

Feb. 7, 1939.

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2,146,147

PROPANE SOLVENT TREATING PROCESS

Filed June 28, 1934

4 Sheets-Sheet 1

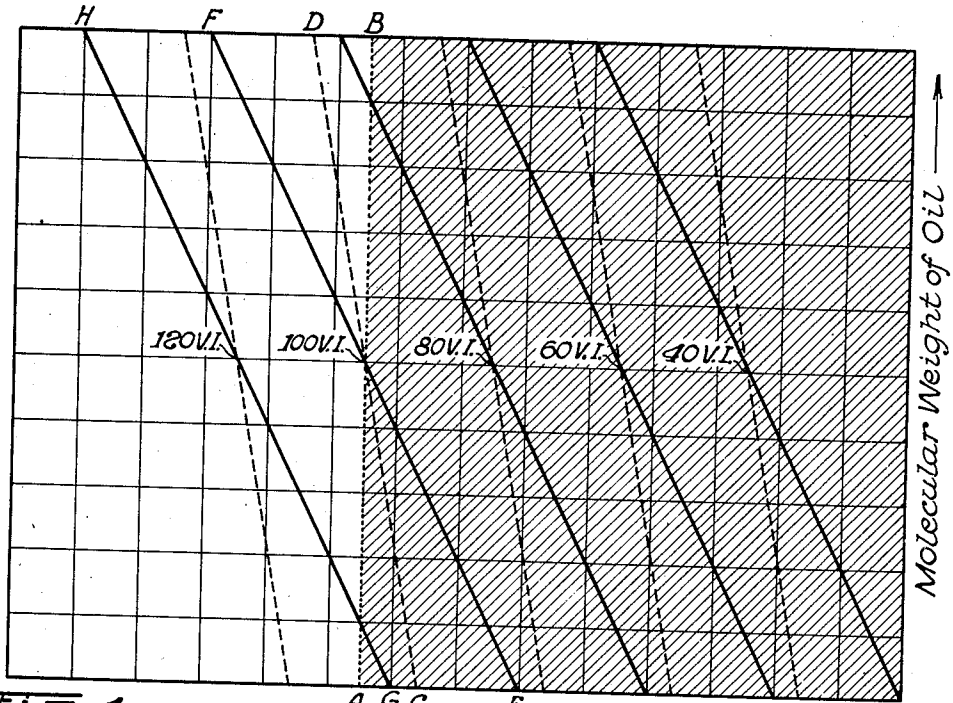


FIG. 1 Solubility of Oil in Solvent

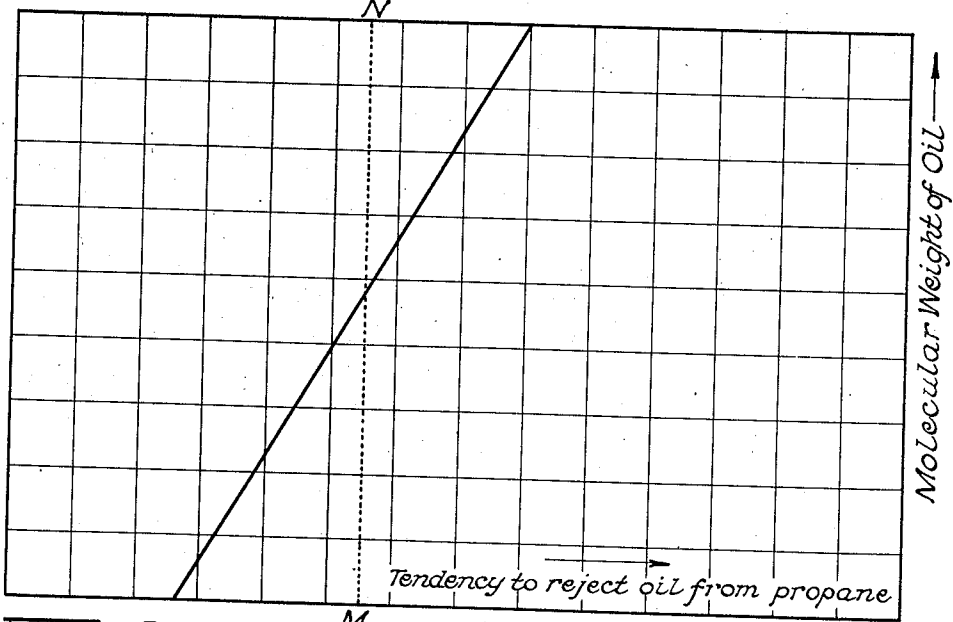


FIG. 2 Solubility of Oil in Propane

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4 Sheets-Sheet 2

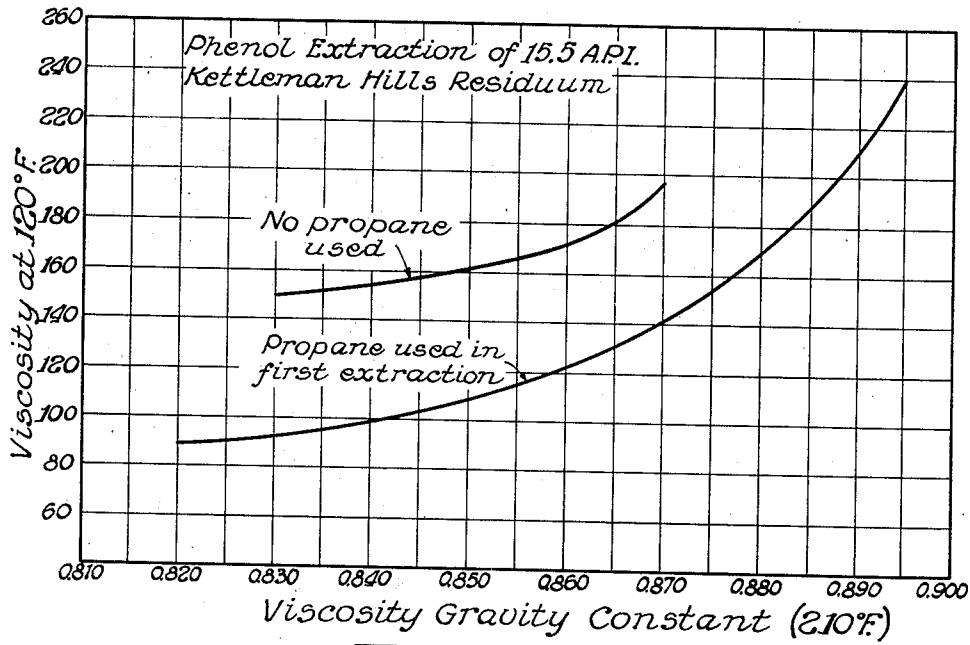


FIG. 3

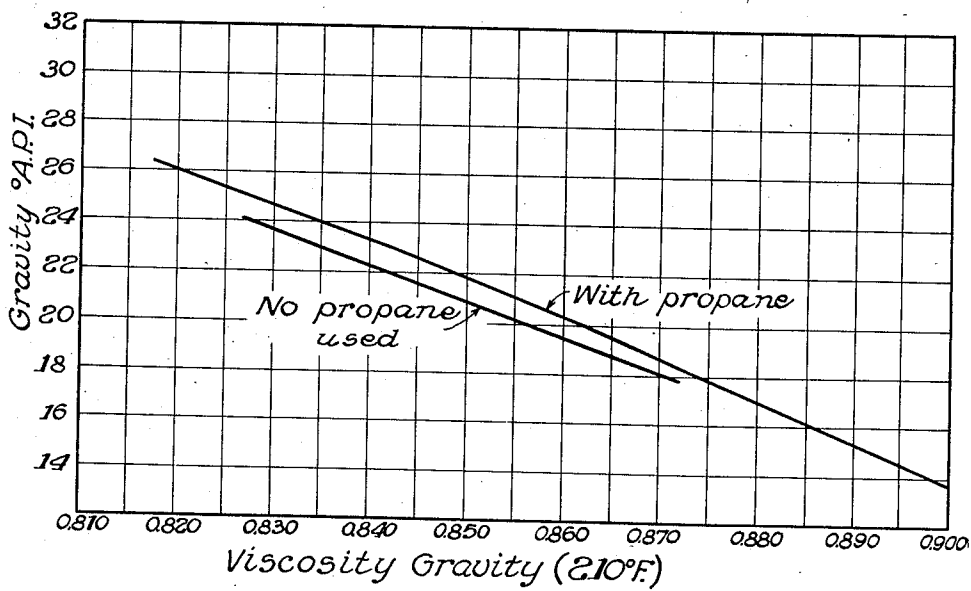


FIG. 4

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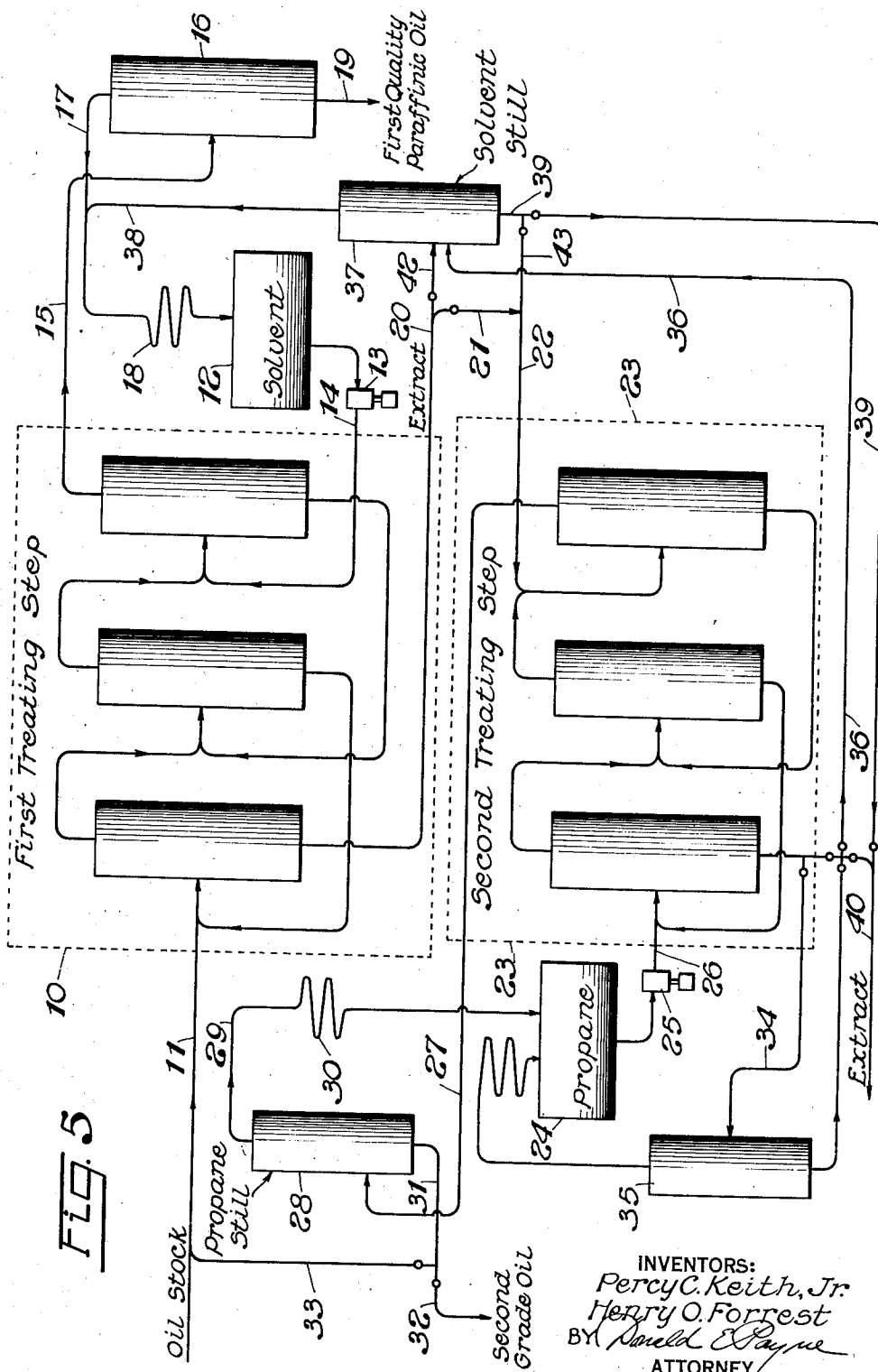
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PROPANE SOLVENT TREATING PROCESS

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4 Sheets-Sheet 3



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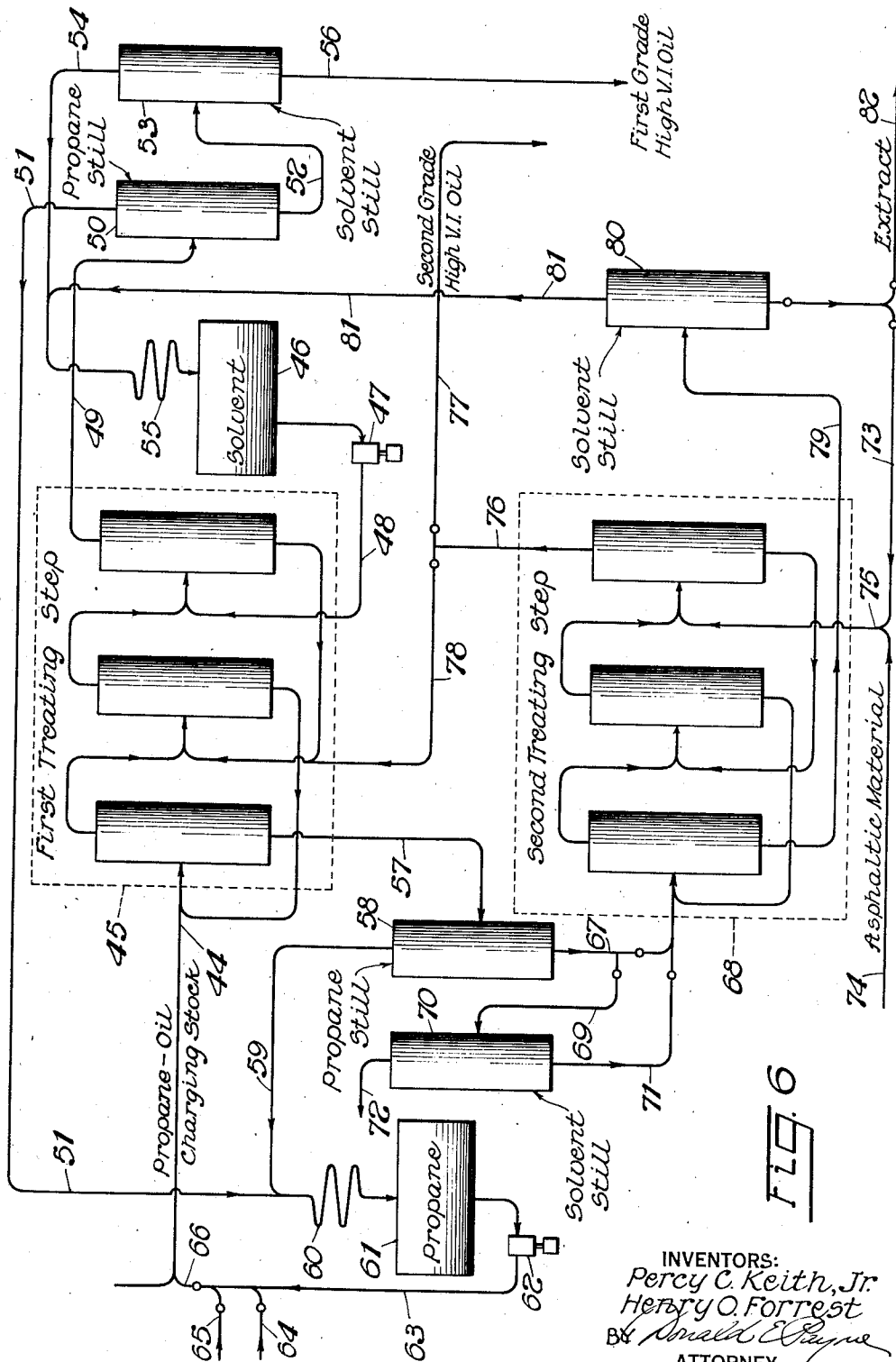
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PROPANE SOLVENT TREATING PROCESS

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4 Sheets-Sheet 4



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2,146,147

PROPANE-SOLVENT TREATING PROCESS

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Application June 28, 1934, Serial No. 732,919

13 Claims. (Cl. 196—13)

This invention relates to improved methods and means for fractionating hydrocarbon oils by means of solvents, and it pertains more particularly to the fractionation of lubricating oil stocks into paraffinic oils of high viscosity index and low grade naphthenic oils.

An object of our invention is to use a selective naphthenic solvent and a light hydrocarbon solvent such as propane in the most effective manner to obtain maximum yields of paraffinic oils of all viscosities. We have discovered that when selective naphthenic solvents are employed without the use of propane and the like, a large amount of low viscosity paraffinic oils is lost in the extract or low grade oils. It is also known that oils may be fractionated by means of propane and the like, in which case the rejected portion consists chiefly of high viscosity oils. In order to obtain the maximum yield of both low and high viscosity paraffinic oils from any given stock, it would seem that both a selective naphthenic solvent and a light hydrocarbon solvent or the like should be used, so that one might modify and supplement the other. We have found, however, that the light hydrocarbon exerts an important effect upon the miscibility temperature, and that in most cases it is impractical to carry out the entire extraction process in the presence of both naphthenic solvent and light hydrocarbon. The object of our invention is to provide a multi-step process wherein one step is primarily designed for the recovery of high viscosity paraffinic oils and the other step is primarily designed for the recovery of low viscosity paraffinic oils, the two steps being so interrelated that maximum oil yields and maximum efficiency are obtainable.

The invention will be more clearly understood from the following detailed description of preferred embodiments and particularly by reference to the accompanying drawings which form a part of the specification and in which:

Figure 1 is a graph showing the characteristics of selective naphthenic solvents;

Figure 2 is a graph showing the corresponding characteristics of propane and the like;

Figure 3 is a graph showing the effect of solvent extraction, with and without propane, on the viscosity of the raffinate;

Figure 4 is a similar graph showing the effect of solvents with and without propane on A. P. I. gravities of raffinates;

Figure 5 is a flow diagram of our process wherein high viscosity paraffinic oils are extracted in the absence of appreciable amounts of propane

and low viscosity paraffinic oils are recovered in another step; and

Figure 6 is another modification wherein the low viscosity paraffinic oils are extracted in the first step in the presence of propane and the high viscosity paraffinic oils are subsequently recovered either by removing propane therefrom or by changing the solvent ratio or recycling final extract or asphaltic material.

Our invention will be described as applied to the fractionation of a 15.5° A. P. I. Kettleman Hills residuum, but it should be understood that the invention is equally applicable to any other lubricating oil stock from Pennsylvania, Mid-Continent or coastal crudes. Our invention is applicable to distillate stocks as well as residuums and to stocks which have had preliminary acid, clay, or dewaxing treatments, as well as untreated stocks. In fact, it is applicable to any solvent extraction system for recovering mixtures of high and low viscosity raffinates.

In our preferred examples we will discuss the use of cresylic acid and phenol as preferred solvents, but it should be understood that our invention is generic in this respect and that we may employ any selective solvent which is known to the art. Examples of suitable solvents include, by way of example (and without limitation), chlorinated phenols, ortho, meta and para cresols and mixtures thereof, coal tar and wood tar acids usually associated with phenol and/or cresol, pyridine, furfural, nitrobenzene, aniline, chloraniline, benzaldehyde, benzonitrile, nitrotoluene, phenyl acetate, beta beta' dichlorethyl ether, sulfur dioxide, crotonaldehyde, nitro-phenols, ethyl chloracetate, glycol diacetate, methyl formate, etc., and/or mixtures of one or more of these compounds with a modifying solvent and/or with another of said compounds.

We refer to propane in this specification as an example of our hydrocarbon solvent. The propane serves the important functions of selectively rejecting the more viscous oil fractions, modifying the miscibility temperatures, and effecting phase separation and fractionation. While we describe propane as our preferred embodiment, it should be understood that we may use ethane, butane, isobutane, pentane, and hexane with perhaps some propylene, butylene, etc., or mixtures of one or more of said hydrocarbons. We prefer to use normally gaseous hydrocarbons, preferably with a vapor pressure of about that of propane. We do not limit ourselves to the use of light hydrocarbons for this purpose and we may employ any light solvents which are equivalent to

the propane in properties of selectively rejecting high viscosity oil fractions.

Theory or explanation

While we do not limit ourselves to our theory, we will describe it in order to explain the significance of the various steps of the process which will be hereinafter described.

The selectivity of naphthenic solvents employed in lubricating oil manufacture may be generally illustrated as shown in Figure 1, poor solvents being illustrated by the solid lines and good solvents being illustrated by dotted lines. These lines are typical of the effect of molecular weight and viscosity index (hereinafter called V. I.) on solubility of oil in any given solvents. A solvent of good selectivity is, therefore, one which tends to dissolve equally all fractions of a given viscosity index. If we assume extraction to be carried out under conditions represented by the line A—B, we will have everything to the left of A—B as a raffinate and everything to the right of A—B (the shaded area) as an extract. If a perfect solvent could be employed, there would be no oil in the extract of higher V. I. than 100 and there would be no oil in the raffinate of lower V. I. than 100.

The best available solvents tend to dissolve low viscosity paraffinic oils in preference to high viscosity oils of the same paraffinicity. C—D may represent a good solvent employed to give a 100 V. I. oil,—all material to the right of line C—D being lower than 100 V. I. and all material to the left being higher than 100 V. I. In this case the fractionation into raffinate and extract will still be along line A—B so that the extract (shaded area) will contain low molecular weight oils of higher V. I. than 100, as represented by triangle AOC. The average V. I. of the raffinate from O to A is higher than 100 because it averages from 100 to about 110. On the other hand, the average V. I. of the raffinate from O to B is lower than 100 because this portion of the raffinate contains material as low as 90 V. I. as indicated by triangle ODB. The average V. I. from A to B is 100, but it will be seen that valuable low molecular weight paraffinic oils are lost in this extract.

Poorer solvents, as indicated by the solid lines, are even worse in their tendency to reject valuable light oils in the extract. Line EF marks the boundary between oils above and below 100 V. I. in this case and line AB marks the separation of extract from raffinate. Here it will be seen that the extract (shaded area) will contain light oil of upwards of 120 V. I. (line GH crosses AB) and the amount of high V. I. low viscosity oil lost in the extract is represented by triangle AOE. The remaining low viscosity oil in the raffinate is enough higher than 100 V. I. to compensate for the high molecular weight low V. I. oil that is in the raffinate as shown by triangle OBF.

The yield of raffinate from the poor solvent is substantially the same as the yield of raffinate with the good solvent, but the distribution of components is quite different. The poorer solvent gives raffinates containing larger amounts of low V. I. high molecular weight fractions, and the poorer the solvent, the more good oil of low molecular weight is lost in the extract.

To produce the maximum obtainable yield of high V. I. oil, it is necessary to include high V. I. low molecular weight oils, which, as illustrated in Figure 1, are usually lost with the extract. The importance of this phenomenon becomes

greater and greater as the length of the cut of the oil to be treated increases and it is of major importance in treating long residua or long distillates.

In Figure 2 we have illustrated the effect of propane tending to reject high molecular weight or high viscosity fractions. At normal temperatures propane precipitates asphalt completely, if no other oil is present, and further separations can be made according to molecular weight by varying conditions of temperature and pressure. Propane tends to protect the light fractions and reject the heavier ones, but only on the basis of molecular weight and not on the basis of viscosity index. Propane is not a preferentially paraffinic solvent because it dissolves naphthenic oils as readily as it dissolves paraffinic oils.

Figures 1 and 2 are not intended to be quantitative, but are intended to aid in understanding Figures 3 and 4 and explaining the invention illustrated in Figures 5 and 6. A large number of solvent extraction tests carried out with and without propane showed that the yields of a given V. G. C. (viscosity gravity constant) are essentially the same regardless of whether or not propane is used in the extraction. Although the V. G. C.'s are substantially the same with and without propane, the actual viscosities and gravities are considerably different in these two cases. In Figure 4 we have shown these differences between experiments with and without propane in comparing viscosities with V. G. C.'s. Thus in treating to .83 V. G. C. the viscosity when propane is used is 92 and when propane is not used is 151.

Since the absence of propane gives yields of considerably higher viscosity oils, it would seem that they should likewise have a lower A. P. I. gravity and such is indeed the case, as illustrated in Figure 4. In treating to .83 V. G. C. with propane, the viscosity of the raffinate is 92 seconds Saybolt at 210° F. and its gravity is 24.8° A. P. I. When no propane is used, the viscosity of the raffinate is 151 seconds Saybolt at 210° F. and its gravity is 23.7° A. P. I.

Since the yields of oils of a given V. G. C. are the same from both methods of operation and since the ratio of low viscosity oil to high viscosity oil is much greater in one case than in the other, it is necessary to conclude that some low viscosity high V. I. oil was lost when operating without propane and that some high viscosity high V. I. oil was lost when operating with propane. These data confirm the previous conclusion that propane tends to reject the high viscosity paraffinic oils and that single solvents tend to dissolve low viscosity fractions thereof.

It might at first appear from this discussion that a proper balance between propane and solvent would result in the maximum yield of high V. I. oil. However, it does not seem to be feasible to balance the propane-solvent ratio for proper extraction conditions relative to V. I. and at the same time relative to miscibility and maximum yield. There are rather narrow limits of operability fixed by miscibility temperatures when propane is used and we have discovered that the preferable method is to treat the lubricating oil stock in two separate steps and under two separate conditions: In one of these steps the propane should play the major part and in the other step the solvent should be dominant. Our invention covers methods and apparatus for practicing such multi-step processes.

Propane absent in first treating step

First we will describe the system wherein propane is substantially absent in the first step,—that step from which the first quality raffinate is removed. Such a system is illustrated in Figure 5. The oil stock enters the first treating step 10, which may be a multi-stage countercurrent extraction system, through line 11 either from a storage tank, from a depropanizer, or from some prior refining step. Solvent from tank 12 is forced by pump 13 and line 14 into the opposite end of the first treating step. Raffinate is removed therefrom through line 15 and introduced into solvent recovery still 16, the solvent being passed through line 17 and condenser 18 to storage tank 12. First quality (high V. I.) paraffin oil is removed from the system through line 19.

The extract is removed from the first treating step through line 20 and it may be passed through lines 21 and 22 to second treating step 23 of our extraction system. Propane from tank 24 is forced by pump 25 and line 26 into the opposite end of the second treating step, which may likewise be a multi-stage countercurrent extraction system. Raffinate from the second treating step is withdrawn therefrom through line 27 and introduced into propane still 28. The propane is passed through pipe 29 and condenser 30 to propane storage tank 24. Depropanized oil is withdrawn through lines 31 and 32 to second quality lubricating oil storage tank or through lines 31 and 33 to line 11 or to some other part of the first treating step.

Extract from the second treating step may be withdrawn through line 34 to depropanizer 35 and thence through line 36 to solvent still 37, the solvent being removed through line 38 to vapor line 17, condenser 18 and tank 12. The final naphthenic oil is then withdrawn through lines 39 and 40 to a suitable storage system (valve 41 being closed).

We may recover the solvent from extract leaving the first treating step before it is introduced into the second treating step. In this case we pass the extract through line 20 directly through line 42 to solvent still 37 and we pass the solvent-free extract through lines 39, 43 and 22 to the second treating step 23. The final extract from the second step is then passed through depropanizer 35 and thence through line 40 to storage, valve 41 being open and the valves in lines 36 and 39 being closed.

We have described the operation of the second treating step both in the presence and absence of solvent, but it will be noted that propane is present in both cases. We may, of course, remove a part and retain a part of the solvent in the second step. The important feature of this system is that high molecular weight high V. I. oils are recovered in the first treating step, low molecular weight high V. I. oils are recovered in the second step and these recovered oils may either be used as a second grade lubricant or they may be recycled to the first step for increasing the yield therein. By operating our process in two steps, we can maintain both countercurrent extraction systems at optimum temperatures and pressures without having the propane in the second step interfere with the miscibility temperatures in the first step. The precise operating conditions will, of course, depend upon the oil to be treated, on the solvents employed, and on the desired end products. In this particular case we may employ about three volumes of phenol to one volume of oil in the first step and we may

extract at about 125° F. In the second step we may operate at about 80° F. and we may use about three to six volumes of propane per volume of extract from the first treating step. If no solvent is present in the second treating step, it may be necessary to heat the propane extract mixture to temperatures of 140–200° F. in order to effect phase separation and to reject the high molecular weight oils. Thus our second treating step acts as a check valve to prevent the loss of high V. I., low molecular weight oils with the final extract.

Propane present in first treating step

In Figure 6 we have disclosed a modification of our invention wherein propane is present in the first treating step and wherein the second treating step is employed as a check valve to prevent the loss of high molecular weight high V. I. oils with the final extract.

Charging stock in this case will probably come from a propane deasphalting step (not shown) or from a propane dewaxing step, so that the oil is already diluted with from about one to five volumes of propane. This diluted propane-oil charging stock is introduced through line 44 to first treating step 45. This step may be a multi-stage countercurrent extraction system with solvent from storage tank 46 being introduced by pump 47 and pipe 48 at the opposite end of the system. Raffinate is removed from the first treating step through line 49 which leads to propane still 50, the propane being removed through line 51. Depropanized raffinate is introduced by line 52 to solvent still 53, the solvent being withdrawn through line 54 and condenser 55 to storage tank 46. The first grade high V. I. oil is withdrawn from the system through line 56.

Extract from the first treating step is withdrawn through line 57 to propane still 58, the propane being withdrawn through line 59 and condenser 60 to propane tank 61. From this tank the liquefied propane may be forced by pump 62 and line 63 to line 64 leading to a deasphalting system, line 65 leading to a dewaxing system, or line 66 leading to incoming charging stock.

Depropanized or partially depropanized extract from still 58 is withdrawn through line 67 to second treating step 68. Instead of introducing this extract into the second treating step with all of its contained solvent, we may partially remove the solvent from this extract by passing it through line 69 into solvent still 70, the extract being returned through line 71 to the second treating step and removed solvent being returned through line 72 to solvent storage tank 46. Either naphthenic extract from line 73 or asphaltic material from line 74 or a mixture thereof is introduced through line 75 into the second treating step for recovering high molecular weight high V. I. oils from the extract from the first treating step. The paraffinic oils recovered in this second treating step are withdrawn through line 76 and are either passed through line 77 to second grade high V. I. oil storage tank or they are returned through line 78 either to the first or one of the succeeding stages of the first treating step.

Extract is removed from the second treating step through line 79 to solvent still 80, from which solvent is returned through lines 81, 54 70 and 55 to solvent tank 46. Final extract is withdrawn through line 82.

The outstanding feature of this modification is the fact that desirable high molecular weight oils which are lost with the extract from the pro-

pane-solvent countercurrent extraction system are recovered in the second treating step wherein the proportion of solvent, naphthenic and/or asphaltic materials is maintained high enough to cause the paraffinic oils to be thrown out of solution. We may use the second grade lubricating oil as such or we may return it to the first treating step, in which case our yield of high V. I. oil will be greatly increased because of the fact that neither the high viscosity nor the low viscosity oils are permitted to escape with the final extract. The ratio of solvent to oil in the second treating step of Figure 6 should be about two or three to one and, as hereinabove pointed out, the effect of this ratio can be obtained by recycling solvent-free extract by introducing asphaltic material, or by removing about half of the solvent in preliminary solvent still 70.

The modification in Figure 5 gave a second grade oil of relatively low viscosity while the modification of Figure 6 gave a second grade oil of relatively high viscosity. When it is desired to produce first and second grade oils of more nearly the same viscosity, we may return the raffinate oils from the second treating step to the first treating step, as indicated by line 33 of Figure 5 and line 78 of Figure 6, and we may then subject the combined fractions of high V. I. raffinate to a second solvent extraction system, preferably in the absence of propane and by means of a good solvent. In this case our two-step process prevents any high molecular weight or low molecular weight good oil from being lost with the extract and the extraction of the first raffinate with good solvent gives a second extract which may be used as an intermediate grade lubricating oil.

As hereinabove stated, our invention is applicable for the treatment of all types of oils, including light oils, gas oils, lubricating oils, gear oils, transmission oils, paraffin distillates, heavy hydrocarbon oils and residual oils whether obtained by the distillation, destructive distillation, hydrogenation, destructive hydrogenation or cracking of coals, tars, pitches, lignite, shales, bitumens, resins, petroleum or other oils or carbonaceous materials. The invention is also applicable to heavy oils prepared by polymerization or condensation of gaseous, liquid or solid hydrocarbons in the presence or absence of catalysts such as sulfuric acid, halides of aluminum, zinc, iron, tin, antimony, or boron, etc. The invention is also applicable to oils prepared by voltolization by means of silent electric discharges and the oils which contain varying amounts of said voltolized oils. The invention is particularly useful for the treatment of long residua or long distillate stocks for the preparation of lubricating oils.

The hydrocarbon oil to be treated may be preliminarily and/or subsequently subjected to various refining treatments such as dewaxing, acid and clay treating, stabilizing, etc., and these treatments may be accomplished by any well known means.

It should be noted that our light hydrocarbon solvent is not a preferential paraffinic solvent since it dissolves naphthenic oils to essentially the same extent that it dissolves paraffinic oils. This solvent may be considered selective on the basis of molecular weight and not on the basis of paraffinicity.

As hereinabove stated, we have found it undesirable to effect the entire solvent extraction process in the presence of both the preferentially naphthenic solvent and the light hydrocarbon solvent because of the difficulty in obtaining

proper miscibility temperatures, phase separations, yields, etc. The simultaneous use throughout the system of both naphthenic solvents and light hydrocarbon solvents necessitates the use of much larger quantities of both of these solvents than are required in our process. The use of the light hydrocarbon solvent requires the use of much larger amounts of naphthenic solvent near the raffinate end of the system and these increased amounts of naphthenic solvent tend to dissolve larger amounts of good oil at the extract end of the system. By operating our system in two steps we markedly decrease the amount of each solvent required, we obtain even greater yields of high viscosity index oils, and we avoid large solvent losses since the solvent losses may be a function of the total amount of solvent which has to be recovered by distillation. Likewise, our invention makes it possible to greatly increase the capacity of treating towers and equipment because they can operate with lesser amounts of solvent and consequently with greater amounts of oils. It will be seen that our process is capable of great flexibility and that it may be operated at maximum over-all efficiency due to the fact that optimum conditions for each solvent may be used in the separate parts of the system.

While we have described our invention in some detail and in connection with a certain theory, it should be understood that we do not limit ourselves to these details or this theory except as defined by the following claims, which should be construed as broadly as the prior art will permit.

We claim:

1. The method of refining lubricating oil stocks to recover both high viscosity and low viscosity paraffinic oils from naphthenic oils, which comprises treating said oil stocks in one system with a preferentially naphthenic solvent in the absence of appreciable amounts of light hydrocarbon solvent, withdrawing raffinate from said system, removing substantially all of said naphthenic solvent from the extract, then treating said extract in another system with a light hydrocarbon solvent at a sufficiently high temperature and pressure to remove low viscosity paraffinic oils therefrom, returning said low viscosity paraffinic oils to said first-named system, and withdrawing the final extract from the second named system.

2. The method of refining a lubricating oil stock which comprises extracting a propane solution of said lubricating oil stock with a selective naphthenic solvent, removing propane from both the extract and raffinate phases thus produced, extracting the depropanized extract with a selective naphthenic solvent in the absence of appreciable amounts of propane to recover high viscosity paraffinic oils therefrom, and returning said high viscosity paraffinic oils to the step of solvent extraction with the propane-naphthenic solvent.

3. The method of refining a lubricating oil stock with selective solvents which comprises extracting said oil with a preferentially naphthenic solvent in the absence of substantial amounts of propane whereby low viscosity paraffinic oils are left in the extract, removing substantially all of the solvent from the extract, treating the solvent-free extract with propane to reclaim low molecular weight high viscosity index oils from high molecular weight low viscosity index oils, and returning said low molecular weight oils to said first extraction system whereby maximum yields of high viscosity index oils are obtained and no

appreciable amounts of high or low viscosity paraffinic oils remain in the final extract.

4. The combination of claim 3 wherein the propane treatment is at temperatures of 140-200° F.

5. The method of claim 1 wherein the naphthenic solvent is selected from the class of solvents which consists of phenol, cresol, ortho, meta and para cresylic acid, wood tar acids, coal tar acids, nitrobenzene, sulfur dioxide, aniline, chloraniline, chlorphenols, beta beta' dichlorethyl ether, furfural, pyridine, acetone, crotonaldehyde, benzonitrile, benzaldehyde, phenyl acetate, nitrotoluene, nitrophenols, ethyl chloracetate, glycol diacetate, ethyl formate and mixtures of one or more of said solvents.

6. The process of claim 1 wherein the light hydrocarbon solvent comprises one or more hydrocarbons having from two to six carbon atoms.

7. The process of claim 1 wherein the light hydrocarbon solvent is propane.

8. The process of claim 1 wherein the naphthenic solvent is a phenolic compound and the light hydrocarbon solvent is propane.

9. The process of claim 1 wherein the naphthenic solvent is nitrobenzene and the light hydrocarbon solvent is propane.

10. The method of refining a lubricating oil stock which comprises extracting a propane solution of said lubricating oil stock with a selective naphthenic solvent, removing propane from both the extract and raffinate phases thus produced, and extracting the depropanized extract with a selective naphthenic solvent in the absence of appreciable amounts of propane to recover high viscosity paraffinic oils from the final extract.

11. The method of refining a lubricating oil stock which comprises extracting said oil stock with a preferentially naphthenic solvent in the

absence of light hydrocarbon diluents whereby a high quality, high viscosity paraffinic oil is produced, removing at least a portion of the solvent from the extract, and countercurrently extracting the extract with a liquefied normally gaseous hydrocarbon to produce a second grade paraffinic oil of relatively low viscosity and a final extract which is substantially free from paraffinic components.

12. The method of refining a lubricating oil stock which comprises extracting said oil stock with a mixture of a selective naphthenic solvent and propane to recover the low viscosity paraffinic components, removing propane from the extract and subsequently extracting it with at least two or three volumes of a naphthenic solvent in the absence of propane to recover high viscosity paraffinic oils from the final extract, blending said, high viscosity paraffinic components with said low viscosity paraffinic components and finally extracting said mixture of paraffinic oils with a selective solvent to separate a first grade paraffinic oil from an inferior grade paraffinic oil.

13. The method of refining a lubricating oil stock which comprises countercurrently extracting said stock with a mixture of a naphthenic solvent and a saturated liquefied normally gaseous hydrocarbon, removing said normally gaseous hydrocarbon from the extract produced by said countercurrent extraction and countercurrently extracting said remaining extract with a naphthenic solvent for recovering high viscosity paraffinic oils which were discarded from the first countercurrent extraction system by the liquefied normally gaseous hydrocarbons.

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