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McClaren et al.

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[54] **ASPHALT MANUFACTURE**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 880,629, Nov. 28, 1969, Pat. No. 3,607,722.

[52] **U.S. Cl.** **208/44**

[51] **Int. Cl.** **C106 3/02**

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

[56] **References Cited**

UNITED STATES PATENTS

3,258,419	6/1966	Hanson	208/44
3,607,722	9/1971	McLaren et al.	208/44

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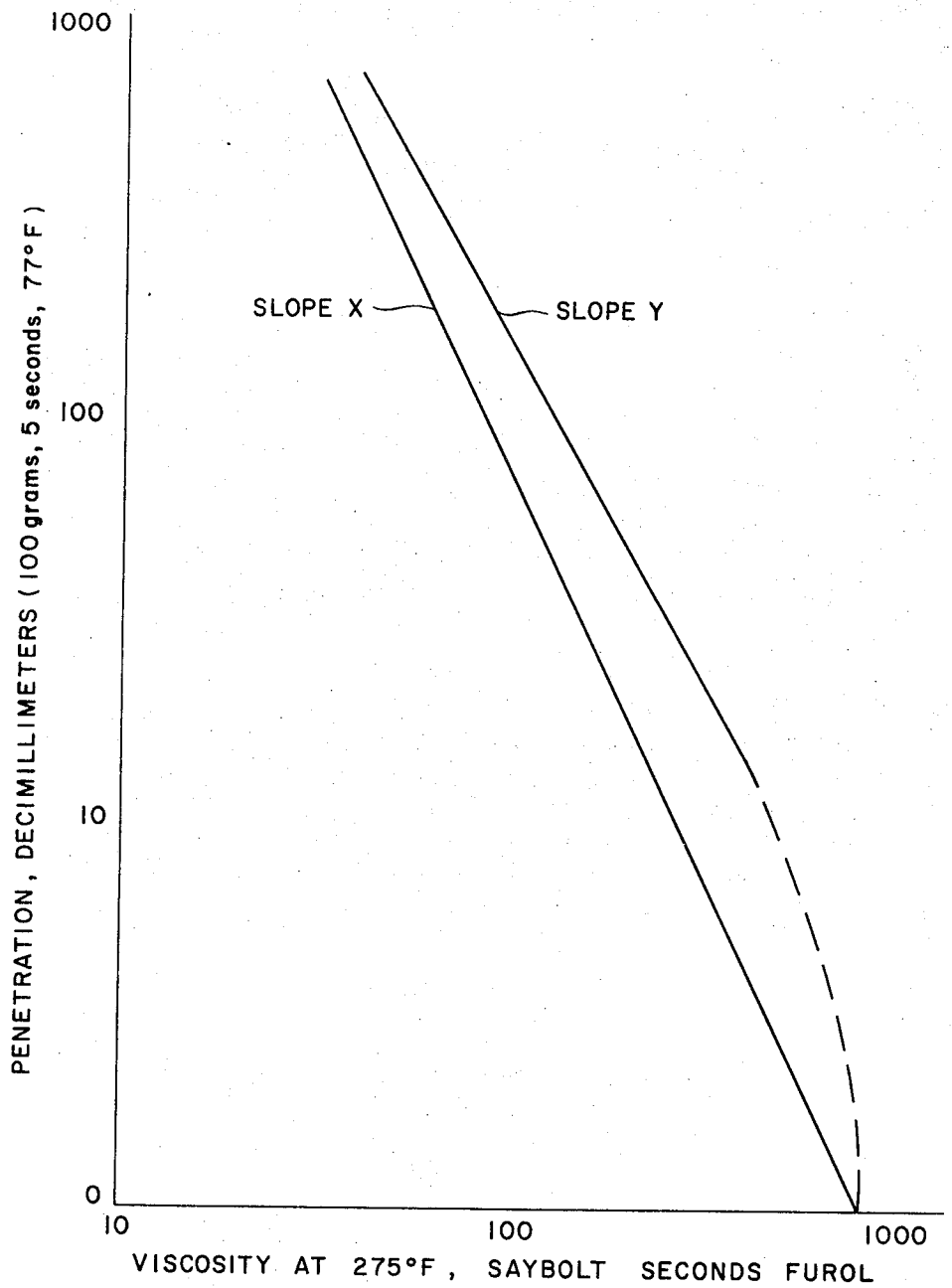
[57] **ABSTRACT**

An asphalt flux having improved rheological properties is prepared from a straight run asphalt residue by means of catalytic hydrogenation under moderate conditions.

7 Claims, 1 Drawing Figure

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ASPHALT MANUFACTURE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. application Ser. No. 880,629, filed Nov. 28, 1969, now U.S. Pat. No. 3,607,722 issued Sept. 21, 1971.

BACKGROUND OF THE INVENTION

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 1000 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.

SUMMARY OF THE INVENTION

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.

DETAILED DESCRIPTION OF THE INVENTION

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 advantagous 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 90 penetration grade asphalt produced by the present process has a viscosity at 275°F of 130 SSF as compared to a viscosity of only 95 SSF 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.

Another advantageous application of the invention is in preparing an asphalt flux, suitable for processing into a variety of useful products, from a straight-run residue obtained from crudes which normally do not have utility in this respect. For example, straight-run asphalt residues obtained from California and certain heavy Venezuelan crudes and generally not suitable for use in preparing roofing flux because upon air blowing of the vacuum flashed residues from such crudes to the requisite softening point, a hard asphalt having a penetration of 0–7 dmm is formed which is well below the 16–22 dmm penetration typically specified for roofing materials. The use of less severe vacuum flashing or the addition of cutter stocks, while effective in increasing the penetration of the flux, adversely affects other properties of the blown product such as softening point and spread-of-flame test properties, hence the product is still unsuitable.

However, it has been found that if the straight-run residue is hydrotreated under the previously specified conditions prior to distillation, and the product is fractionated to remove those components boiling below 840°F, an asphalt flux is obtained that upon being blown with air forms an excellent roofing material. The present process has been found to substantially improve the properties of the flux in respect to penetration, viscosity, penetration index and in a number of other important aspects. In general the penetration at 77°F of the asphalt flux product is at least 40 dmm higher than the penetration of the corresponding boiling fraction in the straight-run residue feed. Preferably the flux product will have a penetration at 77°F of about 250 to 600 dmm, more preferably from 250 to 500 dmm. The desired flux product is normally obtained with relatively low conversion to lower boiling hydrocarbons, e.g., generally less than 15%*w* and usually less than 10%*w* of the straight-run residue feedstock is converted to products boiling below 600°F. In fact, very suitable fluxes can normally be obtained with less than 15%*w* conversion of the feedstock to products boiling below 932°F.

In addition to having utility in preparing roofing materials, the asphalt flux produced in accordance with the invention can be used in preparing a variety of related industrial fluxes, coatings and saturants, and has also been favorably employed as a blending component for paving asphalts. Thus, the present process offers a means of converting straight-run residues of the type which normally have very limited utility in the production roofing materials and related products, into a "multipurpose" flux suitable for preparing a broad range of asphalt products.

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 invention 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 psig to about 5,000 psig, preferably 1,500 psig to about 3,500 psig. 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 SCF/bbl of pitch can be employed, more normally from about 5,000 to 10,000 SCF/bbl of pitch.

Under the specified hydrogenating conditions, generally less than about 15%*w*, and normally less than about 10%*w* 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 zone 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%*v* 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 700°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. Such catalysts

generally comprise 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 or nickel and molybdenum on an alumina carrier. The metals are generally employed in an amount ranging from about 0.1%w to about 25%w 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 commerical 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

Source	Pitch Feedstock 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	1900
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, ppm	195
Nickel, ppm	215
Vanadium, ppm	105

TABLE II

	I	II	III	IV
hydrogenating Conditions				
catalyst Age (1), Days	64	69	74	85
temperature, °F	725	738	752	770
pressure, psig	1800	1800	1800	1800
weight hourly space velocity	0.69	0.59	0.61	0.43
Ratio H_2/pitch, scf/bbl	7,400	9,300	11,800	8,000
H_2 consumption, scf/bbl	350	410	510	830
total liquid product %w yield basis feed	98.8	98.8	97.8	98.9
%w product boiling below 572°F	2.3	3.2	5.0	9.3
%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
%w yield basis total liquid product	98.21	97.70	96.46	93.36
removal of Heteroatoms, %w				
Sulfur	47	57	55	66
Nitrogen	8	9	12	20
Oxygen	49	53	58	59
metals removal from total product,%w				
Iron	92	85	87	-
Nickel	65	57	64	-
Vanadium	47	67	68	-

(1) 1/16 inch 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 emminently 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, psig	2000	1000	2000	2000
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

EXAMPLE III

Straight run residue obtained from a 60 percent California/40 percent Alaska crude was hydrogenated in the presence of the same catalyst employed in Example I under the conditions shown in Table V. The total liquid product from Run IX and X was vacuum distilled to remove fractions boiling below 901°F and 932°F respectively. The properties of the asphalt fluxes thereby obtained are compared to the properties of a corresponding boiling fraction of unhydrotreated straight-

run residue and also to a typical premium coating flux (PCF) prepared from a Venezuelan crude (identifired in Table IV as Lagomar PCF).

TABLE IV

	IX	X	Unhydro treated straight-run res.	Lagomar PCF
Hydrotreating conditions				
Temperature, °F	734	726	-	-
Pressure, psig	1800	18000	-	-
Liquid Hourly space velocity	0.50	0.50	-	-
Properties of Flux				
Boiling point, °F	>901	>932	>932	>857
Softening point, °F	81	84	129	90
Penetration at 77°F dmm	500 (1)	400 (1)	36	350 (1)

(1) Calculated from the viscosity and softening point.

The above data indicate that hydrotreating of a straight-run asphalt generally considered unsuitable for preparing roofing materials and similar products, effectively increases the penetration and modifies other characteristics of the asphalt so as to produce an asphalt flux having properties similar to a premium coating flux of the type typically employed in preparing roofing materials, coatings, saturants, etc.

EXAMPLE IV

To illustrate the utility of asphalt flux obtained in accordance with the invention in preparing asphalt coatings, the products of Run IX and X were blown with air under the conditions shown in Table V. The properties of the blown products were compared to a coating prepared by air blowing the premium coating flux shown in Table IV. Typical specifications for coatings of this type require softening points of from 215° to 222°F and penetrations at 77°F of from 15 to 25 dmm.

TABLE V

	IX	X	Typical PCF Lagomar
Blown Run Conditions			
Temperature, °F	475	475	475
rate of air flow, ft³ air/min	0.5	0.5	0.5
Charge, kg	6	6	6
Time to 220°F softening point, hrs.	5.3	6.9	4.0–4.5
Properties of coating			
Penetration at 77°F, dmm	21	17	18
Penetration Index	5.2	4.4	4.8
Oil Loss During Blowing, %w	0.8	1.1	0.4

EXAMPLE V

To further illustrate the utility of the present process, the properties of two 90 penetration grade paving asphalts prepared from hydrogenated base materials were compared to a 90 penetration grade asphalt blended from unhydrotreated basestocks derived from the same source, i.e., a blend of 90 percent California/10 percent Alaska crude. The results of this comparison (presented in Table VI) indicate that paving asphalts having low heptane-xylene equivalencies and which exhibit negative Oliensis Spot Tests can be prepared from asphalt basestocks which normally do not possess these desirable properties. The blown fluxes employed in preparing these blends were blown with air to a 220°F softening point. Straight-run residue has been abbreviated as SRR.

TABLE VI

	viscosity 275°F, SSF	Oliensis spot test[1] 24 hours	Heptane Xylene equivalent[2] 24 hours
53% Hydrotreated SRR flux/47% blown hydrotreated SRR Flux	240	Negative	20/80
57% hydrotreated SRR Flux/21.5% blown hydrotreated SRR Flux/21.5% Vacuum flasher pitch	145	Negative	20/80
60% unhydrotretated SRR flux/40% Blown unhyrotreated SRR flux	152	Positive	35/65

(1) AASHO Method T-102

(2) California Test Method No. 325. This test is a modification of the Oliensis Spot Test and indicates the percentage of xylene that must be mixed with heptane to suppress the Oliensis spot.

Various modifications can be made in procedures of the specific examples to provide other embodiments which fall within the scope of the present invention. For example, it is possible to prepare penetration grade asphalts directly by blending the air-blown coating grade asphalts made from the hydrogenated fluxes with unblown hydrogenated flux or a three-component blend of air-blown hydrogenated flux, unblown hydrogenated flux and non-hydrogenated vacuum flasher pitch (or admixtures with unhydrogenated flux) to give a wide range of asphalt viscosities at a given penetration level both before and after an aging step.

We claim as our invention:

1. A process for producing an asphalt flux from a straight-run asphalt residue which comprises
   1. contacting said straight-run asphalt residue with hydrogen in the presence of a hydrogenation catalyst at a temperature in the range of from about 600°F to about 850°F and a pressure of from about 1,000 to about 5,000 pounds per square inch gauge,
   2. fractionating the hydrotreated liquid product obtained in step 1 to remove materials boiling below 840°F, and
   3. recovering an asphalt flux having a penetration at 77°F at least 40 decimillimeters higher than the corresponding boiling fraction in the straight-run residue feed.

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

3. The process of claim 2 wherein the catalyst comprises nickel-molybdenum supported on alumina.

4. The process of claim 1 wherein the recovered asphalt flux is air blown to produce a coating grade asphalt having a softening point of 215° to 222°F and a penetration at 77°F of between 15 and 25 decimillimeters.

5. The process of claim 1 wherein less than 15 percent of the straight-run residue asphalt feed is converted to products boiling below 600°F.

6. The process of claim 2 wherein the recovered asphalt flux has a penetration at 77°F of about 250 to 600 decimillimeters.

7. The process of claim 1 wherein recovered asphalt flux is air blown to produce a coating grade asphalt which is subsequently blended with a portion of the recovered asphalt flux or an unhydrogenated flux to produce a paving grade asphalt.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,755,139 **Dated** August 28, 1973

Inventor(s) GORDON A. McLAREN and JOHN W. GIBSON

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On first sheet of patent inventor's name should be corrected to read as

Gordon A. McLaren

Signed and sealed this 19th day of February 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents