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[54] **ASPHALT MANUFACTURE**
5 Claims, 1 Drawing Fig.

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[50] **Field of Search** 208/44

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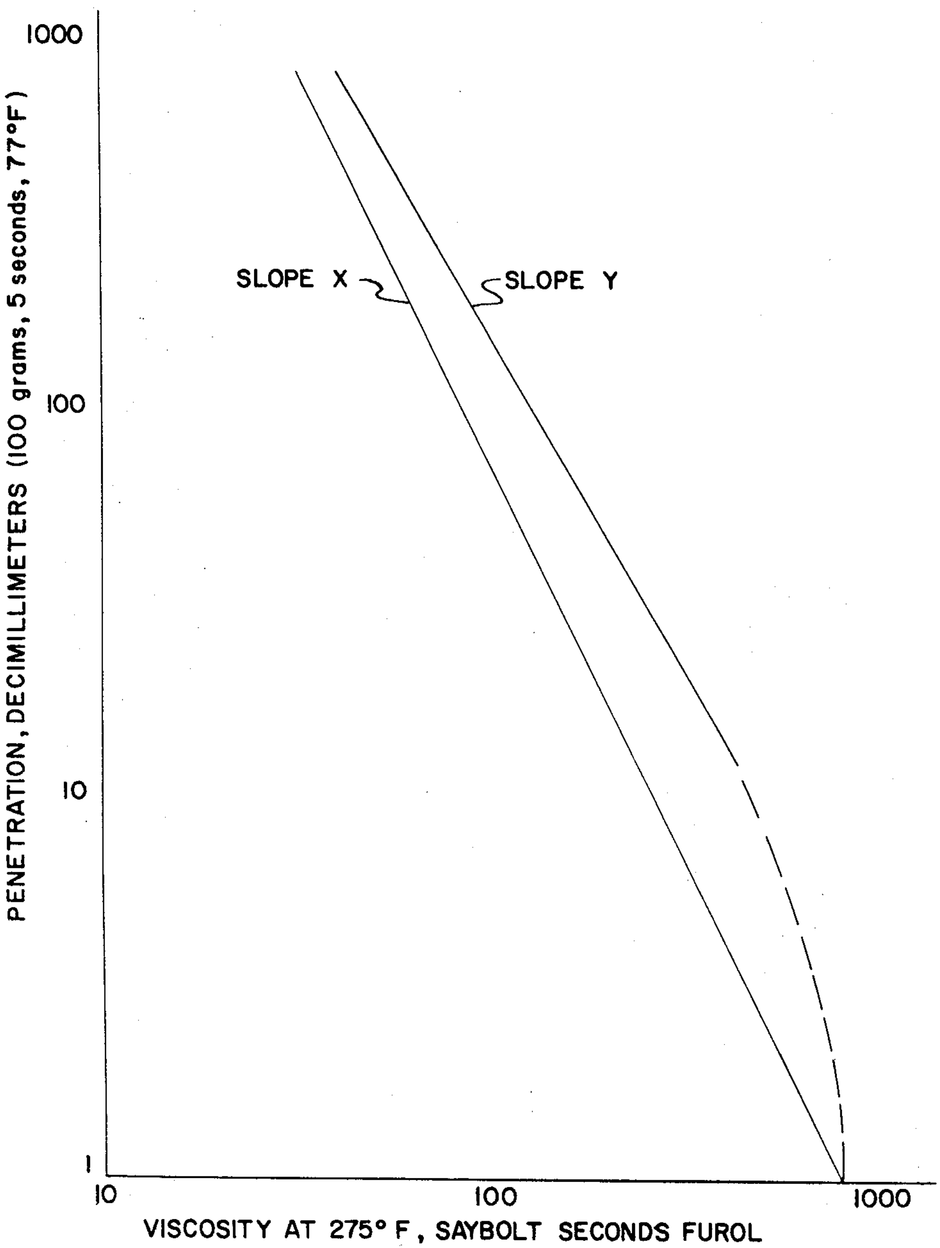
ABSTRACT: Asphalt products having improved rheological properties are prepared from asphaltic residues by means of catalytic hydrogenation under moderate conditions.



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ASPHALT MANUFACTURE

This invention relates to a process for producing asphalt products having highly desirable rheological properties from asphaltic pitch by means of catalytic treatment with hydrogen.

Conventional asphalt manufacture involves the reduction of soft straight run residues, typically having penetrations above 1,000 decimillimeters (dmm.) at 77° F., to a consistency permitting their use as asphalt products by vacuum flashing, solvent extraction or air blowing at an elevated temperature. In the first two of the aforementioned procedures, reduction to specification grade is accomplished by removing a proportion of the heavy oil fraction contained in the straight run residue. In the latter process the desired consistency is obtained through condensation and polymerization of the heavy oil and resinous fractions contained in the residues.

Because the heavy distillate oil fraction contained in straight run residue is valuable, for example, as conversion feed for catalytic cracking, there has been an increasing trend toward reducing these residues to a hard asphaltic pitch thereby maximizing distillate oil recovery. The resulting pitches are usually hard, relatively brittle materials, having very low penetrations, e.g., 5 dmm. or less at 77° F. Due to their inherent physical properties, such pitches have limited utility and are not suitable for most asphaltic applications unless blended with a cutter stock such as a flashed distillate or other oil. Obviously, the use of such an oil or oil-containing residue for blending, frustrates the objective of maximizing the recovery of valuable oil fractions from the residue. Hard pitch can be disposed of by conversion to coke for use as fuel, but this likewise is not a very satisfactory alternative, since pitch residues frequently contain high concentrations of sulfurous and nitrogenous compounds which when burned result in the release of noxious sulfur and nitrogen oxides to the air.

Therefore, there exists in the art a need for a practicable method of converting asphaltic pitches to useful products. The present invention provides such a process; a process wherein asphalt products are prepared having rheological properties superior to those of asphalts prepared from straight run residues by conventional methods of manufacture.

It has now been found that asphalt products having highly desirable rheological properties can be prepared from asphaltic pitch by means of catalytic hydrogenation under moderate conditions. Hydrogenation under the conditions hereinafter described has been found to alter the chemical and physical characteristics of the pitch in such a manner as to produce products having viscosimetric properties superior to those of asphalts prepared by conventional manufacturing techniques. In addition, it has been found that good product yields are attained at relatively low levels of hydrogen consumption, and that good catalyst life can also be achieved. This latter aspect is particularly surprising considering the chemical nature of pitch, which in addition to containing a substantial proportion of asphaltenes that would be expected to deposit on the catalyst, also contains sizable quantities of sulfur and nitrogen compounds, and metals such as vanadium and other elements considered to be detrimental to catalyst life.

As an additional benefit of the present process, concomitant distillate products are freed of a substantial proportion of heteroatoms and trace metals. Since sulfur and nitrogen compounds and metalliferous contaminants are relatively innocuous in asphalt, it is preferred to only partially remove these contaminants from the residue. Metal deposition on catalyst is thus limited thereby extending catalyst life.

The rheological properties of asphalt are generally expressed in terms of their penetration, viscosity, softening point and ductility. These properties are considered indicative of the nature of the asphalt and are related to the inherent structure of bituminous materials. Asphalts of equivalent penetration grade are not necessarily suitable for the same application, since penetration is but one measure of the asphalt' s rheological properties. For example, it is known that penetration together with viscosity can be used to predict the "setting properties" of asphalt when hot-mixed with aggregate in paving applications. It has been found through experience that asphalts of equivalent penetration grade will set slower or faster depending on their viscosity. Generally those having the highest viscosity at or near the hot-mix temperature will have the fastest setting time and thus be the more advantageous for actual use.

A highly significant advantage of the present invention is that for a given penetration, the asphalt products prepared by the inventive procedure, have appreciably greater viscosities than those produced directly from straight run residue by conventional vacuum flashing. The catalytic hydrogenation of the pitch apparently results in a molecular rearrangement which not only increases its penetration without the use of cutter-stocks, but additionally imparts highly desirable viscosimetric properties to the resulting asphalt products.

The improved viscosimetric properties of asphalts prepared in accordance with the invention will be more readily apparent by reference to the accompanying drawing. The drawing is a graph showing the relationship between penetration and viscosity of asphalts prepared by conventional vacuum flashing of a straight run residue (Slope X), compared with the penetration-viscosity relationship of asphalts prepared by catalytic hydrogenation of pitch (Slope Y) derived from the same straight run residue. It is evident from the graph, that at most any given penetration the viscosity at 275° F of the asphalt prepared by vacuum reducing to grade, is lower than that of the asphalt prepared by the process of the invention, e.g., a πb penetration grade asphalt produced by the present process has a viscosity at 275° F. of 130 S.S.F. as compared to a viscosity of only 95 S.S.F. for the asphalt obtained by reducing straight run residue to a 90 penetration grade. The hydrogenated product would, therefore, set faster and be more desirable in paving applications than the conventionally prepared asphalt.

The starting material or feedstock to the process of the invention can be any asphaltic residue of petroleum, e.g., cracked residue, straight run residue (bottoms product from the atmospheric or vacuum distillation of crude oils), residue from solvent deasphalting processes and the like. Such residues comprise predominantly high boiling fractions, i.e., those fractions boiling above 650° F. of which the asphaltic (pitch) fraction generally comprises the highest boiling materials therein. Such asphaltic pitch-containing residues can be catalytically hydrogenated directly and the improved asphaltic pitch fraction subsequently recovered by fractionation, or if desired the residue can be fractionated prior to hydrogenation to recover the distillate fraction beforehand, in which case the feed to the process will be predominantly the heavy pitch fraction.

Lower boiling hydrocarbon fractions can be included in the asphaltic residue feed if desired and in some cases can be quite advantageous as the low boiling fractions tend to be a wash oil in the catalytic hydrotreatment and would be improved in quality, e.g., through partial removal of sulfur and nitrogen compounds. The process of the invention is particularly advantageous in preparing asphalt products from hard asphaltic pitch, i.e., pitch having a penetration below about 5 dmm. at 77° F. as determined by ASTM Method D5, and boiling point essentially above about 900° F. Such pitch is obtained, for example, by deep flashing straight run or cracked residue.

Catalytic hydrogenation processes in general, are well known and thoroughly described in the art, and need not be discussed in detail herein. In accordance with the an asphaltic residue feedstock is subjected to catalytic treatment with hydrogen at temperatures ranging from about 600° F. to about 850° F., preferably from about 675° F. to 775° F., and at pressures of about 1,000 p.s.i.g. to about 5,000 p.s.i.g., preferably 1,500 p.s.i.g. to about 3,500 p.s.i.g. The weight hourly space velocity can be varied from about 0.2 to about 2.0, but preferably is maintained at about 0.5 to about 1.0. A hydrogen circulation rate of between about 1,500 and 15,000 s.c.f./bbl. of pitch can be employed, more normally from about **5,000** to **10,000** a.c.f./bbl. of pitch.

Under the specified hydrogenating conditions, generally less than about 15 percent w/o and normally less than about 10 percent w/o of the feedstock is converted to products boiling below 600° F. to obtain relatively high yields of asphalt. If desired, somewhat higher conversions to light boiling products can be obtained which are recoverable and could suitably be used for distillate fuels, jet fuels or other purposes.

Effluent from the catalytic hydrotreating e.g. is separated into one or more fractions. For example, a gas phase is separated from the liquid product and desirably is recycled to the hydrotreating zone, with or without a suitable treatment to remove any undesirable impurities such as hydrogen sulfide or ammonia. Makeup hydrogen can be added as needed. Pure hydrogen is not necessary as gases rich in hydrogen can be used, e.g., hydrogen gases produced in catalytic reforming of naphthas which are on the order of 70 –80 percent v/o by volume of hydrogen or more, but correspondingly higher operating pressures are required to maintain adequate hydrogen partial pressures.

Liquid product from the hydrotreating zone is suitably fractionated to remove any low boiling hydrocarbons and to recover an asphalt fraction boiling essentially above about 600° F., and preferably above about 650° F., and having a penetration at 77° F. of at least about 20 dmm. higher and preferably at least 40 dmm. higher than the corresponding asphaltic fraction in the residue feed. Thus by practice of the invention asphalt products of most any desired penetration can be prepared from asphaltic pitch or pitch-containing residues. In a preferred embodiment of the invention hard pitch having a penetration at 77° F. of less than about 5 dmm. is converted to asphalt products having penetrations of about 30 to about 500 at 77° F. and viscosities between about 50 and about 500 centistokes at 275° F.

In general, any of the catalysts conventionally employed in the hydrogenation of heavy petroleum oils can be utilized in the present process. In general, the catalyst comprises a hydrogenation component on a suitable refractory oxide support. Examples of suitable catalytic components are the Group VIB and Group VIII metals such as molybdenum, tungsten, chromium, cobalt, nickel, iron and their oxides and sulfides. Mixtures of these materials or compounds of two or more of the oxides can also be employed. These catalytic components are generally composited, with a suitable carrier of the solid refractory type, e.g., alumina, silica, or combinations thereof. Supports having an acidic character such as silica alumina or fluorided alumina are also suitable. Especially suitable are the oxides and/or sulfides of nickel and molybdenum on an alumina carrier. The metals are generally employed in an amount ranging from about 0.1 percent w/o to about 25 percent w/o or higher. The preparation of hydrogenation catalysts is well known and practiced commercially.

The invention will be further described by means of the following examples which demonstrate various embodiments of the invention. It should be understood, however, that these examples are given for illustrative purposes only and that the invention in its broader aspects is not limited thereto.

EXAMPLE I

Flasher pitch having the properties indicated in table I was hydrogenated in the presence of a commercial hydrogenation catalyst under the conditions shown in table II. The total liquid product from each of these runs (I–IV) was fractionated to free the asphalt product of water and light ends. The properties of the asphalt product having a boiling range above 572° F. is shown in table II, as well as product yields and percentages heteroatom and metallic contaminant removal.

TABLE I

Pitch Feedstock	
Source	Vacuum Flashed Straight Run Residue of a Heavy San Joaquin Valley, California Crude
Properties	
Penetration at 77° F., dmm.	0–1
Viscosity at 275° F., CS	1,900
Softening Point, ° F.	177° F.
Components boiling above 932° F., %w	99.4
Sulfur, %w	1.6
Nitrogen, %w	1.5
Oxygen, %w	1.1
Iron, p.p.m.	195
Nickel, p.p.m.	215
Vanadium, p.p.m.	105

TABLE II

	I	II	III	IV
Hydrogenating conditions:				
Catalyst age [1]	64	69	71	85
Temperature, ° F	725	738	752	770
Pressure, p.s.i,g	1,800	1,800	1,800	1,800
Weight hourly space velocity	0.69	0.59	0.61	0.43
Ratio H_2/pitch, s.c.f./bbl	7,400	9,300	11,800	8,000
H_2 consumption, s.c.f./bbl	350	410	510	830
Total liquid product:				
Percent w. yield basis feed	98.8	98.9	97.8	98.9
Percent w. product boiling below 572° F	2.3	3.2	5.0	9.3
Percent w. product boiling above 932° F	89.9	85.9	82.9	70.9
Properties of 572° F. plus asphalt product:				
Penetration at 77° F., dmm	40	78	100	470
Viscosity at 275° F., cs	415	270	216	86
Viscosity at 140° F., poises	4,090	1,545	1,040	136
Percent w. yield basis total liquid product	98.21	97.70	96.46	93.36
Removal of heteroatoms, percent w.:				
Sulfur	47	57	55	66
Nitrogen	8	9	12	20
Oxygen	49	53	58	59
Metals removal from total product, percent w.:				
Iron	92	85	87	....
Nickel	65	57	64	....
Vanadium	47	67	68	....

[1] 1/16" extruded pellets of alumina-supported nickel-molybdenum, 3% nickel, 10% molybdenum was employed as catalyst.

From the above data it is evident that useful asphalt products can be manufactured from pitch without the inclusion of valuable cutter stocks. The products produced in above runs have penetrations and viscosities within the general range of paving grade asphalts and would be eminently suitable for this purpose. The above data further demonstrate that virtually the entire range of asphalt consistencies can be produced by catalytic hydrotreatment of pitches, e.g. from low penetration grade asphalts to soft fluxes. The response to penetration increase has been found to be more strongly dependent on temperature of the catalytic hydrotreatment than on pressure. By modifying the hydrogenation temperature and controlling the other variables, asphalt products of most any desired consistency can be obtained.

It is noted that the catalyst after 85 days still possessed good activity indicating such a catalyst can be effectively employed in the treatment of heavy asphaltic charge stocks for relatively long periods of service.

EXAMPLE II

To further demonstrate the inventive process, asphalts of varying consistencies were prepared under the conditions and having the properties shown in table III. The feedstock was the same as that of Example I.

TABLE III

	V	VI	VII	VIII
Hydrogenation Conditions				
Temperature, °F.	662	707	707	752
Pressure, p.s.i.g.	2,000	1,000	2,000	2,000
Properties of 572° F. Plus Asphalt Product				
Penetration at 77° F., dmm.	18	29	114	120
Viscosity at 275° F., cs	726	594	237	240

Various modifications can be made in the procedures of the specific examples to provide other embodiments which fall within the scope of the present invention. For example, while it is possible to prepare penetration grade asphalts directly from asphaltic pitch without the necessity of employing a cutter stock, it may be desirable in some instances to blend minor amounts of a cutter stock with the hydrogenated asphalt products of the invention to prepare a particular penetration grade material. Likewise, it is understood that asphalts produced by the inventive process can be diluted with petroleum solvents to form road cutbacks, and can also be employed in the form of an emulsion or be used in any other application for which conventional asphalts are employed.

We claim as our invention:

1. A process for producing asphalt products from asphaltic pitch which comprises contacting asphaltic petroleum residue having a penetration of less than 5 decimillimeters at 77° F. with hydrogen in the presence of a hydrogenation catalyst at a temperature in the range of from about 600° F. to about 850° F., F. a pressure of from about 1,000 to about 5,000 pounds per square inch gauge, and recovering an asphalt having a penetration at 77° F. of about 30 to about 500 decimillimeters and a viscosity at 275° F. between about 50 and about 500 centistokes.

2. The process of claim 1 wherein the asphaltic residue is composed predominantly of fractions boiling above 650° F.

3. The process of claim 1 wherein the catalyst comprises nickel molybdenum supported on alumina.

4. A process for producing asphalt products from asphaltic pitch which comprises contacting hard asphaltic pitch having a penetration of less than 5 decimillimeters at 77° F. with hydrogen in the presence of a nickel molybdenum supported on alumina catalyst at a temperature in the range from about 600° F. to about 850° F., a pressure of from about 1,000 to about 5,000 pounds per square inch gauge and a weight hourly space velocity of about 0.2 to about 2.0 and recovering an asphalt product having a penetration at 77° F. of about 30 to about 500 decimillimeters and a viscosity at 275° F. between about 50 and about 500 centistokes, wherein less than about 15 percent w/o of the pitch feed is converted to products boiling below 600° F.

5. The process of claim 4 wherein the catalytic hydrogenation is performed at a temperature in the range of about 675° F. to about 775° F. at a pressure of about 1,500 to about 3,500 pounds per square inch gauge.