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2,991,241

PROCESS FOR THE PRODUCTION OF PITCH COMPRISING HEATING AND CONCURRENTLY AIR-BLOWING THE BOTTOMS OF A DISTILLED CATALYTICALLY CRACKED GAS OIL**Jack F. Renner, Calumet City, Ill., assignor to Sinclair Refining Company, New York, N.Y., a corporation of Maine****No Drawing. Filed Sept. 11, 1957, Ser. No. 683,223
6 Claims. (Cl. 208-4)**

This invention relates to a method of producing a petroleum base pitch and more particularly to the production of a novel petroleum base pitch having physical characteristics more comparable to coal tar pitch than conventional petroleum asphalts and pitches.

With the development of new applications in recent years for coal tar products there has consequently been created an increasing demand for salable coal tar pitch. However, most coal tar products plants in the United States are operated by steel companies and the pitch produced by the distillation of coal tar is utilized by these companies as fuel for their open hearth furnaces. Consequently, of the total volume of coal tar produced in the country only a very small percent is available as salable pitch. To meet the increasing demand for coal tar pitch attempts have been made to find a petroleum pitch comparable in all respects to coal tar pitch. Investigations have proved fruitless particularly in uncovering a petroleum pitch possessing the low needle penetration, low molten viscosity and high insolubility in benzene, naphtha and kerosene that characterizes the coal tar pitches.

It has now been found that a homogeneous petroleum base pitch that compares favorably with coal tar pitch may be produced by heating at a temperature of about 300 to 650° F., a feedstock composed of petroleum bottoms obtained from distilling a cracked oil produced by catalytic cracking processes, simultaneously subjecting the feedstock to a blowing operation with an oxygen-containing gas and concurrently or subsequently removing unreacted wax and oil components. The effect of my novel process is the condensation or polymerization of aromatic material present in the feedstock to form higher molecular weight ring compounds that subsequently yield the pitch material of my invention. A petroleum pitch produced in this manner is found to exhibit physical characteristics markedly similar to those of coal tar pitch. In addition to high insolubility in benzene and petroleum naphtha, the pitch displays low penetration and low molten viscosity.

The feedstock of my invention must possess certain specific properties to yield a suitable pitch. An ideal feedstock would be composed substantially completely of aromatic ring compounds with little or very slight side chain substitution and a minimum molecular weight of 190. However, all commercially available feedstocks contain other components such as paraffins and non-reactive naphthenes and aromatics which tend to hinder pitch production and should for that reason, be removed as a part of the processing sequence. If the latter materials are not removed, a non-homogeneous, valueless material is produced.

Feedstocks suitable for this process are characterized by the following approximate properties:

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Gravity, ° API (ASTM D287-55)	max.	18.0
Flash, ° F. (ASTM D92-52)	min.	200
Average molecular weight	min.	190
Initial boiling point, ° F.	min.	400
Chromatographic analysis:		
Saturates, wt. percent	max.	50
Aromatics and polar compounds, wt. percent	min.	50
Aromatic fraction: Average molecular weight	min.	190
Hazelwood ring analysis—		
Average No. of rings per molecule	min.	3.5
Average No. of aromatic rings per molecule	min.	3.0
Average No. of naphthenic rings per molecule	max.	1.0
Average No. of carbon atoms in aromatic ring structure	min.	13.0
Average No. of carbon atoms in naphthenic rings and paraffin side chain structures	max.	5.0

A petroleum refinery stock found to meet all of these requirements and yield a suitable pitch is the bottoms fraction obtained by the distillation of the cracked oil produced from the catalytic cracking of petroleum gas oils in the presence of catalyst such as the silica-alumina catalysts. In such processes, the catalyst usually comprises about 65 to 95% silica and 5 to 35% alumina and is frequently employed in the fluidized state.

The cracked oil produced as a result of the fluid catalytic cracking process is then subjected to distillation at about 7 to 25 p.s.i. pressure to a maximum temperature of about 650 to 750° F. The residue or distillation bottoms obtained as a consequence of the above distillation process are transferred to a slurry settler for removal of catalyst and the resultant oil has been found to be a suitable refinery stock for the production of my novel petroleum base pitch. This petroleum bottoms fraction will be hereafter referred to as fluid unit clarified oil and the novel petroleum pitch produced as clarified oil pitch. Although the present invention will be described with reference to the employment of fluid cracking unit clarified oil as the suitable feedstock, any petroleum feedstock meeting the property requirements set forth above may be used. Typical tests on satisfactory fluid unit clarified oils are shown below:

		Tests on clarified oil
Gravity, ° API (ASTM D287-55)	4.5-12.5	
Flash, ° F. (ASTM D92-52)	375-315	
Fire, ° F. (ASTM D92-52)	450-420	
Viscosity at 210° F., SSU (ASTM D88-53)	40-40	
Aniline point, ° C. (ASTM D611-55T)	45-70	
Molecular weight	280-330	
Boiling range (90% distilled), ° F.	500-1000	
Chromatographic analysis:		
Paraffins, wt. percent	23.0-38.0	
Polar compounds, wt. percent	2.0-2.0	
Aromatics, wt. percent	75.0-60.0	
Tests on aromatic fraction—		
Refractive index, 20/D	1.68-1.66	
Density, 20/4° C.	1.12-1.09	
Molecular weight	250-280	
Hazelwood ring analysis—		
Average No. of rings per molecule	4.4-4.2	
Average No. of aromatic rings per molecule	3.7-3.6	
Average No. of carbon atoms per molecule	20.8-19.0	
Average No. of carbon atoms in ring structure	19.6-18.2	
Average No. of carbon atoms in aromatic ring structure	16.8-16.2	

Chromatographic analysis of various fluid unit clarified oil feedstocks show them as characterized by an aromatic content ranging from 50 to 75 weight percent of these feedstocks; best yields being obtained from those possessing the highest aromatic content. The aromatic content of the clarified oils has been found to be dependent to some degree on fluid unit conversion levels (yield of 400 E.P. gasoline). For example, at 78.5% conversion pitch yield from the resultant clarified oil is 59.0%;

whereas at 60% conversion yield is 45.0%. Generally speaking the cracking unit must be operated at a minimum 50% conversion (50% yield at 400 E.P. gasoline) to yield a clarified oil that is an economical feedstock for my process.

Although a large variation is found in the aromatic content of the many fluid unit clarified oils, ring analyses of the aromatic fractions from both the clarified oils and their respective distillation cuts indicate very slight differences in composition. The average molecular structure by Hazelwood ring analyses, Analytical Chemistry 26, 1073 (1954) of the aromatic fractions from clarified oils has been found to contain about 3.5 to 3.7 aromatic rings, 0.4 to 0.7 naphthenic ring, and 0.5 to 1.3 carbon atoms attached to the ring structure. Thus, the aromatic fractions are characterized as containing condensed ring molecules with slight side chain substitutions.

In carrying out the present invention a clarified oil meeting the property requirements set forth above is heated at a temperature of about 300 to 650° F., preferably about 350 to 600° F., and simultaneously oxidized by means of a blowing operation with an oxygen-containing gas like air to aid in the polymerization and condensation of the aromatic fraction contained in the clarified oil. The unreacted lower molecular weight materials are removed concurrently or subsequently by steam stripping, vacuum distillation or solvent (e.g. propane, butane, pentane, etc.) extraction. However, concurrent air blowing and steam distillation has been found to be the most economical modification. A petroleum base pitch is formed which exhibits low solubility in petroleum solvents, low molten viscosity and low needle penetration at 77° F.

In this process the air blowing temperatures do not markedly affect the product quality, but do affect the processing time, that is greater temperatures require less time. An air rate of about .01 to 5.0 cubic feet per hour per pound of clarified oil is a satisfactory operating range. Higher temperatures result in substantial feed stock carry-over, and the reaction rate is too slow below 350° F. The air oxidation may be effected in either a batch or continuous oxidation unit. In the case of batch operations, the steam stripping of the unreacted material may be carried on simultaneously or subsequently to the blowing operation. If a continuous oxidation process is used, removal of the unreacted material could occur subsequent to the blowing operation. The fluid clarified oil feed should be of sufficient molecular weight (above about 190) so that it will not distill overhead during the oxidation process.

The following example will further illustrate my invention, but it is not to be considered limiting.

EXAMPLE

One thousand barrels of fluid unit clarified oil possessing the physical properties described above is charged to a gas-fired blowing still. The oil is heated to 500–550° F. and initially air blown for 3 to 4 hours with air supplied by a 2000 s.c.f.m. blower at a rate of one cubic ft./hour/lb. of charge. Following the initial oxidation the air rate is lowered to about 0.2 cubic foot/hour/lb. of charge and steam admitted to the still at the rate of 0.75 pound per 1.0 pound of overhead oil for stripping the pitch of undesirable wax-oil components representing approximately 50 weight percent on charge. The steam and vaporized oil are taken overhead at approximately 500° F. and passed through a condenser. The condenser can possibly be controlled to prevent emulsification of the oil and condensed steam. However, a gas-fired 1000 barrel holding tank is provided to vaporize the water if an emulsion forms. The air-steam mixture then passes through a spray condenser for condensation of remaining light hydrocarbons and steam. If desired, subsequent to the stripping operation,

the air rate can be increased to one cubic foot/hour/lb. of charge, and the resultant soft pitch blown to any required specifications. The minimum softening point of the pitch is about 100° F. and preferably about 150° F.

Typical tests on the resultant pitch and overhead oil are as follows:

Yield of clarified oil, wt. percent:	
Pitch.....	41.2
Overhead oil.....	53.0
Experimental loss.....	5.8
Tests on pitch:	
Specific gravity, 77° F./77° F.....	1.1579
Softening point (R. & B.), ° F.....	171.5
Needle penetration at 77° F., 100 gm./5 sec.....	2
Needle penetration at 115° F., 50 gm./5 sec.....	13
Needle penetration at 140° F., 50 gm./5 sec.....	103
Viscosity at 350° F., SFS.....	22.2
Viscosity at 300° F., SFS.....	90.0
Insoluble in benzene, wt. percent.....	8.5
Insoluble in 86° naphtha, wt. percent.....	86.1
Carbon residue (con.), wt. percent.....	32.1
Ash, wt. percent.....	1.58
Sulfur, wt. percent.....	53.0
Tests on overhead oil:	
Overhead oil yield, wt. percent.....	13.0
Gravity, ° API.....	59.4
Viscosity at 130° F., SUS.....	36.4
Viscosity at 210° F., SUS.....	54.6
Aniline point, ° C.....	262
Molecular weight.....	35.0
Eby chromatography—	
Paraffins, wt. percent.....	3.6
Resins, wt. percent.....	61.4
Aromatics, wt. percent.....	1.6579
Tests on aromatic fraction—	
Refractive index, 20/D.....	1.0794
Density, 20/4° C.....	200
Molecular weight.....	

As shown in Table I below, there is a marked similarity between coal tar pitch and the clarified oil pitch produced by the process of my invention.

Table I

COMPARISON OF THE PHYSICAL PROPERTIES OF CLARIFIED OIL PITCH, COAL TAR PITCH AND BLOWN ASPHALT

	Clarified Oil Pitch	Coal Tar Pitch	Blown Asphalt
Specific gravity, 77° F./77° F.....	1.1579	1.1605	1.0190
Softening point (R. & B.), ° F.....	172	187	178
Needle penetration at 77° F.....	2	0	26
Needle penetration at 115° F.....	13	0	49
Needle penetration at 140° F.....	103	37	
Viscosity at 300° F., SFS.....	90	164.9	
Viscosity at 350° F., SFS.....	22	34	199.6
Insolubles in benzene, Wt. percent.....	8.5	36.9	0.4
Insolubles in 86° naphtha, Wt. percent.....	86.1	94.5	33.0
Insolubles in kerosene, Wt. percent.....	59.7	72.7	38.8
Insolubles in carbon disulfide, Wt. percent.....	4.5	23.9	0.7
Conradson carbon residue, Wt. percent.....	32.1	52.4	22.8
Iodine number.....	77.8	83.2	33.4

The pitch yielded by my invention exhibits high insolubility in petroleum fractions, vegetable oils and aromatic solvents as compared to normal petroleum asphalts and pitches. The pitch gives about a 5% maximum overhead when distilled to 640° F. and preferably this is about 1%. These physical characteristics make it particularly suitable for use as a fuel resistant airport paving cement, a fuel resistant pipe coating enamel, a fiber pipe impregnant, a saturant for weatherboard, siding and insulating board, a rubber plasticizer, a sandmold binder, a molding compound, an additive for paints and a waterproofing compound. It is to be understood that the clarified oil pitch of the invention is not limited to the above applications but may also be employed anywhere coal tar pitch has been used or wherever its novel physical properties offer advantageous results.

I claim:

1. A process for producing a petroleum base pitch which comprises heating at a temperature of about 300 to 650° F. a petroleum bottoms feedstock obtained from the distillation of the cracked oil produced by the catalytic

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cracking of petroleum gas oils, said feedstock having the following approximate properties:

Gravity, ° API (ASTM D287-55).....	max..	18.0
Flash, ° F. (ASTM D92-52).....	min..	200
Average molecular weight.....	min..	190
Initial boiling point, ° F.....	min..	400
Chromatographic analysis:		
Saturates, wt. percent.....	max..	50
Aromatics and polar compounds, wt. percent.....	min..	50
Aromatic fraction—		
Average molecular weight.....	min..	190
Hazelwood ring analysis—		
Average No. of rings per molecule.....	min..	3.5
Average No. of aromatic rings per molecule.....	min..	3.0
Average No. of naphthenic rings per molecule.....	max..	1.0
Average No. of carbon atoms in aromatic ring structure.....	min..	13.0
Average No. of carbon atoms in naphthenic rings and paraffin side chain structures.....	max..	5.0

while simultaneously subjecting said feedstock to an air blowing operation, and removing by distillation the unreacted lower molecular weight components from the pitch obtained to produce a homogeneous petroleum-base pitch giving a maximum overhead of about 5% when distilled to 640° F.

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2. The process of claim 1 wherein the petroleum bottoms feedstock is obtained from the distillation of the cracked oil produced by the fluid catalytic cracking of petroleum gas oil.

3. The process of claim 1 wherein the heating is conducted at a temperature of about 350 to 600° F. and the air blowing rate about .01 to 5.0 cubic feet per hour per pound of feedstock.

4. The process of claim 1 wherein unreacted wax and oil components are removed by steam distillation.

5. A petroleum base pitch produced by the method of claim 1.

6. A petroleum base pitch produced by the method of claim 2.

References Cited in the file of this patent

UNITED STATES PATENTS

2,068,845	Collins	Jan. 26, 1937
2,767,102	Edson	Oct. 16, 1956
2,862,867	Rehner et al.	Dec. 2, 1958