United States Patent Office

3,488,277

Patented Jan. 6, 1970

3,488,277

PROCESS FOR PREPARING MINERAL OIL-DERIVED PITCH

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No Drawing. Filed Feb. 28, 1967, Ser. No. 619,147
Int. Cl. C07c 3/08; F16l 9/14
U.S. Cl. 208—4 14 Claims

ABSTRACT OF THE DISCLOSURE

A mineral oil-derived pitch suitable, for instance, for impregnating fibrous and other materials, is prepared by the process of solvent extracting clarified oil to obtain an intermediate pitch product having a penetration of about 10–300 at 77° F. and then blowing the intermediate to a lower penetration suitable for a given utility of the product. In a preferred specific aspect, a fiber pipe having superior strength and corrosion resistance is prepared by impregnating a fiber pipe with a pitch prepared by the instant process and having a needle penetration of about 0–2 at 77° F.

This invention relates to a novel procedure for making a mineral oil-derived pitch suitable, for instance, for impregnating fibrous and other materials. The invention further pertains to novel pitches made by the new process and fiber pipe impregnated therewith.

It is known in the art to impregnate various fibrous materials such as cardboard or fiber pipes with substances such as wax, asphalt or coal tar pitch to render the fibrous materials more waterproof and resistant to abrasion or corrosion. It has now been found that an impregnant having superior properties may be prepared by blowing a product separated from clarified oil by solvent extraction using a paraffinic solvent.

Clarified oil is the bottoms derived from gasoline-producing catalytic cracking process. The clarified oil may be the residual oil produced as a result of the cracking of suitable mineral oil cracking feedstocks such as gas oils in the presence of catalysts such as silica-alumina, crystalline aluminosilicate or other catalysts, usually silica-based cracking catalysts, which are frequently employed in the fluidized state. In distillation of the cracked oil, generally at about 7 to 25 p.s.i. pressure, to a maximum or end point of about 650 to 750° F., to obtain gasoline and gas oils overhead, there is produced a heavy residue or distillation bottoms containing entrained catalyst. To remove the catalyst, the residue is usually permitted to remain quiescent for a sufficient period of time to allow the catalyst particles to settle out, at which time the residual oil, substantially free of catalyst, may be decanted. In lieu of settling, the catalyst particles may be filtered or centrifuged from the oil, or such operations may be used in conjunction with settling.

In any case, there is obtained a clarified slurry oil, often referred to in the art as clarified oil. Clarified oil feeds suitable for production of the pitch of the present invention boil primarily in the range of about 400 to 1000° F. and may have a 5 volume percent distillation point of at least about 500° F. or even about 600° F. and 95 volume percent distillation point of at least about 800° F. with at least 100° F. units or even at least about 200° F. units, separating the 5 percent distillation point and the 95 percent distillation point. The clarified oil feed for solvent extraction can be the full range clarified oil, that is, the entire bottoms obtained as aforementioned by the distillation of the oil from the cracking unit or it can be suitable bottoms fractions of the full range clarified oil, for example, a bottoms fraction having a 5 volume percent distillation point of below about 700° F. obtained, for instance, by vacuum distillation of the clarified oil to about 50%, and usually not less than about 25% bottoms. It is preferred that the cracking unit from which the clarified feed is obtained be operated at at least 50 percent conversion. Also for reasonable yields of pitch it is preferred that the clarified oil feed have an API gravity of up to about 25.

The clarified oil feed is solvent extracted to provide an intermediate pitch as a raffinate or bottoms phase, an upper extract phase containing solvent and deasphalted oil being produced. Separation of the upper phase provides the intermediate pitch of the invention, usually after any solvent in the raffinate is removed. Solvents suitable for use in the extraction are paraffin hydrocarbons such as lower alkanes, for example, C_3 to C_5 paraffins, especially normal paraffins, with propane being preferred. Any solvent remaining in the pitch separated can be removed by simply heating at an elevated temperature generally about 300° F. for a few minutes.

The solvent to oil ratios and temperatures employed in the extraction may vary depending, for example, on the boiling range of the clarified oil feed, the solvent selected and the purpose for which the ultimate pitch product is intended, but in any event are selected to provide an intermediate pitch product having a penetration (ASTM D5–65) at 77° F. up to about 300 and often in the range of about 10 and 300, preferably about 40–300. Additionally it is preferred that this pitch also have the following approximate properties:

Flash, COC, ° F., 450° F. minimum
Specific Gravity at 60° F., 1.159 minimum
Vis. SUS at 210° F. maximum values vs. penetration

Viscosity	Penetration
900	40
550	120
400	200
340	250
250	300

Generally, the solvent to oil volume ratios employed in the extraction will be at least about 2, preferably about 3 to 15:1, and the temperature utilized for the extraction will often range from about 130° F. to 200° F. Although a single extraction may provide the desired pitch, a number of extractions may be employed. Ordinarily the solvent extraction conditions are those which reduce the clarified oil to at least about 5% bottoms or raffinate, generally about 5 to 50% bottoms, based on the full range clarified oil. In cases where a select bottoms fraction of the full range clarified oil is solvent extracted, the percent bottoms based on the select fraction may, of course, be greater than 50% and may be up to about 85% or more.

Following the extraction operation, the intermediate pitch is blown sufficiently to produce an additional decrease in penetration value of at least about 25%, preferably at least about 50%. Blowing can be effected by employing a suitable oxygen-containing gas, usually air, at about 350–550° F., preferably about 400 to 525° F. The amount of gas employed can vary as known in the art of air blowing, for instance, a convenient amount is about 1 to 4 cubic feet per hour per pound of pitch being treated. The rate at which this gas is introduced will affect the length of time required to blow the pitch to the desired hardness, which generally will be from about 0.5 to 12 hours, preferably about 0.5 to 6 hours.

The hardness to which the pitch is blown may depend on the use for which it is intended. For example, if a pitch product is desired for use in impregnating a fiber pipe, air blowing may be continued until a pitch having a penetration of up to about 5, preferably about 0–2, at

77° F. is obtained. If it is intended to impregnate paperboard, the blowing may be terminated when the pitch reaches a penetration of less than about 125 and preferably about 30–80. Other uses for the pitches of the invention include use as a roofing felt saturant or paving asphalt component.

In the event air blowing is continued until a penetration of about 0–2 at 77° F. is reached, a pitch product may be obtained having the properties summarized in Table I and especially suitable for impregnating pipes made of fibrous materials such as newsprint or other paper pulp.

Impregnation of the paperboard may conveniently be carried out at temperatures of about 340–360° F. since at this temperature the impregnant will possess a viscosity of about 40–70 centipoises, which is most desirable for impregnation. Impregnation may be performed by dipping the paperboard into the impregnant, then draining and cooling. The process is facilitated if impregnation is carried out in a vacuum since this enhances removal of air from the paperboard and thereby allows the impregnant to better permeate the paperboard. The final impregnated paperboard may often contain from about 65–80% by weight, based on the weight of the paperboard, of impregnant.

TABLE I

	Range, minimum	Typical	Preferred
Specific gravity at 60° F	1.18	1.196	1.19–1.21
Softening point (R & B), ° F	160–170	162.5	162–165
Needle penetration at 77° F	0–2	0	0–1
Brookfield viscosity, cps.:			
At 350° F	40–70	56	56
At 340° F	60–85	69	69
At 330° F	80–105	92	92
At 320° F	100–140	117	117
At 310° F	135–200	167.5	168
At 300° F	180–400	225	225
At 280° F	400–600	485	485
Distillation percent:			
At 300° C	0–1.0	0	0
At 355° C	3.0–8.0	4.97	3.0–5.0
Wt. percent H_2O	0–2.0	1.47	0–1.5

Comparative tests made on fibrous pipes impregnated at 350° F. with 75.4% by weight coal tar and pipes impregnated with 74.9% by weight mineral oil-derived pitch obtained by employing the solvent extraction-blowing process of this invention show a marked superiority for the mineral oil-derived pitch impregnated pipe. The results of such tests are given in Table II.

TABLE II.—PHYSICAL TESTS

	Acceptable	Coal tar pitch pipe	Mineral oil pitch pipe
Dry crush, lb. ft	1,100 minimum	1,500	1,750
Wet crush, lb. ft	do	1,450	1,647
Kerosine crush, lb. ft	do	1,300	1,447
Boiling water crush, lb. ft	990 minimum	1,400	1,536
Beam, lb	2,200 minimum	2,600	2,776
Flattening, percent	3 maximum	.6	.74
Water absorption, wt. percent	2 maximum	1.0	.79

Additionally, tests were made by exposing the impregnated pipe of the present invention to outside weathering for a nine-month period. No degradation or other change was observed in the pipe, and in fact, its appearance at the end of the test period was the same as at the beginning.

The present invention will be illustrated by the following specific examples which are not to be considered limiting.

A petroleum-derived clarified oil having a Saybolt Universal Viscosity at 210° F. of 43 seconds and an API gravity of 13.6° was extracted using a propane to oil ratio of 12.1 to 1. After settling, the bottom phase containing the intermediate pitch-like material was separated from the upper phase containing the deasphalted oil. The small amount of propane contained in the pitch was removed by heating for a few minutes at 300° F. The pitch obtained had a viscosity at 210° F. of 511, a needle pentration at 77° F. of 127, a softening point of 105° F. and a specific gravity 60/60 of 1.1624.

That pitch was then air blown at 500° F. and at a rate of 3.3 cubic feet of air per hour per pound of pitch. Samples were tested after 2½ and 4½ hours of air blowing with the following results observed.

	At 2½ hours	At 4½ hours
Softening point (R & B) ° F	121	165
Specific gravity 60/60	1.1780	1.1930
Flash, ° F	485	510
Brookfield Viscosity, cps.:		
At 300° F	22.6	
At 325° F	15.8	
At 350° F		54.6
Needle penetration at 77° F	49	1
Needle penetration at 115° F		21
Viscosity at 275° F		176

It has also been found that the pitch of the present invention has the unique property of being completely compatible in all proportions with coal tar pitch. This is unusual for mineral oil products as most are compatible with coal tar pitch in only very limited concentration ranges. Such compatibility is significant as it permits both coal tar pitch and mineral oil pitch to be either combined and used together as an impregnant, for instance, in compositions containing at least about 10 weight percent of each or to be used in separate applications to the pipe. Results obtained when a 50–50 mix of coal tar pitch and the 0-penetration mineral oil pitch of the present invention were applied to fiber pipe are shown in Table III.

TABLE VIII

	Acceptable	50-50 blend
Dry, crush, lb. ft	1,100 minimum	1,596
Wet crush, lb. ft	do	1,593
Kerosine crush, lbs. ft	do	1,460
Boiling water crush, lb. ft	990 minimum	1,536
Beam, lb	2,200 minimum	2,713
Flattening, Percent	3 maximum	.40
Water absorption, wt. Percent	2 maximum	.88

If desired, the pitch of the present invention may be cut back with suitable solvents, for instance, normally liquid hydrocarbons, such as aromatics, e.g., toluene. The cut back material has a lower viscosity which may enhance its handling properties when used as an impregnant. Also, elevated temperatures may be used during impregnation, whether the pitch is cut back or not, and this will often improve penetration of the pitch into the material being impregnated.

I claim:

1. A process for preparing a mineral oil-derived pitch comprising the steps of solvent extracting clarified oil produced by the catalytic cracking of mineral gas oil with a C_3 to C_5 paraffinic solvent to obtain a propane-insoluble intermediate pitch product having a needle penetration at 77° F. of about 10 to 300, and blowing said intermediate pitch product with an oxygen-containing gas to reduce the penetration of the pitch by at least about 25 percent.

2. The process of claim 1 in which the propane-insoluble intermediate pitch product is blown by the oxygen-containing gas to a penetration at 77° F. of less than 125.

3. The process of claim 2 in which the oxygen-containing gas is air.

4. The process of claim 2 in which the propane-insoluble intermediate pitch product is blown to a pitch product having a needle penetration at 77° F. of about 0 to 5.

5. The process of claim 2 in which the blowing is continued until the pitch has a penetration at 77° F. of about 0–2.

6. The process of claim 2 in which the propane-insoluble intermediate pitch product is blown to a pitch product having a penetration at 77° F. of about 30 to 80.

7. A process for preparing a petroleum-derived pitch comprising the steps of solvent extracting clarified oil produced by the catalytic cracking of petroleum gas oil with a C_3 to C_5 paraffinic solvent to obtain a propane-insoluble intermediate pitch product having a needle penetration at 77° F. of about 40 to 300, and air blowing said intermediate pitch product to reduce the penetration at least about 50 percent.

8. The process of claim 7 in which the solvent is propane.

9. An article of manufacture comprising a fiber pipe impregnated with the final pitch product of claim 4.

10. An article of manufacture comprising a fiber pipe impregnated with the final pitch product of claim 5.

11. An article of manufacture comprising a fiber pipe impregnated with a composition consisting essentially of the pitch product of claim 5 and coal tar pitch, each pitch being at least about 10% of the composition.

12. The article of claim 11 in which the composition contains about 50% of each type of pitch.

13. The pitch produced by the process of claim 4.

14. The pitch produced by the process of claim 5.

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U.S. Cl. X.R.

138—178; 208—3