of column 1, according to the invention, shows a considerable improvement in penetration resistance as the temperature is increased. In other respects the pitches are comparable.

It is also within the scope of this invention to prepare the improved pitches by blending a pitch prepared as shown in Figure 1 with a pitch prepared from conventional petroleum pitch producing feed stocks. This blending operation is preferably carried out by admixing the two products as they leave the final vacuum flash steps in the liquid state.

The invention also contemplates admixing a highly aromatic oil with the conventional feed to a thermal cracking step, thermally cracking the admixture in a single zone rather than separately as in Figure 2, and producing an improved pitch by vacuum flashing of the resulting fuel oil.

Among the valuable industrial uses for which the pitches of this invention are suited may be mentioned coal briquetting, making electrodes for aluminum refining, and the manufacture of certain types of pressed board products.

The term "fuel oil" as employed herein is intended to include any liquid or liquefiable petroleum product obtained from the products of thermal cracking and similar refinery operations. In some instances the fuel oils employed in my process can be viscous liquids or even solids at ordinary temperatures.

As can be noted from the above disclosure, one skilled in the art will understand that the invention produces pitches entirely from petroleum oils or related oils and not by oxidation processes. Herein and in the claims, the term "non-oxidized" is intended to distinguish the pitches of the present invention from the oxidized soft fluxes of the prior art which are made in said art by oxidizing said fluxes in air at an elevated temperature.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, drawing and the appended claims to the invention, the essence of which is that coal-tar-pitch-like improved pitches from petroleum have been produced by thermally cracking an aromatic oil and then vacuum reducing a fuel oil obtained from said cracking operation, as described.

I claim:

1. The production of a petroleum pitch having a softening point in the approximate range 185° F.–330° F., which comprises cracking an essentially aromatic oil at a temperature in the range 900° F. to 1050° F., under a pressure in the range 10–1000 p. s. i. g. for a time in the range 30 to 300 seconds sufficient to produce a fuel oil suitable as a feed to a vacuum reduction, recovering said fuel oil and distilling same at a pressure of the order of 1 mm. mercury at a temperature in the range 440–650° F. so as to obtain a pitch having a normal pentane solubility not greater than 37.5 percent.

2. A production according to claim 1 wherein there is admixed with said aromatic oil extract an aromatic oil derived from at least one of shale oil, coal hydrogenation and the production of pyridines.

3. A production according to claim 1 wherein there is admixed with said fuel oil prior to vacuum distillation thereof a fuel oil obtained by thermal cracking of a reduced crude oil.

4. A production according to claim 3 wherein the fuel oil derived by thermal cracking of a reduced crude is obtained by cracking a vacuum reduced crude.

5. A production according to claim 3 wherein the fuel oil obtained from the reduced crude is vacuum distilled before it is admixed with the fuel oil derived by cracking said aromatic oil extract.

6. The production of a petroleum pitch having a softening point in the approximate range 185° F.–330° F. which comprises extracting an aromatic gas oil with sulfur dioxide to obtain an aromatic oil extract; cracking said aromatic oil extract at a temperature in the range 900° F. to 1050° F., under a pressure in the range 10–1000 p. s. i. g. for a time in the range 30 to 300 seconds sufficient to produce a fuel oil suitable as a feed to a vacuum reduction, recovering said fuel oil and distilling same at a pressure of the order of 1 mm. mercury at a temperature in the range 440–650° F. so as to obtain a pitch having a normal pentane solubility not greater than 37.5 percent.

7. A production according to claim 6 wherein there is admixed with said fuel oil a fuel oil obtained by thermally cracking a vacuum reduced residuum oil.

8. A production according to claim 7 wherein the fuel oil derived from said residuum is vacuum distilled before it is admixed with the fuel oil derived from said aromatic extract.

9. A non-oxidized coal-tar-pitch-like pitch obtained solely from petroleum oils by treatment thereof, said pitch having a softening point in the approximate range 185° F.–330° F., a specific gravity of at least approximately 1.11, a normal pentane solubility in the range of about

5.5 to 29 percent, and a penetration at 115° F. and at 150° F. (5 seconds with 100 grams standard needle) of zero.

References Cited in the file of this patent

UNITED STATES PATENTS

1,643,521	Reeve	Sept. 27, 1927
2,024,106	Levin	Dec. 10, 1935
2,068,845	Collins	Jan. 26, 1937
2,093,450	Jacobsohn	Sept. 21, 1937
2,128,885	Poole	Aug. 30, 1938
2,266,360	Edwards	Dec. 16, 1941
2,278,671	Roediger	Apr. 7, 1942
2,400,067	Best et al.	May 14, 1946
2,409,437	La Crosse	Oct. 15, 1946
2,662,051	Pelzer	Dec. 8, 1953
2,691,621	Gagle	Oct. 12, 1954

OTHER REFERENCES

Abraham: "Asphalts and Allied Substances," fourth ed., pp. 227 and 237 and table facing p. 453. Publ. by D. Nostrand Co., New York, New York, 1938.