Sept. 14, 1965 A. C. PITCHFORD 3,206,388

TREATMENT OF ASPHALTIC CRUDE OILS

Filed July 31, 1961 3 Sheets-Sheet 1

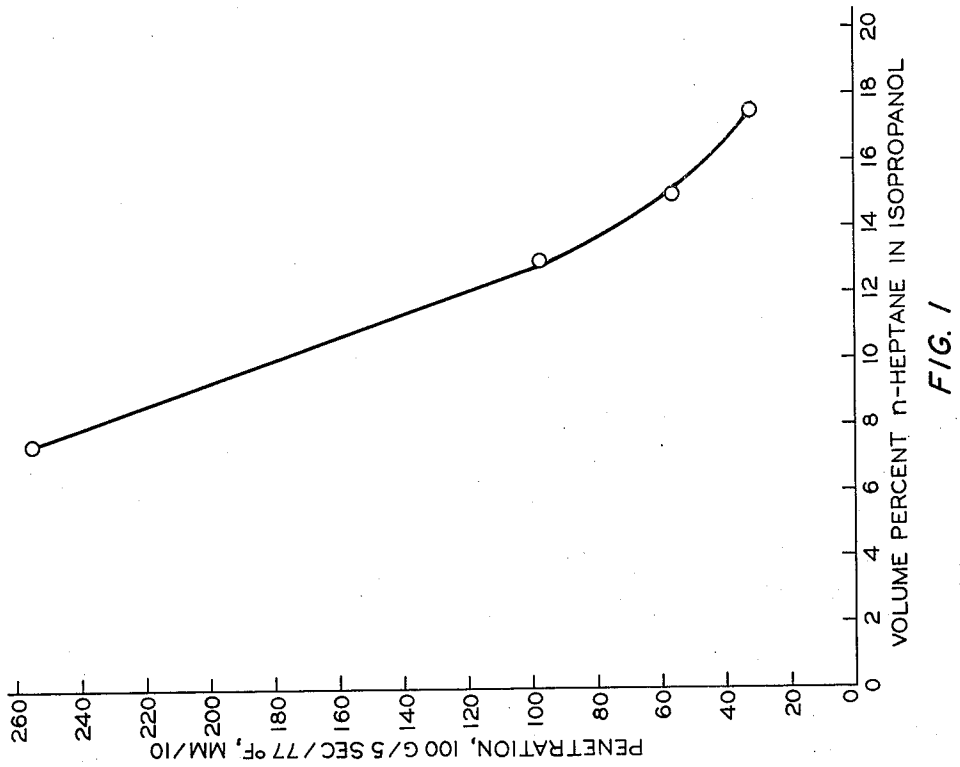


FIG. 1

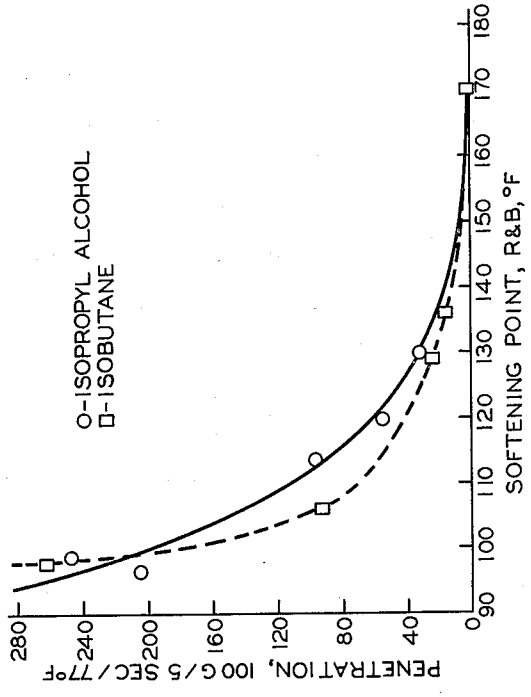


FIG. 2

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TREATMENT OF ASPHALTIC CRUDE OILS

Filed July 31, 1961 3 Sheets-Sheet 2

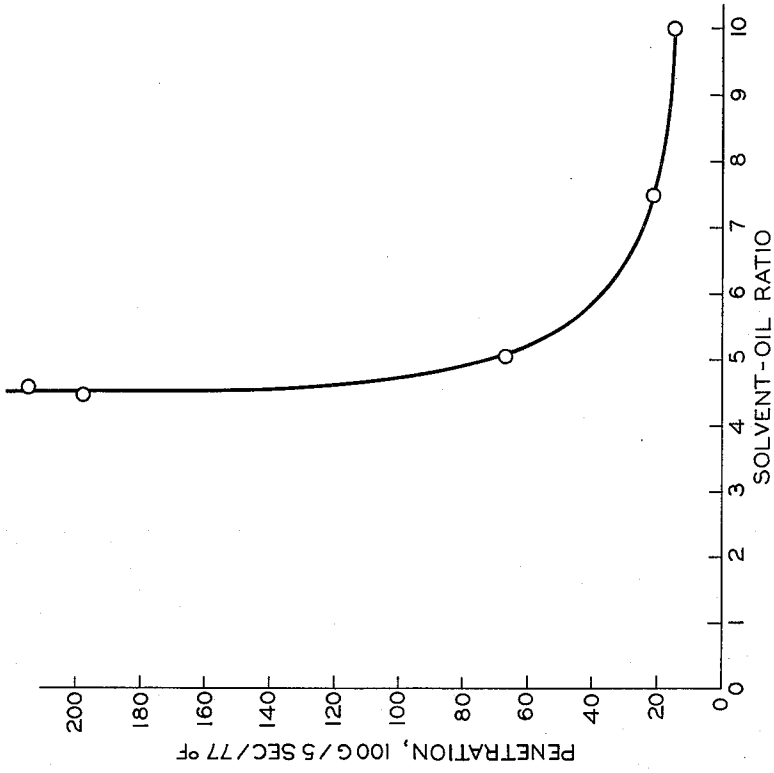


FIG. 3

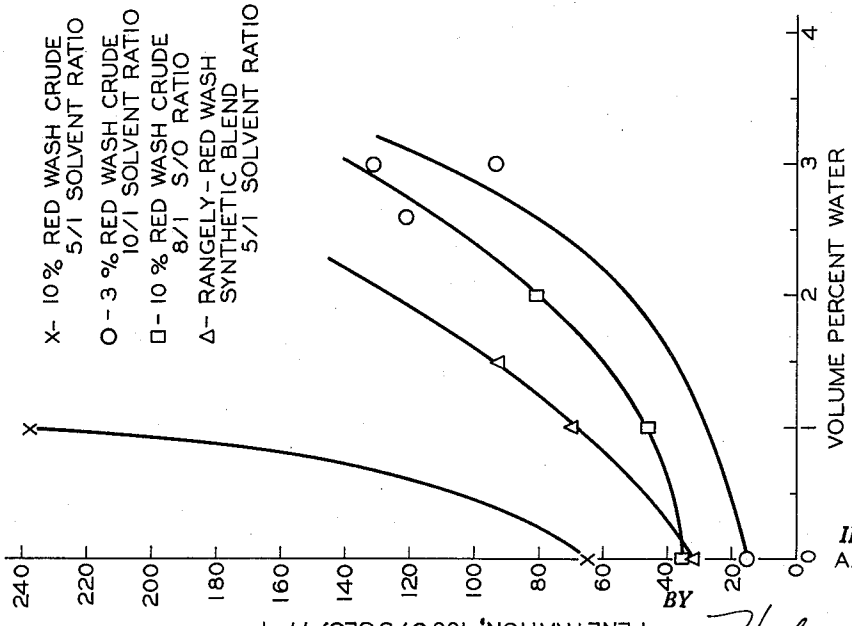


FIG. 4

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TREATMENT OF ASPHALTIC CRUDE OILS

Filed July 31, 1961 3 Sheets-Sheet 3

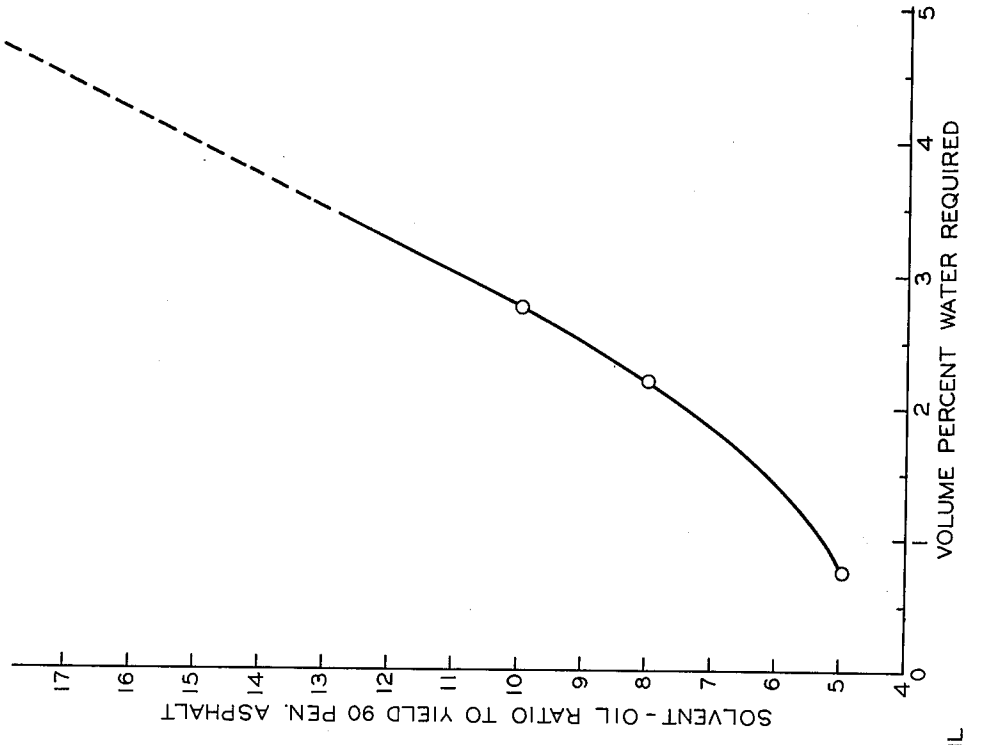


FIG. 5

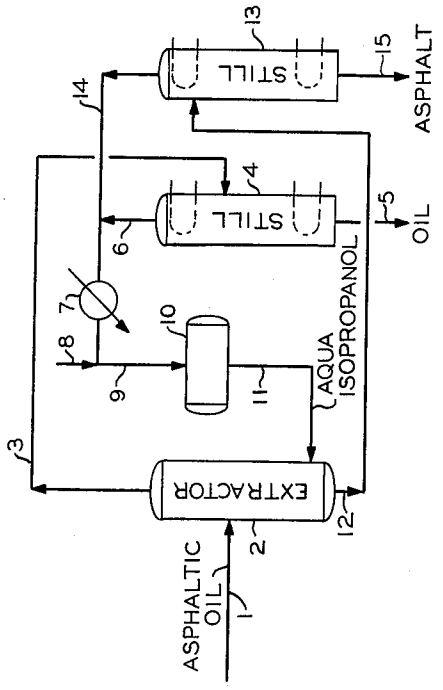


FIG. 6

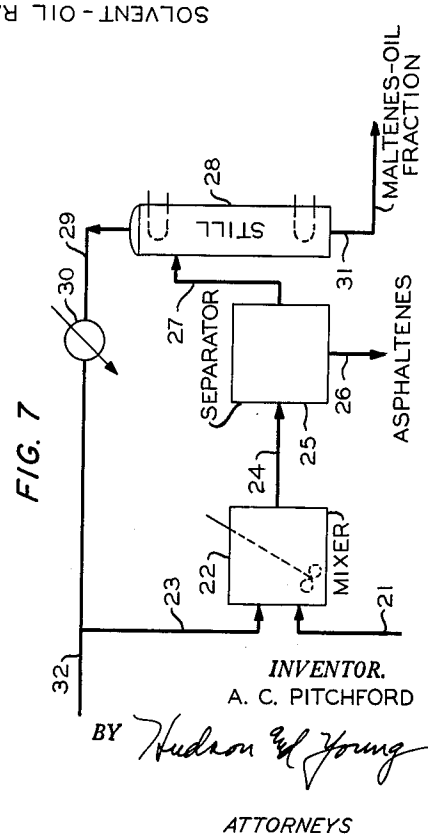


FIG. 7

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United States Patent Office 3,206,388 Patented Sept. 14, 1965

3,206,388

TREATMENT OF ASPHALTIC CRUDE OILS

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Filed July 31, 1961, Ser. No. 128,171
4 Claims. (Cl. 208—45)

This invention relates to the production of an improved hydrocarbon feed stock for the production of motor fuel. In one aspect it relates to the production of asphaltic, and resinous fractions from asphalt containing crude oil. In another aspect it relates to a relatively simple and economical process for separation of asphaltic, resinous and oily materials from crude oils containing these materials with the production of paving quality asphalt and improved quantity feed stock for production of motor fuel.

These improvements include increased yields, lower carbon residue and a reduction in vanadium, nickel and iron contents of the oily fraction.

It is well known in the crude oil processing art that asphaltenes and resins tend to produce coke during cracking and hydro-treating asphalt and resin-containing oils. It is also known that asphaltenes and resins are aromatic type components of crude oils. Thus, removing both of these aromatic components from asphalt-containing crude oils, results in the production of a superior charge stock for ultimate motor fuel production. The efficient utilization of asphaltic crude oils or residual fractions thereof depends upon reducing their viscosity and minimizing the yield of residual product or increasing as much as possible the yield of motor fuel production stocks. By treatment of asphalt-containing oils with pentane the asphalt content is reduced and the viscosity of the extract phase is improved. However, large volumes of pentane or other closely related hydrocarbon solvents are required. The total volume of such solvent hydrocarbons can be reduced by raising the temperature and pressure of the treating operation. At temperatures approaching the critical temperature of pentane asphaltenes are precipitated along with a portion of the resin content of the oil to yield a high melting pitch which is more easily handled than dry asphaltenes which are precipitated at room temperatures. Such high temeratures require high operating pressures and accordingly expensive high pressure vessels and piping all of which contribute to high capital investments.

Paving asphalts are prepared by several methods, (1) by vacuum reduction, (2) vacuum reduction with air blowing, and (3) solvent extraction using normal butane, isobutane or propane. The use of propane or the butanes yields a high quality extract oil suitable for catalytic cracking feed stock for the production of motor fuel blending stocks. The propane or butane extract is essentially a paraffinic oil containing low concentrations of vanadium and nickel metals. However, initial investments for such processes are high because high pressure equipment is required. Also vacuum reduction requires low pressures and high temperatures. Steam costs are high because large volumes of steam are required in the vacuum operation. In many cases of vacuum reduction of asphalt-containing oils paving asphalt cannot be produced without slight or excessive cracking of the asphaltic constituents.

An object of this invention is to provide a process for the separation of asphaltic materials suitable for use as paving asphalts with the simultaneous production of oils suitable for use in catalytic cracking for the production of improved gasoline blending stocks. Another object of this invention is to provide such a process which is relatively simple to operate. Yet another object

of this invention is to provide such a process for the production of paving asphalt and cracking stock which avoids need for use of high pressure equipment. Still other objects and advantages of this invention will be realized upon consideration of the accompanying disclosure.

FIGURE 1 is a curve showing relation of n-heptane content in solvent isopropanol on penetration of asphalt produced from Texas topped crude oil. FIGURE 2 shows curves comparing penetration of asphalts prepared from Texas crude oils using isopropyl alcohol (isopropanol) and isobutane as selective solvents. FIGURE 3 is a curve showing relation of solvent-oil ratio to penetration of asphalt of a Rangely, Colorado, topped crude oil using isopropyl alcohol as solvent. FIGURE 4 shows curves illustrating the effect of water in isopropanol on control of penetration of asphalt from Rangely, Colorado, crude oil. FIGURE 5 is a curve showing the water content required in isopropanol to produce 90 penetration asphalt from Rangely, Colorado, topped crude oil at various solvent (isopropanol-water) ratios at 175° to 180° F. FIGURE 6 is a flow diagram showing arrangement of equipment for carrying out an embodiment of this invention. FIGURE 7 is a flow diagram showing arrangement of equipment for carrying out another embodiment of this invention.

When it is desired to produce from an asphalt-containing oil an oil free of asphaltic materials, such as a lubricating oil stock, my solvent extraction system is particularly appropriate, because it leaves very little residual oil in the asphaltic phase. In other words the yield of the oil fractions is high. Furthermore, my process requires lower volumes of solvent than prior art processes, and it can be operated at atmospheric pressure and at lower temperatures than previously employed. If the purpose of the operation is to obtain a paving asphalt product, I am able to adjust the operating conditions to produce an asphalt meeting paving specifications. I will now describe and illustrate my invention from the point of view of the operating conditions which give optimum results. Control of the process depends chiefly on the solvent additives which are used with the propyl alcohol (normal propyl alcohol, isopropyl alcohol) to, first, increase solvency or solvent power of the alcohol and, second, to decrease the solvent power of the alcohol. These two categories are herein described and illustrated separately.

The employment of an additive to increase the solvent power of the alcohol is particularly beneficial when treating a crude oil containing about 2 to about 8 percent of 100 penetration asphalt, or an asphalt-containing fraction of such crude oil. Such a crude oil or fraction thereof is treated with a solvent in a solvent-oil volume ratio in the range of about 4 to about 20, the solvent comprising about 5 to 20 volume percent of a normal paraffin hydrocarbon containing from 5 to 15 carbon atoms per molecule of the paraffin hydrocarbon, and the remainder of the solvent being isopropanol or normal propanol, that is isopropyl alcohol or normal propyl alcohol, at a temperature within the approximate range of 175° to 180° F.

This embodiment of my invention is particularly adapted to the treatment of asphaltic crude oils containing less than 7 percent of 100 penetration asphalt. Such a crude oil is a West Texas crude oil. Ordinarily such a crude oil is topped, that is, fractions boiling up to and through the gas oils are removed leaving a thick oil-asphaltic residue which in the refining art is termed "topped crude."

It is frequently very difficult to produce paving asphalt of acceptable specifications from crude oils by vacuum reduction because of limitations of commercial units such

as temperature and pressure. Vacuum reduction of such low asphalt content crude oils frequently results in cracking of the residual asphaltic material. The presence of cracked material in asphalt usually makes such material unacceptable for paving uses.

In some instances when processing low asphalt content crude oils for the production of paving asphalts, propane, isobutane or normal butane extraction of the topped crude can be employed. Propane extraction requires pressure vessels because of the very high vapor pressure of propane. When using isobutane or normal butane, high solvent-to-charge oil ratios are ordinarily required for the production of acceptable paving asphalt. Unmodified propanol or isopropanol can be used similarly. However, when using propanol or isopropanol, solvent requirements may also be excessive as illustrated in the following table.

EXAMPLE I

Table I

EXTRACTION OF TEXAS VACUUM RESIDUE WITH ANHYDROUS ISOPROPYL ALCOHOL

Run No.	Solvent	Solvent ratio	Extraction temperature, ° F.	Asphalt		
				Yield, weight percent	Pen., 77° F.	R and B, ° F.
1	Isopropanol	10/1	178	58.4	Too soft	91
2	do	15/1	178	46.7	do	97
3	do	20/1	178	51.0	do	93
4	do	30/1	178	60.5	do	101
5	do	40/1	178	31.0		110
6	do	60/1	178	28.9	94	115

In the runs illustrated in Table I isopropanol (isopropyl alcohol) was used in the solvent-oil ratios given to extract the vacuum residue of a West Texas crude oil. Only sufficient pressures were employed to maintain the solvent in the liquid phase. It will be noted from the data in this table that a 60 to 1 solvent-oil ratio was required to yield an asphalt having a penetration of 94 at 77° F. The smaller or lower solvent-oil ratios yielded asphalts too soft for paving purposes.

In the following Table II are given results illustrating the use of the solvent isopropanol containing paraffinic hydrocarbon additives to increase the solvent power of the isopropanol.

It will be noted in Table II, that Run 7 which employed only 7.5 volume percent normal heptane in the isopropanol, the penetration of the produced asphalt was 255, which value obviously is too high for grades of paving asphalt normally in demand. In Run 8, 13 volume percent n-heptane was employed with the isopropanol and an asphalt having a penetration of 98 was produced. It is pointed out that this Run 8 yields an asphalt quite similar to that asphalt produced in Run 6 illustrated in Table I. Thus, by the use of 13 volume percent of such a normal paraffinic hydrocarbon as normal heptane with the isopropanol, the entire or complete solvent being used in the ratio of 10 to 1, solvent to oil, that a suitable paving asphalt was obtained. Thus, the use of only 10 volumes of solvent per volume of charge in contrast to 60 volumes of solvent per volume of charge oil illustrates the marked advantage of using normal heptane with the isopropanol.

The effect of the hydrocarbon additive on the extracting power of isopropanol is illustrated graphically in FIGURE 1. From this figure it is noted that in order to produce asphalts having penetrations from 85 to 100 requires the use of about 12.6 to 13.4 volume percent of normal heptane in the isopropanol when using a solvent oil ratio of 10 to 1 at about 176° F. In the following Table III is given the minimum and maximum as well as the optimum volume percent normal heptane to be used with isopropanol for the production of the stated penetration grade asphalt.

EXAMPLE II

Table II

EXTRACTION OF TEXAS VACUUM RESIDUE WITH ISOPROPANOL CONTAINING A HYDROCARBON ADDITIVE

Run No.	Solvent	Percent n-Heptane (of total solvent)	S/O Ratio	Temp., ° F.	Asphalt		
					Yield, wt. percent	Pen., 77° F.	R and B, ° F.
7	Isopropanol	7.5	10/1	174	45.5	255	99
8	do	13.0	10/1	176	27.5	98	114
9	do	15.0	10/1	174	20.7	57	120
10	do	17.5	10/1	172	13.0	32	131
11	do	0.0	10/1	178	58.4	Too soft	91

Table III

Penetration grade	Volume percent n-Heptane		
	Minimum	Optimum	Maximum
40–50	15.5	16	16.5
50–60	14.8	15.2	15.5
60–70	14.2	14.5	14.8
70–85	13.5	13.8	14.2
85–100	12.8	13.2	13.5
100–120	11.8	12.2	12.8

In FIGURE 2 is a curve showing the relation between the softening point, by the ring and ball method in degrees F. and the penetration at 77° F. of the asphalts of Runs 7, 8, 9 and 10 in Table II.

Other paraffinic hydrocarbon additives can be used in place of normal heptane, illustrated above, such other hydrocarbons being hexane, octane, nonane, decane, pentane, cyclohexane, kerosene, naphtha or other distillate fraction, preferably having a boiling point or range near the boiling point of isopropyl alcohol at about atmospheric pressure. This boiling range of the paraffinic hydrocarbon material can be extended somewhat if sufficient pressure is imposed on the system to maintain the hydrocarbon in the liquid phase at the operating temperature.

The second embodiment of my invention involves the use of an additive to decrease the solvent power of the propanol and isopropanol. This embodiment is particularly adapted to treating crude oils which contain from about 8 percent to about 80 percent of 100 penetration asphalt, or a fraction of such crude oil. In this case the crude oil or the fraction thereof, is treated with a solvent in the solvent-oil-ratio in the range of about 4 to 20 volumes of solvent per volume of oil. This solvent comprises from about 0.75 to about 4.5 volume percent water and the remainder of the solvent is isopropanol or normal propanol, the treating temperature being in the range of about 175° F. to about 180° F. Topped crude oil fractions from Monagas (Venezuela) crude oil, some West Kansas and some Southern Oklahoma high asphalt crude oils and Rangely (Colorado) intermediate asphalt content crude oil are operable with the process of this invention in which the solvent power of the alcohol is reduced with water.

The production of paving asphalt from crude oils or topped crude oils containing large amounts, that is, from 8 to 80 percent asphalt, of 85 to 100 penetration, presents a problem which requires careful control, usually a reduction in the solvent power of the extraction solvent. In the following Table IV are given data illustrating the preparation of asphalt from Monagas full range crude oil by isopropyl alcohol extraction, with and without water.

EXAMPLE III

Table IV

PREPARATION OF ASPHALT FROM MONAGAS TOPPED CRUDE BY ISOPROPYL ALCOHOL EXTRACTION, WITH AND WITHOUT WATER

Run No.	Solvent ratio	Temp., ° F.	Asphalt yield, wt. percent	Asphalt properties	
				Pen., 77° F.	R&B, ° F.
12	5/1	178	36.7	4	182
13	7.5/1	179	35.3	2	191
14	15/1	180	30.0	0	219
15	5/1	120	49.7	83	119
16	5/1	110	51.5	92	117
17	5/1 (1% H_2O)	180	39.7	13	163
18	5/1 (2% H_2O)	178	42.7	21	149
19	5/1 (4% H_2O)	180	49.2	33	136
20	5/1 (4.5% H_2O)	181	51.9	42	131
21	5/1 (5% H_2O)	184	58.9	199	100
22	5/1 (13% n-C_7)	178	30.2	0	218

In Table IV, it is noted than in Run 22, 13 percent normal heptane was used with isopropyl alcohol at a temperature of 178° F. This run produced a very low yield percent of asphalt of 0 penetration at 77° F. Thus, the use of this amount of normal heptane with the isopropanol yielded an asphalt far too hard for use as a paving asphalt.

Crude oils such as those from Rangely, Colorado, contain from about 8 to 12 percent of 85 to 100 penetration asphalt. In addition, the asphalt produced from this crude oil contains a microcrystalline wax which is associated with the asphaltene fraction of the asphalt. The crude oil appears to be deficient in a middle-range molecular weight fraction (1000–2000 M.W.) commonly referred to as resins. These composition variations make the control of a solvent extraction process very difficult since with propane, a slight change in temperature or in solvent-oil ratio produces a magnified change in yield and grade of asphalt.

In the following Table V are given data illustrating the marked change in 77° F. penetration of an asphalt produced in the propane extraction of a Rangely topped crude oil fraction with small temperature changes. When the temperature of extraction was increased from 191° to 196° F. the penetration increased from 13 to 48, and a further increase in extraction temperature to 204° F. produced an asphalt having a penetration of 324. Thus, it is noted that slight changes in temperature with the propane-to-oil ratio remaining substantially constant yielded asphalts having very great differences in penetration. In an operation using propane as the solvent for the production of paving asphalt temperature control would be very difficult.

EXAMPLE IV

Table V

PROPANE FRACTION OF 28% RANGELY TOPPED CRUDE

Run No.	Temperature, ° F.	S/O Ratio	Asphalt, Vol. percent	Penetration, 77° F.
23	131	6.97	33.3	13
24	196	7.08	35.8	48
25	204	7.00	44.8	324

In the following Table VI are illustrated data showing the effect of temperature and solvent-to-oil ratio using anhydrous isopropanol with 16 percent Rangely reduced topped crude oil. When the solvent-to-oil ratio changed from 3 to 1 to 10 to 1 the penetration was reduced from 186 to 2.

EXAMPLE V

Table VI

16% RANGELY REDUCED TOPPED CRUDE

Run No.	Solvent	S/O ratio	Temperature, ° F.	Asphalt	
				Yield, Wt. percent of crude	Penetration
26	Isopropyl alcohol	3/1	179	10.6	186
27	do	4/1	180	9.7	112
28	do	5/1	183	8.4	48
29	do	7.5/1	179	6.9	17
30	do	10/1	178	5.9	2

In the following Table VII are given data showing the quality of asphalt produced when using anhydrous isopropanol with a blend of Rangely, Colorado, and Red Wash topped crude oil (97–3 percent blend).

EXAMPLE VI

Table VII

ISOPROPANOL EXTRACTION OF RANGELY RED WASH TOPPED CRUDE (97-3% BLEND)

Run No.	Solvent	S/O ratio	Temperature, ° F.	Asphalt	
				Yield, wt. percent	Pen., 77° F.
31	Isopropanol	10/1	175–180	34.3	16
32	do	7.5/1	175–180	38.3	22
33	do	5/1	175–180	47.9	67
34	do	4.5/1	175–180	56.3	198
35	do	4.6/1	175–180	57.1	215
36	do	4.5/1	175–180	52.3	84

These data of Table VII are plotted in the form of a curve which is shown in FIGURE 3. This curve shows that the 85–100 penetration grade asphalt lies in the vertical portion of the curve and solvent-to-oil ratio to produce specification penetration of 85 to 100 would be very difficult to control. This difficulty can be easily overcome by using aqueous isopropanol as a solvent in place of the anhydrous isopropanol. In Table VIII are given the volume percentages of water used with the isopropanol and the solvent-to-oil ratios given represent the total solvent, that is, the isopropanol plus water.

EXAMPLE VII

Table VIII

AQUEOUS ISOPROPANOL EXTRACTION OF RANGELY TOPPED CRUDES TO PRODUCE PAVING ASPHALT

Run No.	Percent H_2O	S/O ratio	Temperature, ° F.	Asphalt	
				Yield, wt. percent	Pen., 100/5/77° F.
37	5.0	10–1	175–180	68.5	Too soft
38	3.0	10–1	175–180	52.9	93
39	2.6	10–1	175–180	53.4	121
40	1.0	5–1	175–180	59.5	238
41	0.0	5–1	175–180	48.3	65
42	0.0	8–1	175–180	42.0	36
43	1.0	8–1	175–180	48.3	46
44	2.0	8–1	175–180	52.3	81
45	0.0	5–1	175–180	59.8	33
46	1.0	5–1	175–180	69.0	70
47	1.5	5–1	175–180	70.8	93

The several categories of solvent-to-oil ratios as shown in Table VIII are plotted as curves in FIGURE 4. These curves are drawn to illustrate the relation between the volume percent of water in the solvent and penetration at 77° F. It will be noticed that in all of these curves there is an appreciable horizontal component, that is relative to the water content of the solvent in the range of penetration of 85 to 100 with the exception of the upper curve. Thus, in view of these relatively large horizontal components illustrating the volume percent water in the isopropanol extractant, the control of such an operation is relatively simple. As will be well understood by those skilled in the art, the control of the volume percent of water in the isopropanol is much easier than to control temperatures of the extraction column within, for example, 1, 2 or 3 degrees.

Cross plotting of the data illustrated in FIGURE 4 and given in Table VIII is illustrated in FIGURE 5 to show the volume of water necessary to produce 90 penetration asphalt at various solvent-oil ratios from similar charging stocks.

The 90 penetration values from curves 1, 2 and 3 only are used in plotting the curve illustrated in FIGURE 5.

This cross plotting of the data (FIGURE 5) shows that the water content of the isopropanol varies from about 0.75 to about 4.5 volume percent at solvent-to-oil ratios from about 5 to 1 to 17.5 to 1, respectively, at extraction temperatures between 175° and 180° F.

As mentioned hereinbefore Rangley crude oil contains small quantities of micro-crystalline wax which tends to degrade the specification properties of asphalt prepared by vacuum reduction of propane extraction. These properties include penetration ratio, solubility of asphalt in carbon tetrachloride and the oilensis spot test. By using aqueous isopropanol these properties are improved as shown in the following example. In the following Table IX are given paving asphalt specifications for the State of Oklahoma for comparison with paving asphalt produced by vacuum reduction and isopropanol extraction of the identical topped crude charge stock.

EXAMPLE VIII

Table IX

	Oklahoma specifications for paving asphalt	Vacuum reduction	Isopropanol extraction	
			R-8	R-7
Penetration, 100/5/77° F.	120-150	134	131	121
Penetration ratio: $\frac{\text{Pen. at } 39.2° \text{ F.}}{\text{Pen. at } 77° \text{ F.}} \times 100$	(Min. 25)	22.4	33.6	33.1
Solubility, CCl_4, wt. percent	99.0-100	98.5	99.0	98.9
Spot test, naphtha, 24 hours	Negative	Positive	Pos.	Neg.

While the data given above illustrating the operation of this invention involves use of isopropanol, I disclose the use of normal propanol as an equivalent of the isopropanol in all respects. However, relative to cost of the material isopropanol is preferred because it is less expensive to purchase commercially than is the normal propanol.

The apparatus required for carrying out the operations of this invention is relatively simple as will be noted in reference to FIGURE 6. The crude oil, or strictly speaking, topped crude oil passes from a source, not shown, through a conduit **1** into an extractor vessel **2**. This extractor can be countercurrent, liquid-liquid contracting column or it can be merely a mixing vessel in which the solvent aqueous isopropanol and the asphaltic oil are mixed. In such a mixer upon addition of the isopropanol and asphaltic oil contacting is achieved by use of a stirring device of any suitable type. However, for most operations, a countercurrent extraction operation is preferred. Thus, from extractor **2** the oily material in solution in the aqueous isopropanol is removed through a conduit **3** and is introduced into a still **4**. In this still the aqueous isopropanol is distilled from the oil, the oil being removed from this vessel through a conduit **5** for such disposal as desired. The aqueous isopropanol vapors are removed from still **4** through a conduit **6**, condensed in condenser **7** and condensate is passed on through a conduit **9** to a run storage vessel **10** and thence through a conduit **11** to the extractor **2**. Make-up aqueous isopropanol is added to the system through a conduit **8**. Since the aqueous isopropanol is specifically lighter than the asphaltic oil being treated the solvent is introduced at a level near the bottom of the column. Upon introduction into vessel **2**, this specifically light aqueous isopropanol passes upward in countercurrent contact with the relatively heavy and down-flowing asphaltic oil. This extractor vessel can be provided with suitable liquid-liquid contact promoting apparatus. The dissolved oil and solvent pass from extractor **2** through an overhead conduit **3** and this extract phase is introduced into still **4**. The asphalt containing phase with a very minor proportion of solvent is withdrawn from extractor **2** through a conduit **12** and is passed into a still **13**. In this vessel the small amount of solvent is removed by distillation through a conduit **14** and these vapors are added to those from conduit **6** prior to passage to condenser **7**. The hot solvent-free asphalt is removed from still **13** through a conduit **15** for such disposal or such use as desired. Relative to operations of stills **4** and **13** refluxing and reboiling operations are not difficult because there is considerable spread in temperature between the boiling points of the oily fraction of the topped crude materials and the asphaltic bottoms materials and the boiling point of the solvent being separated.

If it were desired to produce an asphaltene product and also a separate resin product from the crude oils or topped crude oils disclosed hereinabove it will then be necessary to dilute the original topped crude material with pentane within a temperature range of from about 60° to about 90° F. using a solvent-to-oil ratio of about 5 to 1 to 15 to 1 under pressures of from about 1 to 2 atmospheres. This portion of the process, however, is operable over a greater temperature range such as from about 50° to about 450°, when using a solvent-to-oil ratio by volume of 2 to 1 to about 100 to 1 and at pressures varying about 1 to about 50 atmospheres. As examples of the operation of the pentane separation portion of this operation a charge of Wafra (Kuwait) vacuum reduced crude oil was slurried with an equal volume of pentane. This slurry was then added to an additional 9 volumes of pentane, the mixture stirred for an hour and allowed to settle for about 16 hours. The pentane soluble material was decanted and filtered. The precipitated asphaltenes were washed with approximately 5 volumes of fresh pentane. These washings were added to the pentane soluble material and the pentane from the entire mixture was recovered by fractional distillation.

In the following Table X are given four sets of run data using pentane for treating asphalt-containing oil for the separation of an asphaltenes product.

EXAMPLE IX

Table X

PENTANE EXTRACTIONS OF WAFRA 1025 F+ RESIDUUM

Run No	A-1	A-2	A-3	A-4
Wt. of Asphalt, lbs	38.26	36.0	38.0	38.0
Vol. of Asphalt, gals	4.52	4.26	4.5	4.5
Vol. n-Pentane, gals	45.9	44.9	44.6	45.1
Solvent Ratio	10.1	10.5	9.9	10.0
Temperature, ° F	78	80	85	86
Settling Time, hrs	16	16	72	48
Filtrate + 10-gal Wash, gals	52.1	53.3	52.5	52.5
n-C_5 Evaporation Loss, gals	3.8	1.6	2.1	2.6
Yields:				
Asphaltenes, lbs	5.47	5.62	5.37	6.23
Asphaltenes, wt. percent	14.8	15.6	14.13	16.3
Maltenes, lbs	20.84	33.39	29.88	33.2
Maltenes, wt. percent	54.4	92.2	78.7	87.5
n-C_5 Recovered, gal	43.7	50.4	47.0	47.0
n-C_5 Loss in Stripping, gal	8.4	2.9	5.5	5.5

In these four runs the solvent-to-oil ratio varied from 9.9 to 10.5 and temperatures of treating varied from 78° to 86° F. It will be noted that from 5.37 pounds of asphaltenes to 6.23 pounds of asphaltenes were produced from 36 to 38 pounds of original Wafra residuum. In Example A-1 from 38.26 pounds of asphaltic charge stock, there were recovered 5.47 pounds of asphaltenes and 20.84 pounds of maltenes. This quantity of maltenes plus the quantity of asphaltenes total only 26.31 pounds; there being an appreciable loss. This loss was in the maltenes fraction because some of the maltenes were carried into other parallel runs with pentane used for washing. In the total operation, ten individual parallel runs were made using a total weight of asphaltic feed stock of 375.39 pounds. There was recovered from the ten parallel operations 54.69 pounds of asphaltenes and 320.7 pounds of maltenes. These two products totaled

375.39 pounds, the exact weight of the asphaltic material used as charge stock. This 100 percent recovery of the combined maltenes and asphaltenes is relatively simple because of the extremely high boiling points of these materials.

The asphaltene separation by way of pentane precipitation is carried out in an apparatus as illustrated in FIGURE 7. The topped crude material is fed into a mixer **22** by way of ac onduit **21**. Normal pentane as solvent enters the mixer **22** by way of a conduit **23**, from a source to be disclosed hereinafter. After sufficient and thorough mixing in mixer **22** the mixture is passed by way of a conduit **24** to a separator vessel **25** in which the precipitated asphaltenes are separated from the pentane-asphaltene liquid phase. The separated asphaltenes are removed from separator **25** through a conduit **26** for a subsequent washing step or for such use as desired. The liquid maltene-containing fraction is removed from separator **25** through a conduit **27** and is passed to a still **28** for recovery of the solvent pentane. This still is operated under such temperature and pressure conditions as to separate normal pentane from the heavy oily maltene fraction. Vaporous pentane leaves still **28** by way of a conduit **29**, is condensed in condenser **30** and condensate is passed on through the before-mentioned conduit **23** for reuse in mixer **22**. The maltene-oil fraction is withdrawn through a conduit **31** from the kettle section of still **28**. Make-up pentane as required is added to the system through a line **32** from a source, not shown.

The heavy maltene-oil fraction withdrawn from the kettle section of still **28** through a conduit **31** can, if desired, be treated in the system illustrated in FIGURE 6 of the drawing. If it is desired to separate and to recover a resin fraction from this maltene fraction then the process described and illustrated hereinabove relative to FIGURE 6 is employed. By treating the maltenes-oil fraction free from asphaltenes in the apparatus and according to the system of FIGURE 6, there will be produced a resin fraction which is removed through conduit **15** from the kettle section of still **13**. The oil fraction removed through conduit **5** is the same oil fraction removed through this conduit when the entire asphalt containing charge oil is treated according to the system of FIGURE 6.

While certain embodiments of the invention have been described for illustrative purposes, the invention obviously is not limited thereto.

I claim:

1. A process comprising contacting an asphaltic petroleum oil in which the concentration of 100 penetration asphalt is in the range of about 8 to 80 volume percent with a solvent consisting essentially of a member selected from the group consisting of n-propyl alcohol and isopropyl alcohol and containing from about 0.75 to about 4.5 percent by volume of water, the ratio of solvent to oil being from about 4:1 to about 20:1, at a temperature within the approximate range of 175° to 180° F. and at sufficient pressure for process flow, and controlling the water concentration so as to produce an asphalt-phase containing paving grade asphalt having a penetration point in the range of 85 to 100 (1/10 millimeters with 100 g. for 5 sec. at 77° F.) and an oil-containing phase suitable for catalytic cracking to gasoline.

2. The process of claim **1** wherein the selected alcohol is isopropyl alcohol.

3. The process of claim **1** wherein the selected alcohol is n-propyl alcohol.

4. A process comprising contacting an asphaltic petroleum oil in which the concentration of 100 penetration asphalt is in the range of about 8 to 80 volume percent with a solvent consisting essentially of a member selected from the group consisting of n-propyl alcohol and isopropyl alcohol and containing from about 0.75 to about 4.5 percent by volume of water, the ratio of solvent to oil being from about 4:1 to about 20:1, at a temperature within the approximate range of 175° to 180° F. and at sufficient pressure for process flow, and controlling the water concentration so as to produce an asphalt-phase containing paving grade asphalt having a penetration point in the range of 40 to 120 (1/10 millimeters with 100 g. for 5 sec. at 77° F.) and an oil-containing phase suitable for catalytic cracking to gasoline.

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