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2,729,589

DEASPHALTING WITH PROPANE AND BUTANE

Filed June 12, 1952

3 Sheets-Sheet 1

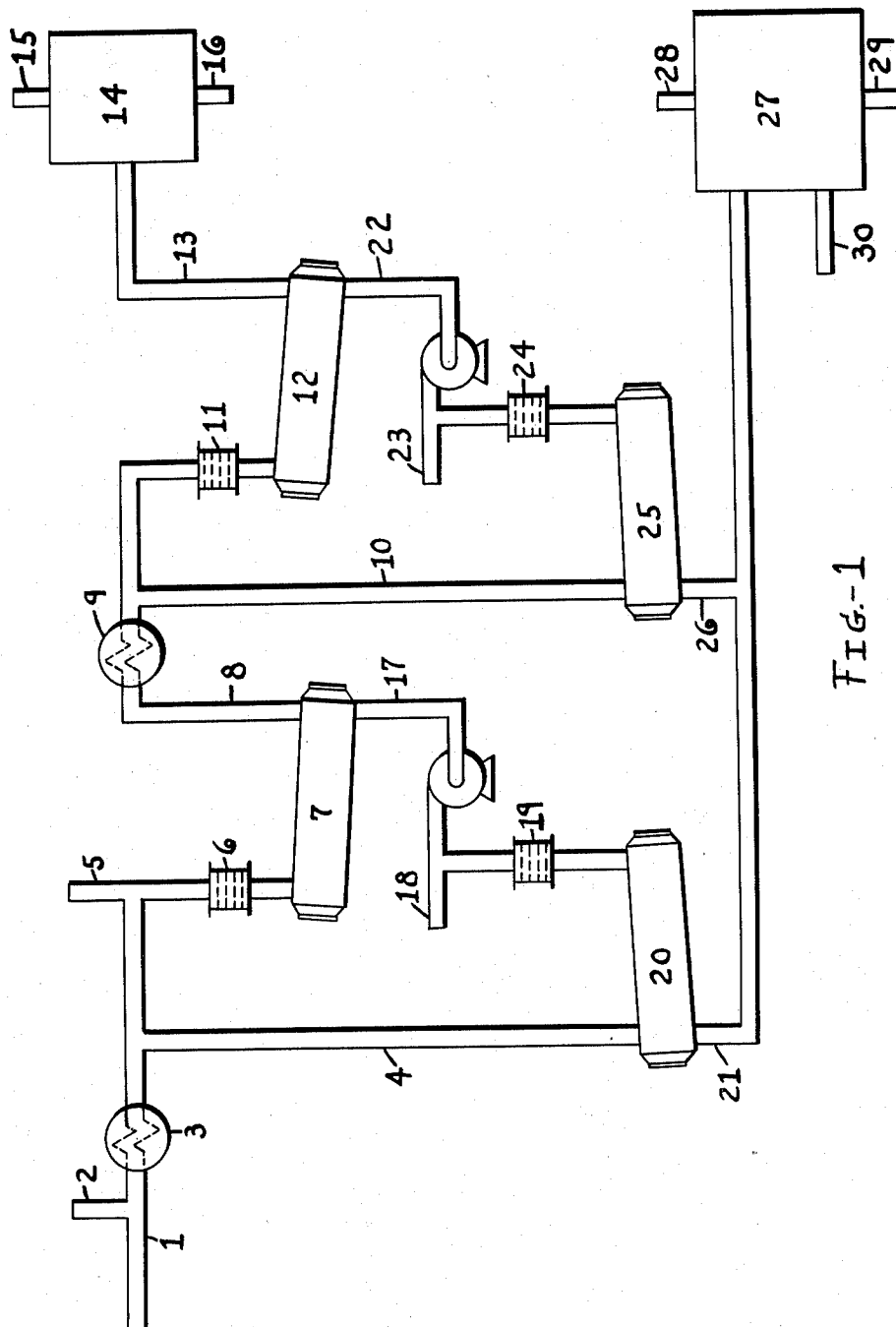


FIG.-1

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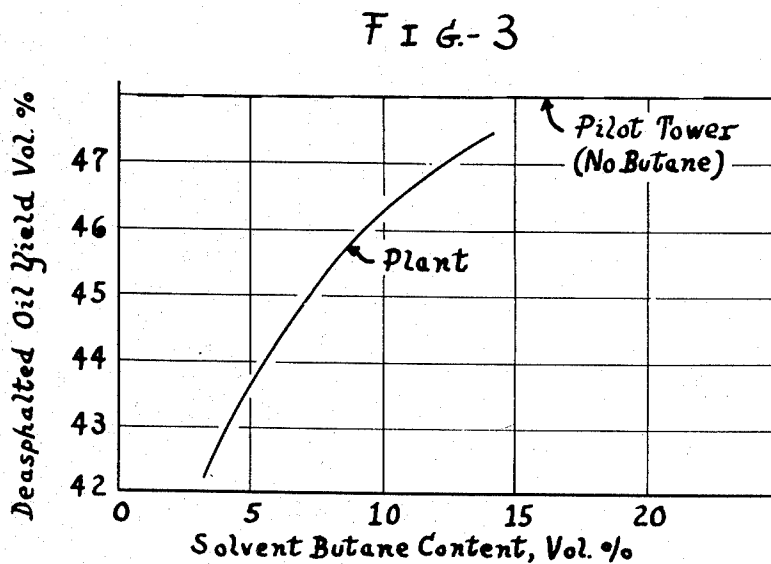
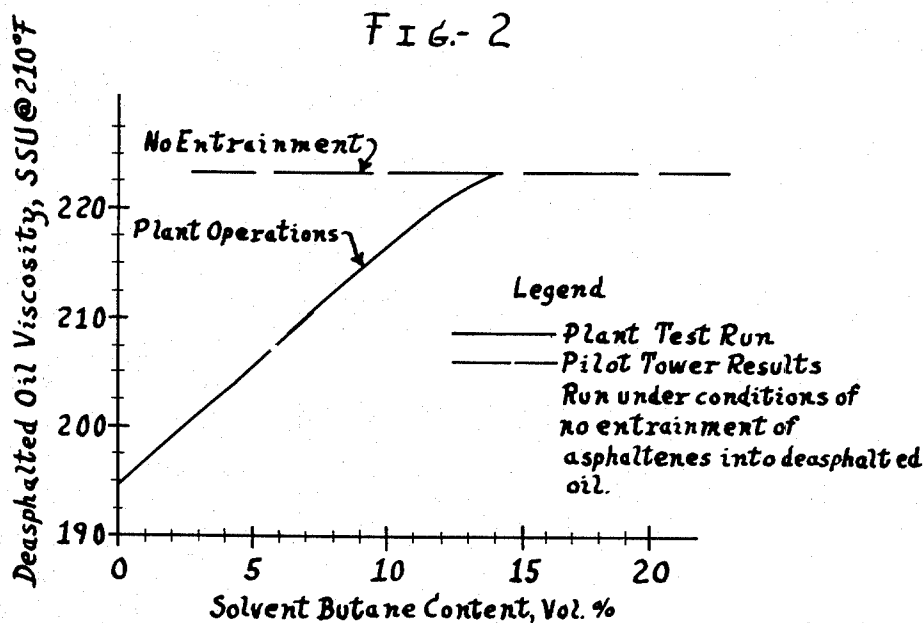
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3 Sheets-Sheet 2



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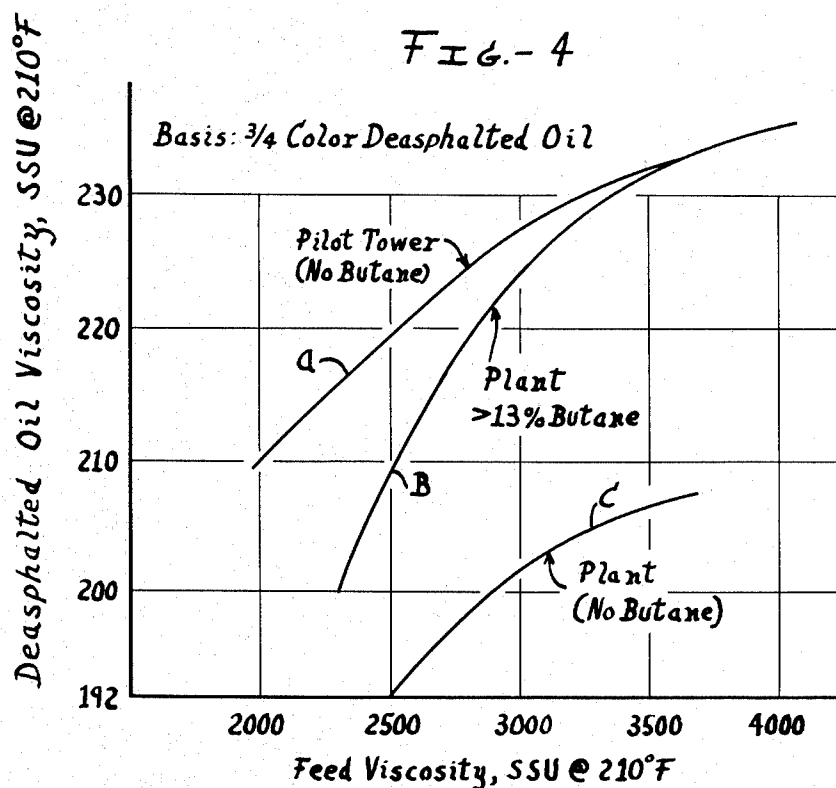
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DEASPHALTING WITH PROPANE AND BUTANE

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3 Claims. (Cl. 196—14.46)

This invention concerns a novel process for the deasphalting of residual petroleum oil fractions to secure high quality lubricating oil stocks. The invention concerns the use of particular proportions of propane and butane in admixture for treatment of residual oils to eliminate asphaltic and resinous constituents of the oils. By employing a deasphalting agent constituting a mixture of propane containing about 14% butane, improved deasphalting results are obtained.

In the refining of crude petroleum oils, distillation is commonly employed to divide the crude oil into a variety of petroleum fractions such as gasoline, kerosene, lubricating oil, etc. Heavier fractions of petroleum oil cannot be successfully segregated by distillation procedures however. For example, those fractions of petroleum oil boiling above the lubricating oil boiling range or above about 700° F. are subject to thermal decomposition during distillation even though vacuum distillation is employed. To permit the treating and upgrading of residual oil fractions, a variety of solvent treating methods are commonly employed. This invention concerns the solvent treating of residual oils in which a low molecular weight paraffinic hydrocarbon is employed to precipitate asphaltic and resinous material from the residual oils to provide valuable lubricating oil blending stocks and deasphalted stocks for a variety of other applications.

The residual oils to which this invention has application are the heavier fractions of petroleum oil boiling above 850° F., and containing asphalts and resins. These oils are generally characterized by their physical properties rather than their distillation characteristics and generally have a specific gravity in the range of about 12.1 to 10.4° API and viscosities of about 2400 to 6000 SSU at 210° F.

It has been appreciated that paraffinic hydrocarbons are capable of rejecting or precipitating high molecular weight portions of residual oils including asphalts and resins. It has also been known that as the molecular weight of the precipitating agent is reduced, its solubility for asphaltic and resinous compounds is also reduced so as to increase the precipitating action. For this reason propane is commonly employed as the deasphalting agent in preference to higher molecular weight paraffins such as butane, pentane, etc.

It has now been found however, that inclusion of a critical amount of butane in the propane serves to provide an improved deasphalting agent. As will be brought out, use of about 14% of butane in admixture with propane serves to substantially improve deasphalting results, re-

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sulting in a higher yield of deasphalted oil, a deasphalted oil of higher viscosity, a deasphalted oil of better color characteristics at equal volume percent yields, and permitting use of higher asphalt settling temperatures.

The process of this invention and graphical data concerning the invention are illustrated in the accompanying drawings, in which:

Figure 1 diagrammatically illustrates a deasphalting flow plan which may be used in the practice of this invention, and;

Figure 2 graphically shows the relation between the viscosity of the deasphalted oil and the butane content of the solvent, and;

Figure 3 graphically shows the relation between the deasphalted yield obtainable and the solvent butane content, and finally;

Figure 4 graphically shows the relation between the viscosity of the deasphalted oil and the feed oil viscosity under conditions of no entrainment and when employing varying proportions of butane in the solvent.

Referring first to Figure 1, a simple diagrammatic flow plan of an operative solvent deasphalting system is shown. This flow plan embodies a system in which multistage mixing and settling of the solvent-residual oil mixture is employed. It is to be understood that the invention may equally be applied to a countercurrent contacting system in which the solvent is flowed countercurrently with the residual oil in a contacting tower. In Figure 1 the residual oil feed is introduced to the system through line 1. Deasphalting solvent, primarily constituting a mixture of propane and butane, is admixed with the oil of stream 1 by introduction through line 2. This mixture of solvent and oil is passed through heat exchanger 3 wherein the mixture is heated to a temperature of about 140 to 160° F. Recycle solvent obtained through line 4 may be mixed with the oil solvent mixture together with additional solvent introduced through line 5. This mixture of oil feed together with the primary solvent, secondary solvent, and recycle solvent, is then passed through a suitable mixing device such as orifice mixer 6. The thoroughly mixed solvent and oil having a solvent to oil ratio of about 4 to 10 or preferably about 4 to 6, at a temperature of about 130 to 150°, is then introduced to a horizontal settling zone 7.

Settler 7 is used to secure a phase separation providing an upper liquid phase consisting of a solvent phase and oil and a lower liquid phase consisting of a solvent phase containing precipitated asphaltic and resinous constituents. The upper solvent-oil phase is removed from the settler through line 8 and is passed through heat exchanger 9 wherein the oil and solvent mixture is heated to about 135° to 155° F. Recycle solvent from line 10 is mixed with the oil-solvent mixture and this mixture is preferably thoroughly mixed in an orifice mixer 11 or the like. This mixture is then passed to a second settler 12 wherein additional high molecular weight constituents are settled from the oil. As described, the first settler 7, is primarily effective in secured precipitation of asphalts while the second settler 12 primarily precipitates resinous materials. In settler 12 an upper liquid phase constituting a mixture of solvent and deasphalted oil may be removed through

line 13 for passage to a deasphalted oil recovery system 14. This system may constitute a steam distillation zone in which steam is employed to strip solvent from the deasphalted oil, permitting removal of the solvent as an overhead stream through line 15. The deasphalted oil is then removed as a bottoms product through line 16.

The asphaltic phase separating in settler 7 is removed from the lower portion of the settler through line 17 and is mixed with wash solvent introduced through line 18. The wash solvent and asphalt phase are mixed in an orifice mixer 19 and are passed to a settling zone 20. The upper solvent phase is removed from the upper portion of settler 20 through line 4 for recycle as described while the precipitated asphalt is removed from the lower portion of the settler through line 21.

Similarly, the resinous phase of settler 12 is removed from the settler through line 22 and is mixed with wash solvent introduced through line 23 by means of orifice mixer 24. This mixture is settled in settler 25 permitting removal of solvent through line 10 for recycle as described and permitting removal of precipitated resins through line 26. The asphaltic and resinous constituents of lines 21 and 26, together with residual solvent, are passed to an asphalt recovery system 27 which may constitute a fractionation zone. Solvent may be removed overhead through line 28 and the asphaltic and resinous constituents may be removed as a bottoms product through line 29. In the case of asphalt manufacture, a low viscosity flux oil may be introduced to this system through line 30 for admixture with the asphalt removed through line 29.

In operating a deasphalting system of the character illustrated in Figure 1, in accordance with this invention, the solvent employed constitutes propane containing about 14% of butane. The discovery that inclusion of this quantity of butane in the propane is highly desirable resulted from basic studies of plant performance. In these studies it was found that actual deasphalting plant performance was unaccountably inferior to apparently equivalent pilot plant performance. Thus, in comparing operating results of a deasphalting plant operating at about 4,000 bbls. per day to a pilot plant operating at about 4 bbls. per day, it was found that the yield, color, and viscosity relations of the two systems showed the plant operation to be greatly inferior. This conclusion was established even though the plant and pilot performance was apparently equivalent. Thus, operations were controlled so that equal yields of a given viscosity oil were obtained in both the plant and pilot operations, indicating that the two plants provided about the same stage equivalence. Nevertheless, the color of the refined plant oil was much darker than the refined pilot unit oil, clearly indicating inadequate resin and asphaltene removal.

In studying this anomaly, it was unexpectedly found that there is a sharp relation in plant performance between the viscosity of the residual oil treated, and the molecular weight of the deasphalting solvent employed. It was surprisingly found, for example that, contra to the common understanding, when treating high viscosity residual oils, a solvent having a molecular weight somewhat greater than propane is particularly selective. This discovery is opposed to the general principle that no change in selectivity is obtained when varying a molecular weight of the deasphalting agent. Nonetheless, it was determined that greatly improved plant performance may be obtained by increasing the molecular weight of a propane deasphalting agent by inclusion of butane. Lowering the molecular weight of propane deasphalting agent by inclusion of methane and ethane was found to have the opposite effect, resulting in poorer plant performance. Optimum performance was found to correspond to a mixture of pure propane with pure butane in which the butane constitutes about 14% of the mixture. In the event the solvent also contains small proportions of methane and ethane, somewhat greater quantities of butane must be employed.

These differing solvent compositions can best be expressed to compensate for inclusion of methane and ethane by definition of the average molecular weight of the solvent mixture. Thus, according to this invention, a solvent agent is to be employed having a molecular weight of about 45.8, corresponding to a butane content of about 14%, assuming that only propane and butane are present.

The basic effect attributable to the use of a solvent agent having a molecular weight of about 45.8 is apparently related to the entrainment characteristics of a residual oil-deasphalting solvent mixture. It was found that in the pilot plant tests referred to there was no entrainment of asphalt in the deasphalting solvent after phase separation. However, in plant operations, due to the impracticability of securing equivalent settling in a plant, substantial asphalt entrainment in the deasphalted oil ordinarily occurs. For some reason, increasing the molecular weight of the deasphalting solvent by inclusion of butane in the propane deasphalting agent serves to correct this condition, permitting complete elimination of entrainment under plant conditions when 14% of butane is mixed with propane. This is illustrated in Figure 2 of the drawings showing the relation between the viscosity of deasphalted oil of a constant color and the butane content of a propane-butane solvent mixture used for deasphalting. The feed oil had a viscosity of 3000 SSU at 210° F. In plant operations using pure propane, due to entrainment of asphalt, the deasphalted oil was found to have a viscosity of about 195. Inclusions of small percentages of butane in the propane serve to minimize this entrainment, but about 14% of butane was found to be required in order to completely eliminate asphalt entrainment in the deasphalted oil.

This same relation was established by reference to the yield of deasphalted oil of a constant color as compared to the butane content of the solvent. This is illustrated in Figure 3 wherein it is shown that greatly improved yields of deasphalted oil are obtained as entrainment of asphalt is eliminated by increasing the butane content of the solvent. Again the optimum yield of deasphalted oil is obtainable by the elimination of asphalt entrainment obtained by using a deasphalting agent containing about 14% of butane.

While the advantages of using 14% of butane in admixture with propane are clearly related to elimination of asphalt entrainment as described, the basic reason for this phenomenon is not now known. In the graphs of Figures 2 and 3, it is apparent that greater deasphalted oil yields are obtainable for oils of the same color characteristics since elimination of entrainment of asphalts provides better color characteristics at higher yield levels. Similarly, better precipitation of asphalt permits more selective elimination of higher molecular weight constituents so as to enable obtaining an oil product of higher viscosity. It is presently believed that these effects are probably due to an increased asphalt phase particle size. It is also probable that an increased interphase gravity differential obtainable by inclusion of butane contributes to this effect. In any case, as presented, it has been established that a propane-butane mixture containing about 14% butane is a particularly desirable deasphalting agent. As emphasized, the nature of this agent may be expressed by the average molecular weight of the agent which must be about 45.8.

To exemplify the nature and benefits of this invention, a series of test runs were made in an actual deasphalting plant in which the molecular weight of the solvent composition was varied by inclusion of butane in a solvent consisting predominantly of propane. Each of the runs were made to provide a deasphalted oil having a constant color while determining the yield and viscosity of deasphalted oil obtainable. These tests are fully presented in Table I, showing the operating variables and the deasphalted oil characteristics.

TABLE I

Plant test data showing effect of varying solvent butane content and deasphalted oil color

Run No.	1	2	3	4	5
Feed Rate, B./SD.	3,737	3,814	3,814	3,836	3,938
Feed Viscosity, SSU @ 210° F.	2,990	3,010	3,003	3,060	3,990
Deasphalted Oil:					
Rate, B./SD.	1,610	1,707	1,795	1,818	1,818
Yield, Vol. Percent	43.0	44.8	47.1	47.4	46.2
Viscosity, SSU @ 210° F.	203	209	220	223	234
Color, TR Dil.	1	1	1	1	3/4
Solvent/Feed Ratios, Vol./Vol. Feed:					
Primary	0.77	0.76	0.76	0.70	0.94
Secondary	0.79	0.76	0.78	0.68	0.63
Asphalt Wash	1.12	1.15	1.16	0.97	1.40
Resin Wash	1.22	1.22	1.22	1.19	1.36
Total	3.90	3.89	3.92	3.53	4.33
Settler Temperatures, ° F.:					
Asphalt	132	138	139	146	149
Resin	136	140	145	149	149.5
Asphalt Wash	103	102	103	115	115
Resin Wash	114	115	116	121	124
Solvent Composition:					
Avg. Mol. Wt. ^a	44.61	44.96	45.48	45.77	46.06
Calc. Butane Content, Vol. Percent ^b	4.3	7.2	11.4	13.8	15.8

^a Calculated from mass spectrometer analysis and simple flash vaporization test results.

^b Calculated from average molecular weight assuming only C₃ and C₄ present. Methane content ranged from 0.0 to 0.3%; ethane from 0.3 to 0.8%.

Referring to Table I, it will be observed that in increasing the butane content from 4.3% to 13.8% in the successive runs 1, 2, 3 and 4, the volume percent yield of deasphalted oil was progressively increased from 43% to 47.4%. Similarly, the viscosity of the deasphalted oil was substantially increased by increasing the butane content of the deasphalting solvent. Run No. 5 employing even higher butane contents in the solvent is not strictly comparable to runs 1 to 4 since an oil of somewhat poorer color was obtained. Comparison of the yield and viscosity results however shows that substantially no improvement was obtained by using the higher percentage of butane.

This conclusion was verified by carefully controlled tests in which the butane content of the solvent was increased above 14%. Again the experiments conducted were in an actual deasphalting plant. The results of these experiments are fully given in Table II:

TABLE II

Plant test data showing effect of varying solvent butane content and deasphalted oil color

Run No.	1	2	3
Feed Rate, B./SD.	3,711	3,748	3,728
Feed Viscosity, SSU @ 210° F.	2,530	2,450	2,400
Deasphalted Oil:			
Rate, B./SD.	1,807	1,812	1,792
Yield, Vol. Percent	48.7	48.3	48.1
Viscosity, SSU @ 210° F.	199	202	199
Color TR Dil.	3/4	3/4	3/4
Solvent Ratios, Vol./Vol. Feed:			
Primary	1.02	1.01	1.01
Secondary	0.88	0.87	0.87
Asphalt Wash	1.56	1.53	1.70
Resin Wash	1.67	1.67	1.67
Total	5.13	5.13	5.25
Settler Temperatures, ° F.:			
Asphalt	147	154	161
Resin	147	155	161
Asphalt Wash	112	112	114
Resin Wash	126	138	142
Solvent Composition:			
Avg. Molecular Wt. ^a	45.75	46.60	47.2
Calc. Butane Content, Vol. Percent ^b	13.8	20.0	24.0

^a Calculated from mass spectrometer analysis and simple flash vaporization test.

^b Calculated from average molecular weight assuming only C₃ and C₄ present. Methane content ranged from 0.0 to 0.2%; ethane from 0.1 to 1.3%.

It will be observed from the data of Table II that the yield and viscosity of deasphalted oil of comparable color were not improved by increasing the molecular weight of the solvent above about 45.8 or by including more than

about 14% of butane in the solvent. This data together with the data of Table I therefore establishes that inclusion of about 14% of butane in a propane deasphalting solvent is critically effective in eliminating entrainment of asphalt permitting higher oil yields, better viscosity, etc. In considering the possibility of employing higher percentages of butane, it is necessary to appreciate that butane recovery cannot be accomplished with the efficiency of propane recovery. Thus, butane is selectively lost in the typical solvent recovery facilities of a deasphalting plant. Consequently, it is extremely undesirable to employ more than 14% of butane in the deasphalting solvent. It is for this reason that the amount of butane to be employed is critically set at about 14% and no more and no less than this proportion of butane is to be employed.

In studying the improvement in deasphalting results obtained by adding butane to a propane deasphalting agent, it was also found that higher settler temperatures could be employed when butane was included. Thus, in a typical case, in order to obtain a deasphalted oil of suitable color characteristics, it was found that a settler temperature of about 133° F. was required when using pure propane. However, when 14% of butane was included with the propane it was found that a settler temperature of 148° F. could be employed to obtain deasphalted oil of equal quality. This again is an important advantage, of using the butane-propane mixture as a deasphalting agent. This is particularly important in warm climates or in areas where adequate cooling water is not available, since the temperature which may be maintained in the settler of a deasphalting plant is frequently a limiting process variable.

Further experiments with the deasphalting agent of this invention established that the improvements referred to are primarily obtained in the treatment of high viscosity residual oils. Thus, inclusion of butane in a propane solvent has little effect in improving deasphalting of a low viscosity residual oil. However, when the residual oil has a viscosity above about 2500 SSU, the full benefits of this invention may be obtained. Preferably the invention is employed for the treatment of residual oils having a viscosity above 3,000 SSU at 210° F. This is illustrated by Figure 4 of the drawings showing the relation between the viscosity of deasphalted oil and the feed viscosity. Referring to Figure 4 graphical line A shows the relation of deasphalted oil viscosity to feed oil viscosity in pilot plant operations under conditions wherein there was no entrainment of asphalt in the deasphalted oil. Line B shows the plant results obtainable when using at least 13% of butane in the solvent while line C shows the plant results obtainable when no butane was included in the solvent. It will be observed that below a feed viscosity of about 2500 little improvement in deasphalting results were obtained by inclusion of the butane. However, particularly above feed viscosities of 3,000, inclusion of 13% butane or more permitted obtaining results substantially equivalent to no entrainment conditions. It must be appreciated therefore that the process of this invention is primarily adapted to the treatment of residual oils having a viscosity above about 3,000 SSU at 210° F. In considering the benefits of this invention it is important to note the advantages of obtaining a higher viscosity deasphalted oil than otherwise obtainable. Thus, as emphasized, by using the deasphalting agent of this invention including 14% of butane, a deasphalted oil viscosity increase of as much as 30 units may be obtained. This serves to further magnify the increases in deasphalted oil yields since the higher viscosity deasphalted oil can be blended with greater amounts of low viscosity lubricating oil blending stocks, thereby under comparable conditions, an increase in lubricating oil production of as much as 27% can practically be obtained.

What is claimed is:

1. A deasphalting process in which a residual oil having a viscosity above about 2500 S. S. U. at 210° F. is admixed with a deasphalting agent consisting essentially of propane and butane in which the said butane comprises about 14% by volume of the deasphalting agent.

2. A multi-stage deasphalting process which comprises contacting a residual oil having a viscosity above about 3000 S. S. U. at 210° F. and containing asphaltic and resinous constituents with a deasphalting agent consisting of a C₁ to C₄ paraffinic hydrocarbon mixture having an average molecular weight of about 45.8.

3. The process of claim 2 wherein the reaction mixture

of said residual oil, asphaltic constituents and paraffinic hydrocarbon mixture is settled in a settling zone at a temperature of from about 130° to 150° F.

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