

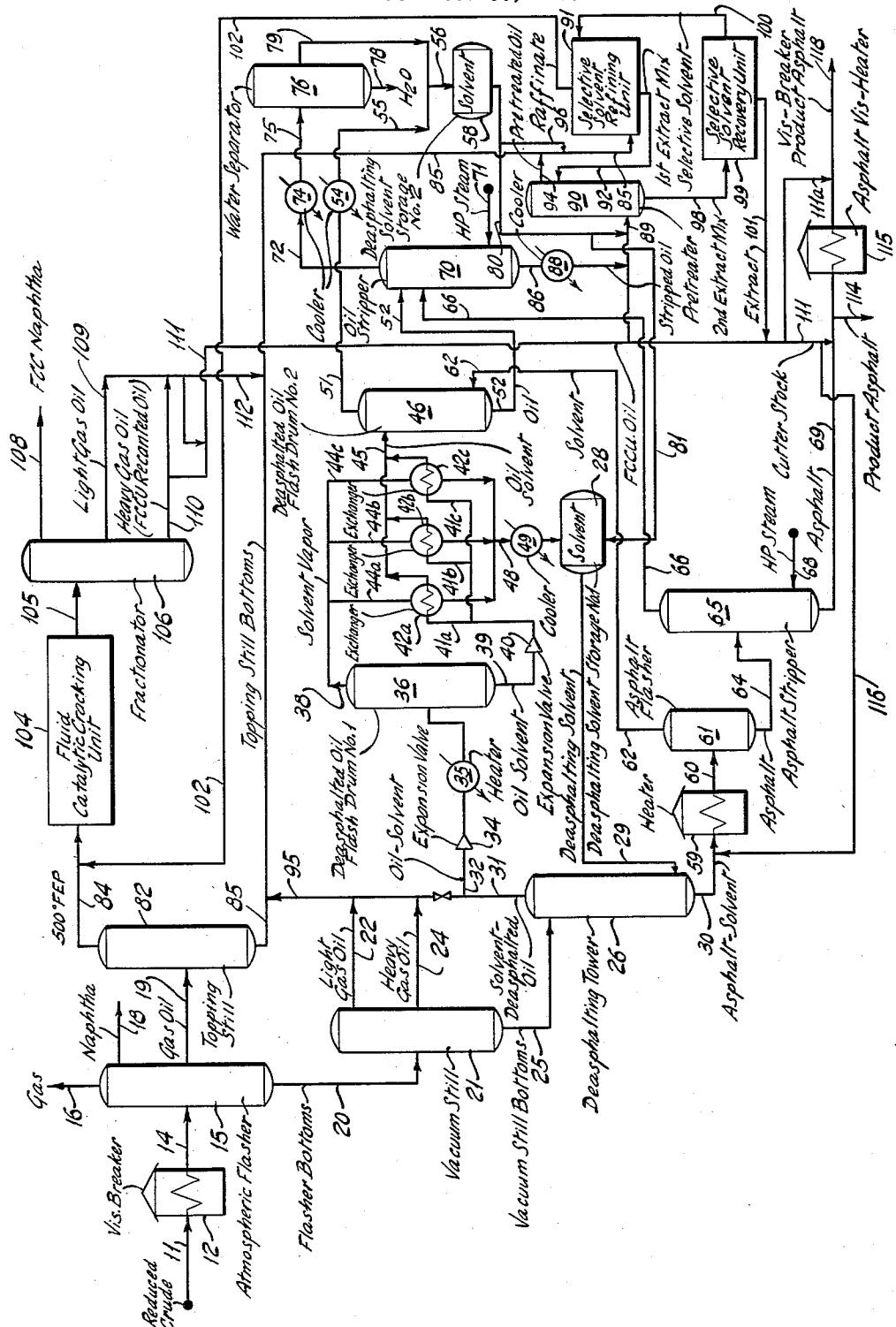
Sept. 2, 1958

R. SMITH

2,850,431

## SOLVENT DEASPHALTING

Filed Dec. 30, 1955



# United States Patent Office

2,850,431

Patented Sept. 2, 1953

1

2,850,431

## SOLVENT DEASPHALTING

Randlow Smith, New Rochelle, N. Y., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

Application December 30, 1955, Serial No. 556,496

8 Claims. (Cl. 196—14.46)

This invention relates to the treatment of asphaltic oils with a deasphalting solvent for the separation of asphaltic constituents therefrom. More particularly, this invention is concerned with the treatment of asphaltic residual hydrocarbon oils for the recovery of asphaltic constituents therefrom and for the production of a deasphalted oil suitable for use as a catalytic cracking feed stock. In accordance with one embodiment, this invention relates to a process for deasphalting residual hydrocarbon oils for the production of an asphalt fraction and a deasphalted oil fraction which is subsequently solvent refined for the preparation of a catalytic cracking feed stock characterized by a relatively low metals content.

It is an object of this invention to provide an improved solvent deasphalting process.

It is another object of this invention to provide an improved solvent deasphalting process employing a volatile deasphalting solvent, such as a normally gaseous hydrocarbon, e. g., ethane, propane, n-butane, isobutane, n-pentane, isopentane and mixtures thereof, wherein the deasphalting solvent after having been employed to separate asphaltic constituents from the asphaltic oil undergoing treatment is recovered in a deasphalting solvent recovery system which does not require the use of compressors to effect liquefaction and recovery of the deasphalting solvent.

It is another object of this invention to provide an improved and economical method for the recovery of deasphalting solvent employed in an operation involving the solvent deasphalting of asphaltic residual hydrocarbon oils.

How these and other objects of this invention are accomplished will become apparent with reference to the accompanying disclosure and drawing wherein there is schematically illustrated an embodiment of the practice of this invention directed to the solvent deasphalting of an asphaltic residual hydrocarbon oil. In at least one embodiment of this invention at least one of the foregoing objects will be achieved.

In accordance with this invention an asphaltic oil is solvent deasphalting by contact with a deasphalting solvent under deasphalting conditions of temperature and pressure to effect separation of asphaltic constituents from said oil. There is recovered from the aforesaid deasphalting operation a liquid deasphalted oil phase having a reduced amount of asphaltic constituents and containing a portion of said deasphalting solvent and a liquid asphalt phase containing another portion of said deasphalting solvent. The deasphalted oil phase at substantially the deasphalting conditions of temperature and pressure is partially volatilized or vaporized, as by pressure reduction, to produce a resulting first liquid phase and a resulting first vapor phase containing deasphalting solvent at a temperature  $T_1$  and at a pressure  $P_1$ . The resulting first liquid phase is further treated, e. g., partial vaporization by pressure reduction, to produce a resulting second liquid phase comprising deasphalted oil and a resulting second vapor phase comprising deasphalting solvent at a tem-

2

perature  $T_2$  and a pressure  $P_2$ ,  $T_2$  being lower than  $T_1$  and  $P_2$  being lower than  $P_1$ . The aforesaid first and second vapor phases are then passed in indirect heat exchange relationship to each other whereby the temperature of said first vapor phase is reduced such that the vapor pressure of the deasphalting solvent therein is substantially lower than  $P_1$ , preparatory to or leading to the ready liquefaction and condensation of the deasphalting solvent in said first vapor phase. The resulting second vapor phase after heat exchange with said vapor phase is then cooled to a temperature sufficiently low to effect condensation of the deasphalting solvent therein. By operating in accordance with the above-broadly-indicated method the deasphalting solvent contained in the deasphalted liquid oil phase issuing from the solvent deasphalting operation is substantially completely recovered in liquid form without requiring the use of compressors and the like and is available for recycle to the solvent deasphalting operation. Also by operating a solvent deasphalting operation in accordance with the above-indicated method, substantial heat economy is possible.

Referring now in detail to the drawing a reduced crude, such as a mixture of reduced California crudes, having an initial boiling point greater than about 650° F., usually having a boiling point greater than about 800° F., amounting to about 35-75% by volume of the original crude, is supplied via line 11 to vis-breaker 12 where it is subjected to temperature, pressure and throughput conditions so as to mildly lower the viscosity of the reduced crude. A temperature in the range 800-1000° F. and a pressure in the range 50-800 p. s. i. g. are usually sufficient to effect mild vis-breaking of the reduced crude.

Vis-breaking of the reduced crude serves to reform or otherwise alter some of the high molecular weight or high boiling constituents of the reduced crude into relatively low molecular weight or low boiling constituents. The vis-breaking operation tends to produce lower boiling, more aromatic constituents which are generally more refractory in a catalytic cracking operation than lower boiling, more paraffinic hydrocarbons which are also produced. The vis-breaking operation complements and otherwise cooperates with a subsequent combination of deasphalting and solvent refining operations described hereinafter. The vis-breaking operation increases the yield of naphtha recoverable from the reduced crude in that the relatively more aromatic hydrocarbons produced during the vis-breaking operations are separated in a subsequent combination of fractionation, and deasphalting and solvent refining steps with the resulting production of a more paraffinic catalytic cracking charge stock suitable for the production of a catalytic cracked naphtha.

The mildly vis-broken reduced crude from vis-breaker 12 is introduced via line 14 into fractionator or atmospheric flasher 15 from which there is recovered overhead via line 16 a gas fraction comprising normally gaseous hydrocarbons such as propane and the butanes, a naphtha fraction via line 18, such as a 430° F. end point naphtha, and a gas oil fraction via line 19. There is also recovered from flasher 15 a bottoms fraction via line 20. The flasher bottoms is then introduced via line 20 into vacuum still or distillation zone 21 where it undergoes further fractionation for the production of a light gas oil fraction recovered via line 22 and a heavy gas oil fraction recovered via line 24. Vacuum bottoms is recovered from vacuum still 21 via line 25.

The vacuum bottoms fraction recovered from vacuum still 21 via line 25, usually having a gravity °A. P. I. in the range 3-12 and a Conradson carbon residue in the range 15-40%, more or less, is introduced via line 25 into the upper part of solvent deasphalting tower or zone 26. The solvent deasphalting operation may be a batch operation, a multiple vessel operation or a substan-

5  
tially continuous liquid-liquid counter-current treating operation, as indicated in the drawing, wherein the vacuum bottoms to be deasphalted is introduced via line 25 into the top of deasphalting tower 26 and flowed therein in countercurrent liquid-liquid contact with a suitable deasphalting solvent, such as a liquefied normally gaseous hydrocarbon, e. g., propane, n-butane, isobutane. The deasphalting solvent is introduced via line 29 into the bottom portion of deasphalting tower 26 from deasphalting solvent storage tank 28.

A suitable deasphalting solvent in accordance with the practice of this invention is a liquefied normally gaseous hydrocarbon such as ethane, ethylene, propane, propylene, normal butane, isobutane, n-butylene, isobutylene, pentane, isopentane and mixtures thereof, either alone or in admixture with a minor amount of additive materials to improve the deasphalting operation or otherwise increase the yield and quality of the deasphalting oil and/or the recovered asphalt. The deasphalting operation is carried out at any suitable deasphalting temperature and pressure, the temperature and pressure being adjusted so as to maintain the deasphalting solvent in the liquid phase during the deasphalting operation. A deasphalting temperature in the range 150-325° F., usually not more than 75 degrees Fahrenheit lower than the critical temperature of the deasphalting solvent, and a pressure in the range 200-800 p. s. i. g., are employed depending upon the composition of the deasphalting solvent employed and to some extent the composition of the vacuum bottoms undergoing deasphalting. Generally, a deasphalting solvent to vacuum bottoms volume charge ratio in the range 2-10 is employed within deasphalting tower 26. Deasphalting tower 26 may be operated under substantially isothermal conditions or under a temperature gradient, e. g., top tower temperature greater than bottom tower temperature by not more than about 40 degrees Fahrenheit. Also deasphalting tower 26 may be operated so that the vacuum bottoms is introduced thereto at a number of points along the height of the tower and/or so that the deasphalting solvent is introduced thereto at a number of points.

Following the deasphalting operation there is recovered from deasphalting tower 26 a deasphalted oil solvent mix via line 31 and an asphalt solvent mix via line 30. The deasphalted oil in the mix in line 31 may have a gravity °A. P. I. in the range 10-25 and a Conradson carbon residue in the range 1-10% and a viscosity in the range 200-600 SUS at 210° F., more or less. The deasphalted oil solvent mix is transferred from line 31 via line 32 through a vaporizing device, such as pressure reducing or expansion valve 34, and through a heater 35 into deasphalted oil flash drum 36. From flash drum 36 there is removed overhead via line 38 a first vapor phase containing deasphalting solvent vapor. There is also removed from the bottom of flash drum 36 via line 39 a first liquid phase containing deasphalted oil admixed with deasphalting solvent. The first liquid phase is passed via line 39 through a second vaporizing device, such as pressure reducing valve 40, whereby it is partially vaporized to a lower temperature and pressure than the temperature and pressure prevailing in line 38. The resulting partially vaporized first liquid phase is then passed in indirect counter-current heat exchange relationship via lines 41a, 41b and 41c by means of heat exchangers 42a, 42b and 42c with said first vapor phase introduced into the heat exchangers via lines 44a, 44b and 44c, respectively. After the above-described heat exchange has taken place the resulting partially vaporized first liquid phase is recovered via line 45 and introduced into deasphalting solvent storage tank 28. The resulting cooled first vapor phase, approaching the temperature of the partially vaporized first liquid phase in lines 41a, 41b and 41c, is recovered via line 48 and, if necessary, after having been cooled in cooler 49 is introduced into deasphalting solvent storage tank 28 from which the result-

5  
ing liquefied deasphalting solvent can be returned to deasphalting tower 26 via line 29.

The partially vaporized first liquid phase introduced into deasphalting oil flash drum 46 via line 45 is separated into an overhead solvent vapor phase via line 51 comprising substantially only deasphalting solvent and a liquid oil phase via line 52 comprising substantially only deasphalted oil. The deasphalting solvent vapor phase in line 51 is cooled in cooler 54 and the resulting liquefied deasphalting solvent is passed via lines 55 and 56 into deasphalting solvent storage tank 58.

The liquid asphalt deasphalting solvent mix leaving deasphalting tower 26 is passed via line 30 through a heater 59 and line 60 into asphalt flasher 61. The resulting vaporized deasphalting solvent is removed overhead from asphalt flasher 61 via line 62 for introduction into deasphalting oil flash drum 46 for the eventual liquefaction and recovery of the deasphalting solvent as indicated hereinabove. There is removed from asphalt flasher 61 a liqued asphalt bottoms via line 64 which is introduced into asphalt stripper 65 for the removal overhead via line 66 of residual deasphalting solvent by the injection of high temperature, high pressure steam into asphalt stripper 65 via line 68. The resulting steam stripped asphalt is removed as liquid bottoms from asphalt stripper 65 via line 69.

30  
35  
3b  
40  
45  
50  
55  
60  
65  
70  
75  
80  
85  
90  
95  
100  
105  
110  
115  
120  
125  
130  
135  
140  
145  
150  
155  
160  
165  
170  
175  
180  
185  
190  
195  
200  
205  
210  
215  
220  
225  
230  
235  
240  
245  
250  
255  
260  
265  
270  
275  
280  
285  
290  
295  
300  
305  
310  
315  
320  
325  
330  
335  
340  
345  
350  
355  
360  
365  
370  
375  
380  
385  
390  
395  
400  
405  
410  
415  
420  
425  
430  
435  
440  
445  
450  
455  
460  
465  
470  
475  
480  
485  
490  
495  
500  
505  
510  
515  
520  
525  
530  
535  
540  
545  
550  
555  
560  
565  
570  
575  
580  
585  
590  
595  
600  
605  
610  
615  
620  
625  
630  
635  
640  
645  
650  
655  
660  
665  
670  
675  
680  
685  
690  
695  
700  
705  
710  
715  
720  
725  
730  
735  
740  
745  
750  
755  
760  
765  
770  
775  
780  
785  
790  
795  
800  
805  
810  
815  
820  
825  
830  
835  
840  
845  
850  
855  
860  
865  
870  
875  
880  
885  
890  
895  
900  
905  
910  
915  
920  
925  
930  
935  
940  
945  
950  
955  
960  
965  
970  
975  
980  
985  
990  
995  
1000  
1005  
1010  
1015  
1020  
1025  
1030  
1035  
1040  
1045  
1050  
1055  
1060  
1065  
1070  
1075  
1080  
1085  
1090  
1095  
1100  
1105  
1110  
1115  
1120  
1125  
1130  
1135  
1140  
1145  
1150  
1155  
1160  
1165  
1170  
1175  
1180  
1185  
1190  
1195  
1200  
1205  
1210  
1215  
1220  
1225  
1230  
1235  
1240  
1245  
1250  
1255  
1260  
1265  
1270  
1275  
1280  
1285  
1290  
1295  
1300  
1305  
1310  
1315  
1320  
1325  
1330  
1335  
1340  
1345  
1350  
1355  
1360  
1365  
1370  
1375  
1380  
1385  
1390  
1395  
1400  
1405  
1410  
1415  
1420  
1425  
1430  
1435  
1440  
1445  
1450  
1455  
1460  
1465  
1470  
1475  
1480  
1485  
1490  
1495  
1500  
1505  
1510  
1515  
1520  
1525  
1530  
1535  
1540  
1545  
1550  
1555  
1560  
1565  
1570  
1575  
1580  
1585  
1590  
1595  
1600  
1605  
1610  
1615  
1620  
1625  
1630  
1635  
1640  
1645  
1650  
1655  
1660  
1665  
1670  
1675  
1680  
1685  
1690  
1695  
1700  
1705  
1710  
1715  
1720  
1725  
1730  
1735  
1740  
1745  
1750  
1755  
1760  
1765  
1770  
1775  
1780  
1785  
1790  
1795  
1800  
1805  
1810  
1815  
1820  
1825  
1830  
1835  
1840  
1845  
1850  
1855  
1860  
1865  
1870  
1875  
1880  
1885  
1890  
1895  
1900  
1905  
1910  
1915  
1920  
1925  
1930  
1935  
1940  
1945  
1950  
1955  
1960  
1965  
1970  
1975  
1980  
1985  
1990  
1995  
2000  
2005  
2010  
2015  
2020  
2025  
2030  
2035  
2040  
2045  
2050  
2055  
2060  
2065  
2070  
2075  
2080  
2085  
2090  
2095  
2100  
2105  
2110  
2115  
2120  
2125  
2130  
2135  
2140  
2145  
2150  
2155  
2160  
2165  
2170  
2175  
2180  
2185  
2190  
2195  
2200  
2205  
2210  
2215  
2220  
2225  
2230  
2235  
2240  
2245  
2250  
2255  
2260  
2265  
2270  
2275  
2280  
2285  
2290  
2295  
2300  
2305  
2310  
2315  
2320  
2325  
2330  
2335  
2340  
2345  
2350  
2355  
2360  
2365  
2370  
2375  
2380  
2385  
2390  
2395  
2400  
2405  
2410  
2415  
2420  
2425  
2430  
2435  
2440  
2445  
2450  
2455  
2460  
2465  
2470  
2475  
2480  
2485  
2490  
2495  
2500  
2505  
2510  
2515  
2520  
2525  
2530  
2535  
2540  
2545  
2550  
2555  
2560  
2565  
2570  
2575  
2580  
2585  
2590  
2595  
2600  
2605  
2610  
2615  
2620  
2625  
2630  
2635  
2640  
2645  
2650  
2655  
2660  
2665  
2670  
2675  
2680  
2685  
2690  
2695  
2700  
2705  
2710  
2715  
2720  
2725  
2730  
2735  
2740  
2745  
2750  
2755  
2760  
2765  
2770  
2775  
2780  
2785  
2790  
2795  
2800  
2805  
2810  
2815  
2820  
2825  
2830  
2835  
2840  
2845  
2850  
2855  
2860  
2865  
2870  
2875  
2880  
2885  
2890  
2895  
2900  
2905  
2910  
2915  
2920  
2925  
2930  
2935  
2940  
2945  
2950  
2955  
2960  
2965  
2970  
2975  
2980  
2985  
2990  
2995  
3000  
3005  
3010  
3015  
3020  
3025  
3030  
3035  
3040  
3045  
3050  
3055  
3060  
3065  
3070  
3075  
3080  
3085  
3090  
3095  
3100  
3105  
3110  
3115  
3120  
3125  
3130  
3135  
3140  
3145  
3150  
3155  
3160  
3165  
3170  
3175  
3180  
3185  
3190  
3195  
3200  
3205  
3210  
3215  
3220  
3225  
3230  
3235  
3240  
3245  
3250  
3255  
3260  
3265  
3270  
3275  
3280  
3285  
3290  
3295  
3300  
3305  
3310  
3315  
3320  
3325  
3330  
3335  
3340  
3345  
3350  
3355  
3360  
3365  
3370  
3375  
3380  
3385  
3390  
3395  
3400  
3405  
3410  
3415  
3420  
3425  
3430  
3435  
3440  
3445  
3450  
3455  
3460  
3465  
3470  
3475  
3480  
3485  
3490  
3495  
3500  
3505  
3510  
3515  
3520  
3525  
3530  
3535  
3540  
3545  
3550  
3555  
3560  
3565  
3570  
3575  
3580  
3585  
3590  
3595  
3600  
3605  
3610  
3615  
3620  
3625  
3630  
3635  
3640  
3645  
3650  
3655  
3660  
3665  
3670  
3675  
3680  
3685  
3690  
3695  
3700  
3705  
3710  
3715  
3720  
3725  
3730  
3735  
3740  
3745  
3750  
3755  
3760  
3765  
3770  
3775  
3780  
3785  
3790  
3795  
3800  
3805  
3810  
3815  
3820  
3825  
3830  
3835  
3840  
3845  
3850  
3855  
3860  
3865  
3870  
3875  
3880  
3885  
3890  
3895  
3900  
3905  
3910  
3915  
3920  
3925  
3930  
3935  
3940  
3945  
3950  
3955  
3960  
3965  
3970  
3975  
3980  
3985  
3990  
3995  
4000  
4005  
4010  
4015  
4020  
4025  
4030  
4035  
4040  
4045  
4050  
4055  
4060  
4065  
4070  
4075  
4080  
4085  
4090  
4095  
4100  
4105  
4110  
4115  
4120  
4125  
4130  
4135  
4140  
4145  
4150  
4155  
4160  
4165  
4170  
4175  
4180  
4185  
4190  
4195  
4200  
4205  
4210  
4215  
4220  
4225  
4230  
4235  
4240  
4245  
4250  
4255  
4260  
4265  
4270  
4275  
4280  
4285  
4290  
4295  
4300  
4305  
4310  
4315  
4320  
4325  
4330  
4335  
4340  
4345  
4350  
4355  
4360  
4365  
4370  
4375  
4380  
4385  
4390  
4395  
4400  
4405  
4410  
4415  
4420  
4425  
4430  
4435  
4440  
4445  
4450  
4455  
4460  
4465  
4470  
4475  
4480  
4485  
4490  
4495  
4500  
4505  
4510  
4515  
4520  
4525  
4530  
4535  
4540  
4545  
4550  
4555  
4560  
4565  
4570  
4575  
4580  
4585  
4590  
4595  
4600  
4605  
4610  
4615  
4620  
4625  
4630  
4635  
4640  
4645  
4650  
4655  
4660  
4665  
4670  
4675  
4680  
4685  
4690  
4695  
4700  
4705  
4710  
4715  
4720  
4725  
4730  
4735  
4740  
4745  
4750  
4755  
4760  
4765  
4770  
4775  
4780  
4785  
4790  
4795  
4800  
4805  
4810  
4815  
4820  
4825  
4830  
4835  
4840  
4845  
4850  
4855  
4860  
4865  
4870  
4875  
4880  
4885  
4890  
4895  
4900  
4905  
4910  
4915  
4920  
4925  
4930  
4935  
4940  
4945  
4950  
4955  
4960  
4965  
4970  
4975  
4980  
4985  
4990  
4995  
5000  
5005  
5010  
5015  
5020  
5025  
5030  
5035  
5040  
5045  
5050  
5055  
5060  
5065  
5070  
5075  
5080  
5085  
5090  
5095  
5100  
5105  
5110  
5115  
5120  
5125  
5130  
5135  
5140  
5145  
5150  
5155  
5160  
5165  
5170  
5175  
5180  
5185  
5190  
5195  
5200  
5205  
5210  
5215  
5220  
5225  
5230  
5235  
5240  
5245  
5250  
5255  
5260  
5265  
5270  
5275  
5280  
5285  
5290  
5295  
5300  
5305  
5310  
5315  
5320  
5325  
5330  
5335  
5340  
5345  
5350  
5355  
5360  
5365  
5370  
5375  
5380  
5385  
5390  
5395  
5400  
5405  
5410  
5415  
5420  
5425  
5430  
5435  
5440  
5445  
5450  
5455  
5460  
5465  
5470  
5475  
5480  
5485  
5490  
5495  
5500  
5505  
5510  
5515  
5520  
5525  
5530  
5535  
5540  
5545  
5550  
5555  
5560  
5565  
5570  
5575  
5580  
5585  
5590  
5595  
5600  
5605  
5610  
5615  
5620  
5625  
5630  
5635  
5640  
5645  
5650  
5655  
5660  
5665  
5670  
5675  
5680  
5685  
5690  
5695  
5700  
5705  
5710  
5715  
5720  
5725  
5730  
5735  
5740  
5745  
5750  
5755  
5760  
5765  
5770  
5775  
5780  
5785  
5790  
5795  
5800  
5805  
5810  
5815  
5820  
5825  
5830  
5835  
5840  
5845  
5850  
5855  
5860  
5865  
5870  
5875  
5880  
5885  
5890  
5895  
5900  
5905  
5910  
5915  
5920  
5925  
5930  
5935  
5940  
5945  
5950  
5955  
5960  
5965  
5970  
5975  
5980  
5985  
5990  
5995  
6000  
6005  
6010  
6015  
6020  
6025  
6030  
6035  
6040  
6045  
6050  
6055  
6060  
6065  
6070  
6075  
6080  
6085  
6090  
6095  
6100  
6105  
6110  
6115  
6120  
6125  
6130  
6135  
6140  
6145  
6150  
6155  
6160  
6165  
6170  
6175  
6180  
6185  
6190  
6195  
6200  
6205  
6210  
6215  
6220  
6225  
6230  
6235  
6240  
6245  
6250  
6255  
6260  
6265  
6270  
6275  
6280  
6285  
6290  
6295  
6300  
6305  
6310  
6315  
6320  
6325  
6330  
6335  
6340  
6345  
6350  
6355  
6360  
6365  
6370  
6375  
6380  
6385  
6390  
6395  
6400  
6405  
6410  
6415  
6420  
6425  
6430  
6435  
6440  
6445  
6450  
6455  
6460  
6465  
6470  
6475  
6480  
6485  
6490  
6495  
6500  
6505  
6510  
6515  
6520  
6525  
6530  
6535  
6540  
6545  
6550  
6555  
6560  
6565  
6570  
6575  
6580  
6585  
6590  
6595  
6600  
6605  
6610  
6615  
6620  
6625  
6630  
6635  
6640  
6645  
6650  
6655  
6660  
6665  
6670  
6675  
6680  
6685  
6690  
6695  
6700  
6705  
6710  
6715  
6720  
6725  
6730  
6735  
6740  
6745  
6750  
6755  
6760  
6765  
6770  
6775  
6780  
6785  
6790  
6795  
6800  
6805  
6810  
6815  
6820  
6825  
6830  
6835  
6840  
6845  
6850  
6855  
6860  
6865  
6870  
6875  
6880  
6885  
6890  
6895  
6900  
6905  
6910  
6915  
6920  
6925  
6930  
6935  
6940  
6945  
6950  
6955  
6960  
6965  
6970  
6975  
6980  
6985  
6990  
6995  
7000  
7005  
7010  
7015  
7020  
7025  
7030  
7035  
7040  
7045  
7050  
7055  
7060  
7065  
7070  
7075  
7080  
7085  
7090  
7095  
7100  
7105  
7110  
7115  
7120  
7125  
7130  
7135  
7140  
7145  
7150  
7155  
7160  
7165  
7170  
7175  
7180  
7185  
7190  
7195  
7200  
7205  
7210  
7215  
7220  
7225  
7230  
7235  
7240  
7245  
7250  
7255  
7260  
7265  
7270  
7275  
7280  
7285  
7290  
7295  
7300  
7305  
7310  
7315  
7320  
7325  
7330  
7335  
7340  
7345  
7350  
7355  
7360  
7365  
7370  
7375  
7380  
7385  
7390  
7395  
7400  
7405  
7410  
7415  
7420  
7425  
7430  
7435  
7440  
7445  
7450  
7455  
7460  
7465  
7470  
7475  
7480  
7485  
7490  
7495  
7500  
7505  
7510  
7515  
7520  
7525  
7530  
7535  
7540  
7545  
7550  
7555  
7560  
7565  
7570  
7575  
7580  
7585  
7590  
7595  
7600  
7605  
7610  
7615  
7620  
7625  
7630  
7635  
7640  
7645  
7650  
7655  
7660  
7665  
7670  
7675  
7680  
7685  
7690  
7695  
7700  
7705  
7710  
7715  
7720  
7725  
7730  
7735  
7740  
7745  
7750  
7755  
7760  
7765  
7770  
7775  
7780  
7785  
7790  
7795  
7800  
7805  
7810  
7815  
7820  
7825  
7830  
7835  
7840  
7845  
7850  
7855  
7860  
7865  
7870  
7875  
7880  
7885  
7890  
7895  
7900  
7905  
7910  
7915  
7920  
7925  
7930  
7935  
7940  
7945  
7950  
7955  
7960  
7965  
7970  
7975  
7980  
7985  
7990  
7995  
8000  
8005  
8010  
8015  
8020  
8025  
8030  
8035  
8040  
8045  
8050  
8055  
8060  
8065  
8070  
8075  
8080  
8085  
8090  
8095  
8100  
8105  
8110  
8115  
8120  
8125  
8130  
8135  
8140  
8145  
8150  
8155  
8160  
8165  
8170  
8175  
8180  
8185  
8190  
8195  
8200  
8205  
8210  
8215  
8220  
8225  
8230  
8235  
8240  
8245  
8250  
8255  
8260  
8265  
8270  
8275  
8280  
8285  
8290  
8295  
8300  
8305  
8310  
8315  
8320  
8325  
8330  
8335  
8340  
8345  
8350  
8355  
8360  
8365  
8370  
8375  
8380  
8385  
8390  
8395  
8400  
8405  
8410  
8415  
8420  
8425  
8430  
8435  
8440  
8445  
8450

contacted therein with a solvent extract mix comprising selective solvent, such as furfural, together with the dissolved hydrocarbons therein, which is recovered from solvent refining unit 91, described hereinafter, and introduced into pretreater 90 via line 92. The resulting deasphalted oil raffinate from pretreater 90 is recovered via line 94 and introduced into line 85 for introduction into selective solvent refining unit 91 in admixture with the bottoms fraction recovered from topping still 82 and the gas oil fractions removed from vacuum still 21 via lines 22, 24 and 95. If desired, liquid deasphalting solvent from deasphalting solvent storage tank 58 may be admixed via lines 80 and 96 with the pretreated deasphalted oil prior to introduction into selective solvent refining unit 91. Also, if desired, a portion of the deasphalted oil solvent mix recovered from deasphalting tower 26 via line 31 may be introduced via line 95 into line 85 for eventual admixture with the pretreated deasphalted oil in selective solvent refining unit 91.

The resulting extract effluent from pretreater 90 is recovered via line 98 and introduced into selective solvent recovery unit 99 wherein the selective solvent, e. g., furfural, is recovered and recycled to selective solvent refining unit 91 via line 100. The resulting separated extract is recovered from selective solvent refining unit 99 via line 101. Various selective solvents may be employed in selective solvent refining unit 91, these include furfural, phenols (Selecto), nitrobenzene, sulfur dioxide,  $\beta,\beta'$ -dichloroethyl ether (Chlorex), dimethyl formamide and other selective solvents for aromatic hydrocarbons.

The resulting admixture in line 85 comprising the bottoms fraction from topping still 82, the gas oil fractions from vacuum still 21, selective solvent pretreated deasphalted oil from pretreater 90 and, if desired, the liquid deasphalting solvent recovered from deasphalting solvent storage tank 58 via lines 80 and 96 or a portion of the deasphalted oil-deasphalting solvent mix recovered from deasphalting tower 26 via lines 31 and 95, is introduced into selective solvent refining unit 91 wherein it flows in liquid-liquid counter-current contact with a liquid selective solvent, such as furfural, which selectively dissolves or extracts the more aromatic hydrocarbons therefrom. As previously indicated, the resulting extract mix from selective solvent refining unit 91 comprising selective solvent and extracted hydrocarbons is recovered via line 92 and introduced into pretreater 90.

The aromatic type hydrocarbons contained in the extract mix introduced into pretreater 90 via line 92 and employed to contact and pretreat the deasphalted oil introduced thereto via line 89 further increase the solvent power of the selective solvent for the metal-containing components in the deasphalted oil being thus pretreated and thus assist in the removal of these metal-containing components (the presence of which is undesirable in a catalytic cracking charge stock) from the deasphalted oil. Furthermore, since the concentration of the metal-containing components would be greater in the deasphalted oil than in the admixture in line 85 introduced into selective solvent refining unit 91 a greater overall degree of metals removal is possible. Also, the selective solvent contained in the deasphalted oil raffinate recovered from pretreater 90 via line 94 serves to predilute the deasphalted oil raffinate introduced in admixture with the gas oils and bottoms fraction via line 85 into selective solvent refining unit 91. This predilution of the feed to the selective solvent refining unit 91 increases the efficiency of the selective solvent refining operation therein. Still further, the deasphalted oil introduced into pretreater 90 via line 89 removes from the extract mix introduced thereto via line 92 the lower molecular weight, more paraffinic hydrocarbons therein which may have been taken into solution in the extract mix during the refining of the combined feed admixture supplied to the selective solvent refining unit 91 via line 85. These more paraffinic ma-

terials are returned continuously to the selective solvent refining unit 91 and thus the overall yield of the raffinate recovered from selective solvent refining unit 91 via line 102 is increased. The contacting or scrubbing of the extract mix within pretreater 90 should result in a reduction in the quantity of the more paraffinic materials withdrawn from pretreater 90 as solvent effluent via line 98 and eventually removed from the system as extract suitable as cutter stock via line 101.

The raffinate removed from selective solvent refining unit 91 via line 102 having a reduced metals content, e. g., vanadium, nickel, copper, iron and similar heavy metals, in the range 0.2-5 p. p. m., after having been freed of its selective solvent content is combined via line 84 with the 500° F. end point naphtha fraction recovered from topping still 82 and introduced as feed stock to fluid catalytic cracking unit 104 where it is contacted with fluidized cracking catalyst.

A cracking catalyst usually comprises an oxide of metals of groups II, III, IV and V of the periodic table, for example, a silica-alumina catalyst containing about 5-30% by weight alumina. The average particle size of the cracking catalyst particles is usually below about 200 microns, a size sufficient to produce a dense fluidized bed of cracking catalyst.

The resulting cracked catalyst effluent from fluid catalytic cracking unit 104 is introduced via line 105 into fractionator 106 wherein it is fractionated into a catalytic cracked naphtha recovered via line 108, a catalytic cracked light gas oil recovered via line 109 and a relatively heavy cycle gas oil, e. g., FCCU decanted oil, recovered via line 110.

To the asphalt recovered from asphalt stripper 65 via line 69, which asphalt may have a ring and ball softening point in the range 180°-325° F., is added at least a portion of the gas oil fractions recovered from catalytic cracking fractionator 106 via lines 109, 110 and 111 and at least a portion of the selective solvent-free extract recovered from selective solvent recovery zone 99 via line 101, the resulting stream of combined catalytic cracked gas oils and selective solvent extract being added via line 111 as cutter stock to the asphalt in line 69.

If desired, at least a portion of the catalytic cracked light gas oil recovered from fractionator 106 via line 109 and/or the heavy gas oil or FCCU decanted oil recovered via line 110 are passed via lines 111 and 89 to pretreater 90 or in admixture via lines 112 and 85 to selective solvent refining unit 91 for the recovery of the more paraffinic constituents therefrom as raffinate via line 102 to provide additional catalytic cracking charge stock and for the eventual recovery of the more aromatic constituents therefrom as extract via line 101 as cutter stock. When the gas oil recovered from catalytic cracking fractionator 106, such as the FCCU decanted oil, possesses a relatively high metals content, e. g., more than about 30 p. p. m. heavy metals, the gas oils are preferably introduced via lines 111 and 89 as feed to pretreater 90 in order to reduce its metals content.

Pretreater 90 is operated at any suitable temperature and pressure for effecting liquid-liquid contacting and for the removal of the more aromatic components contained in the feed thereto. The operating conditions and solvent dosages employed within pretreater 90 are influenced to some extent by the composition of feed thereto and the type of selective solvent employed therein. In the instance where furfural is employed as the selective solvent pretreater 90 is operated at a solvent dosage in the range 75-250%, e. g., 125%, basis oil charge whereas selective solvent refining unit 91, employing the same solvent (furfural), might be operated at a relatively lower solvent dosage in the range 10-100%, e. g., about 25%, basis oil charge thereto. By operating in accordance with this feature of the invention the

yield of recoverable catalytic cracked naphtha is further increased.

Cutback product asphalt is recovered via line 114. Desirably, however, especially when a heavy crude such as a San Ardo, California, crude is the source of the reduced crude introduced into the above-described operations via line 11, the asphalt in line 69, prior to the addition of cutter stock thereto via line 111, is subjected to vis-breaking as indicated by asphalt vis-breaker 115 in the drawing and the cutter stock added to the resulting vis-broken asphalt via line 111a. The resulting cutback vis-broken asphalt is then removed as product via line 118. Desirably a portion of the combined stream employed as cutter stock in line 111 is admixed via line 116 with the solvent asphalt mix recovered from deasphalting tower 26 via line 30 prior to introducing the same into asphalt heater 59. This addition of cutter stock to the asphalt deasphalting solvent mix prior to introduction into asphalt heater 59 is desirable in order to alleviate coke deposition and reduce cracking which might otherwise occur within the furnace heating tubes and upon the heated surfaces within the asphalt-deasphalting solvent recovery system.

The following is illustrative of the practice of this invention. A mixture comprising California crude was atmospherically distilled to about 50-55% volume reduced crude based on the original crude mixture and charged through a heater operated under mild viscosity breaking conditions at an outlet temperature of 850° F. The resulting mildly viscosity broken reduced crude was introduced into an atmospheric flasher from which was recovered overhead approximately 46% total volume yield of gas oil, naphtha and atmospheric viscosity broken gas oil, basis reduced crude, in the following amounts: gas 1% volume; 430° F. end point naphtha 3.5% volume; gas oil 41.5% volume, the atmospheric flasher being operated at a maximum temperature of about 790°-800° F. The atmospheric flasher bottoms having a gravity of about 12° A. P. I. and a Conradson carbon residue of about 15 was introduced into a vacuum still operated at about 25 mm. Hg at a temperature of 665° F. There was recovered overhead from the vacuum still gas oil fractions amounting to about 42% by volume of the vacuum still charge and a heavy bottoms fraction amounting to about 16% by volume basis original crude mixture or about 33.8% volume basis reduced crude. The vacuum still bottoms had a gravity of about 3.6° A. P. I., a penetration (100 gm./5 sec./77° F. cm.  $\times 10^{-2}$ ) in the range 27-29 and a Conradson carbon residue in the range 26-33.

Portions of the above-identified vacuum still bottoms were solvent deasphalting with liquid isobutane as the deasphalting solvent, employing a solvent:oil volume ratio of 5:1 at various temperatures in the range 200°-275° F. and at a pressure in the range 200-500 p. s. i. g. The results of these operations are set forth in accompanying Table No. I.

Table No. I

Solvent	Deasphalting		Deasphaled oil				
	Temp., ° F.	Press., p.s.i.g.	Yield, weight percent	Carbon residue, percent	P. p.m. Fe	P. p.m. Ni	P. p.m. V
Charge							
Isobutane	200	280	46.0	5.9	80	150	350
Do.	235	335	40.1	5.0	6	11	9
Do.	245	385	42.0	4.1	6	8	5
Do.	270	475	35.6	3.0	8	3	3

There was directly recovered from a deasphalting operation carried out in the manner described hereinabove a liquid deasphalting solvent-deasphaled oil mix containing deasphaled oil and isobutane at a temperature of about 248° F. and at a pressure of about 390

75

p. s. i. g.; there was also directly recovered a liquid deasphalting solvent-asphalt mix containing asphalt and liquid isobutane at about the same aforesaid temperature and pressure. The liquid deasphaled oil-isobutane mix leaving the deasphalting operation at a pressure of about 390 p. s. i. g. was partially vaporized by passage through an expansion valve to yield a first vapor phase at a temperature of about 190° F. and at a pressure of at least about 175 p. s. i. g., e. g., about 210 p. s. i. g., and a first liquid phase at substantially the same temperature and pressure as said first vapor phase. The first liquid phase is then partially vaporized by passage through an expansion valve to yield a partially liquefied admixture containing deasphaled oil and vaporous isobutane at a temperature of about 145° F. and at a pressure of at least about 75 p. s. i. g., preferably about 100 p. s. i. g. The resulting vaporous admixture is then passed in indirect heat exchange relationship with said first vapor phase to yield a resulting relatively cooled first vapor phase at a temperature in the range 190°-200° F. (at a pressure about 205 p. s. i. g.) whereby the isobutane deasphalting solvent in said first vapor phase is condensed and liquefied or is readily condensed and liquefied by supplemental cooling to a temperature of about 190° F. the pressure in the resulting cooled first vapor phase being at least about 160 p. s. i. g. and higher if necessary in order to effect liquefaction of the isobutane deasphalting solvent. The resulting admixture of liquid deasphaled oil and vaporous isobutane derived from first said liquid phase, after having been passed in indirect heat exchange relationship with said first vapor phase, now at a temperature of about 160° F. and is passed to a gas liquid separator from which there is recovered overhead, at a pressure of about 100 p. s. i. g., vaporous isobutane which is liquefied and condensed by cooling to a temperature of about 126° F. at a pressure of at least about 95 p. s. i. g. The separated deasphaled oil is then steam stripped to effect substantially complete removal of isobutane therefrom and the resulting steam stripped isobutane is recovered by cooling the effluent resulting from the steam stripping operation to a temperature of about 90°-100° F., more or less, at a pressure of at least about 50 p. s. i. g., preferably above about 75 p. s. i. g. and at least sufficient to effect liquefaction of the deasphalting solvent at said temperature, and passed to storage at a temperature of about 126° F. at a pressure of about 95 p. s. i. g.

The deasphaled oil recovered from a solvent recovery operation described hereinabove has a gravity in the range 15.3°-16.8° A. P. I., a viscosity SUS 210° F. in the range 238-281 and a K factor of about 11.7.

The liquid asphalt deasphalting solvent mix phase containing asphalt admixed with isobutane, after the addition of an amount of cycle gas oil cutter stock, is passed to the asphalt heater and heated to a temperature of about 500° F. at a pressure of about 100 p. s. i. g. The resulting heated asphalt-isobutane stream was passed to an asphalt separator from which there is recovered overhead vaporous isobutane which is admixed with vaporous isobutane from the deasphaled oil flash drum, from which admixture liquid isobutane is condensed by cooling the resulting vaporous stream to a temperature of about 126° F. at a pressure preferably at least about 100 p. s. i. g. The liquid asphalt bottoms recovered from the asphalt separator is then steam stripped for the removal of any residual isobutane and recovered as a product. There was recovered from the aforementioned operations an asphalt having a ring and ball softening point in the range 200°-300° F.

A high boiling petroleum fraction comparable to the deasphaled oil recovered from the asphalt deasphalting operation is subjected to liquid-liquid contact with furfural solvent extract mix at a solvent dosage in the range 100-200% volume, e. g., 125%, basis oil charge, the furfural solvent extract mix having been derived

from the furfural solvent refining of the resulting deasphalted oil raffinate in admixture with VPS gas oil, said subsequent furfural refining being carried out at a solvent dosage in the range 15-75%, basis oil charge. The raffinate resulting from the subsequent furfural refining operation possesses a significantly lower metals content, substantially below 30 p. p. m., in the range 5-20 p. p. m. and lower.

It is also advantageous in the practice of this invention to carry out the subsequent solvent refining operation and/or the selective solvent pretreatment of the deasphalted oil in the presence of a substantial amount of a light liquid hydrocarbon, such as the deasphalting solvent, in an amount in the range 10-200% volume, more or less, based on the deasphalted oil charged to the pretreater or to the selective solvent refining unit. By so operating the metals content of the resulting raffinate (selective solvent refined deasphalted oil) is further reduced, e. g., below about 5 p. p. m. The advantages of carrying out a solvent refining operation in the presence of a liquid low molecular weight hydrocarbon, e. g., deasphalting added thereto or present in the deasphalted oil due to the incomplete removal of deasphalting solvent therefrom is more completely set forth in copending, coassigned patent application Serial No. 547,638, filed November 18, 1955. Also the advantages of carrying out a solvent refining operation by pretreating a deasphalted oil by contact with a solvent extract mix and then subjecting the resulting pretreated deasphalted oil to contact with fresh selective solvent in a selective solvent refining unit in order to produce a suitable catalytic cracking charge stock is more completely set forth in copending, coassigned patent application Serial No. 556,495, filed December 30, 1955. The disclosures of the above-referred patent applications are herein incorporated and made part of this disclosure.

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many substitutions, changes and alterations are possible in the practice of this invention without departing from the spirit or scope thereof.

I claim:

1. A method of treating an asphaltic oil which comprises contacting said oil with a deasphalting solvent under deasphalting conditions of temperature and pressure to effect separation of asphaltic constituents from said oil, recovering from the aforesaid operation a liquid oil phase having a reduced amount of asphaltic constituents and containing a portion of said deasphalting solvent and a liquid asphalt phase containing another portion of said deasphalting solvent, treating said liquid oil phase to produce a resulting first liquid phase and a resulting first vapor phase comprising deasphalting solvent at a temperature  $T_1$  and at a pressure  $P_1$ , treating said first liquid phase to convert the same to a resulting second liquid phase and a resulting second vapor phase comprising deasphalting solvent at a temperature  $T_2$  and a pressure  $P_2$ ,  $T_2$  being lower than  $T_1$  and  $P_2$  being lower than  $P_1$ , passing said first vapor phase and second vapor phase in indirect heat exchange relationship to each other whereby the temperature of said first vapor phase is reduced such that the vapor pressure of the deasphalting solvent therein is substantially reduced, condensing deasphalting solvent from said first vapor phase, heating said liquid asphalt phase to produce a third vapor phase comprising deasphalting solvent and a third liquid phase comprising asphalt, admixing said third vapor phase with said second vapor phase after said second vapor phase has been passed in indirect heat exchange relationship with said first vapor phase, recovering the resulting combined second and third vapor phases and cooling the resulting combined second and third vapor phases to a temperature sufficiently low to condense the deasphalting solvent therein.

2. A method of treating an asphaltic oil which comprises contacting said oil with a deasphalting solvent under deasphalting conditions of temperature and pressure to effect separation of asphaltic constituents from said oil, recovering from the aforesaid operation a liquid oil phase having a reduced amount of asphaltic constituents and containing a portion of said deasphalting solvent and a liquid asphalt phase containing another portion of said deasphalting solvent, treating said liquid oil phase to produce a resulting first liquid phase comprising deasphalting solvent and a resulting first vapor phase comprising deasphalting solvent at a temperature  $T_1$  and a pressure  $P_1$ , treating said first liquid phase to convert the same to a resulting second liquid phase and a resulting second vapor phase comprising deasphalting solvent at a temperature  $T_2$  and a pressure  $P_2$ ,  $T_2$  being lower than  $T_1$  and  $P_2$  being lower than  $P_1$ , passing said first vapor phase and said second vapor phase in the presence of said second liquid phase in indirect heat exchange relationship to each other whereby said first vapor phase is reduced to a temperature such that the vapor pressure of the deasphalting solvent is substantially reduced, condensing deasphalting solvent from said first vapor phase, heating said liquid asphalt phase to produce a third vapor phase comprising deasphalting solvent and a third liquid phase, admixing said third vapor phase with said second vapor phase in the presence of said second liquid phase after said second vapor phase has been passed in indirect heat exchange relationship with said first vapor phase, separately recovering from the aforesaid admixing operation the resulting combined second and third vapor phases and said second liquid phase, cooling the resulting combined second and third vapor phases to a temperature sufficiently low to condense the deasphalting solvent therein, steam stripping said third liquid phase to re-

## 11

move substantially all of said deasphalting solvent therefrom, and to produce overhead a fourth vapor phase comprising steam and deasphalting solvent, steam stripping the recovered second liquid phase to remove substantially all of said deasphalting solvent therefrom and to produce overhead a fifth vapor phase comprising steam and vaporized deasphalting solvent, recovering from the immediate aforesaid steam stripping operation said second liquid phase comprising a deasphalting oil substantially free of deasphalting solvent, admixing said fourth and fifth vapor phases and cooling the resulting combined vapor to a temperature sufficiently low to condense the steam and deasphalting solvent contained in said admixed steam and separately recovering the resulting condensed deasphalting solvent and condensed steam.

4. In a process wherein an asphaltic oil is treated with a deasphalting solvent under deasphalting conditions of temperature and pressure to separate asphaltic constituents from said oil and wherein there is recovered from the aforesaid deasphalting operation a liquid deasphalting solvent-oil mix containing deasphalting oil and deasphalting solvent, the deasphalting solvent being subsequently separated therefrom and liquefied, the improvement which comprises passing said deasphalting solvent-oil mix into a low pressure zone to produce a first vapor phase comprising deasphalting solvent and a first liquid comprising deasphalting oil and deasphalting solvent, passing said first liquid phase into a lower pressure zone to yield a second vapor phase comprising a deasphalting solvent at a temperature lower than said first liquid phase and a second liquid phase containing deasphalting oil, passing

## 12

said first vapor phase in indirect heat exchange relationship with said second vapor phase to substantially reduce the temperature of said first vapor phase to produce a resulting first vapor phase substantially saturated with respect to said deasphalting solvent and recovering liquefied deasphalting solvent resulting from said first vapor phase.

5. A process in accordance with claim 4 wherein said deasphalting solvent comprises isobutane.

6. A process in accordance with claim 4 whereby the pressure differential between said lower pressure zone and said low pressure zone is in the range of 50-200 p. s. i. g.

7. A process in accordance with claim 4 wherein the temperature of said resulting first vapor phase is in a range 20-60 degrees Fahrenheit lower than first said vapor phase.

8. A method in accordance with claim 4 wherein the temperature of said first vapor phase after heat exchange is reduced to a value so that substantially all of the deasphalting solvent therein is liquefied.

## References Cited in the file of this patent

## UNITED STATES PATENTS

25	2,121,517	Brandt	-----	June 21, 1938
	2,192,253	Adams	-----	Mar. 5, 1940
	2,223,192	Swartwood	-----	Nov. 26, 1940
	2,383,535	Dickinson et al.	-----	Aug. 28, 1945
	2,538,220	Willauer	-----	Jan. 16, 1951
30	2,645,596	Axe	-----	July 14, 1953