

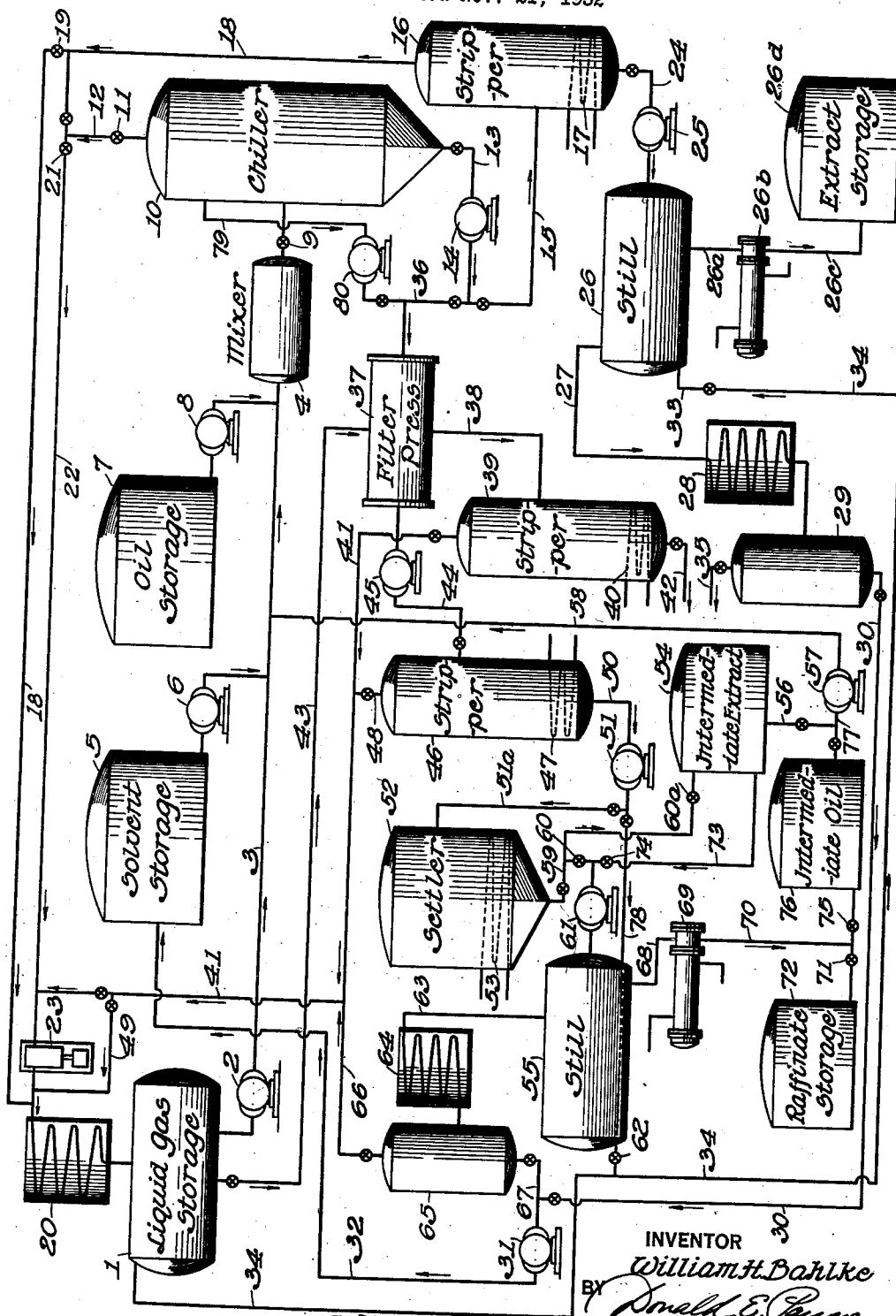
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W. H. BAHLKE

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REFINING LUBRICATING OILS

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**INVENTOR**

William H. Bahlke

BX

Donald E. Payne

ATTORNEY

UNITED STATES PATENT OFFICE

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REFINING LUBRICATING OILS

William Herbert Bahlke, Hammond, Ind., assignor
to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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This invention relates to the refining of lubricating oils and it pertains more particularly to a combination extracting and dewaxing system wherein the dewaxing diluent aids in the extraction and the extraction solvent aids in the dewaxing.

The object of this invention is to produce lubricating oils with low pour points and high viscosity indices from mixed base crude distillates or residues. A further object is to provide an improved means for separating naphthenic and/or asphaltic constituents from lubricating oils. A further object is to provide an improved means for separating wax from oils so that the solvent used in the extraction step may act as an antisolvent in the dewaxing step. A further object is to provide an improved means for removing the extracting solvent from a finished lubricating oil. Other objects will be apparent as the detailed description of the invention proceeds.

In solvent extraction processes heretofore used it has been difficult to separate the raffinate phase from the extract phase because the wax separates out at extraction temperatures and entrains large amounts of both phases in a difficultly workable slurry or buttery mass. Furthermore, the raffinate phase is usually quite viscous, especially at low temperatures, making it difficult to handle. Also it has been difficult to recover the extracting solvent from the separated oils without loss of solvent, and corrosion caused by decomposition of the solvent. The object of the present invention is to overcome all of these difficulties and to improve the efficiency of the recently developed propane dewaxing process.

Before describing the invention in detail it may be well to state a few fundamental principles on which the invention is based. In the first place, it has been found that light hydrocarbon diluents, such as propane, butane, pentane, etc. increase the miscibility between the oil and the extraction solvents, such as beta beta dichlor diethyl ether, hereinafter referred to as "Chlorex", nitrobenzene, etc. and that by using mixtures of such diluents with an oil and solvent, a more intimate contact can be obtained between the solvent and the oil. Then when the diluent, or a portion thereof, is allowed to evaporate from the mixture a low temperature is obtained which assists in the separation of solvent and oil. The refrigerative effect of vaporizing propane is, of course, well known but in the present invention the self evaporation serves another function, namely, by removing the propane from the mixture

of propane, oil and solvent, the miscibility temperature of the remaining components is increased to such an extent that a separation of the raffinate and extract phases may be readily obtained.

In the preferred embodiment of my invention a liquefied hydrocarbon gas, for example, propane, and a suitable extraction solvent, for example, "Chlorex", are mixed under pressure with the oil to be extracted. In general, the components will be completely miscible. The temperature of the mixture is next reduced by allowing a portion of the propane to expand, thereby causing a separation of the mixture into two layers which are separately treated for recovery of solvents, as hereinafter described.

Referring to the drawing which forms a part of this specification, liquefied hydrocarbon gas which may suitably be propane, contained in tank 1 is conducted in regulated quantities by pump 2 and line 3 to mixer 4 where it is intimately mixed with the extraction solvent from tank 5 delivered by pump 6 and the oil to be treated contained in tank 7 delivered by pump 8. The oil may suitably be a distillate from M-C crude or other mixed-base petroleum oil having a viscosity within the lubricating range and ordinarily containing paraffin wax in amounts usually between 1 and 10%, but sometimes as much as 20%. It may also suitably be treated with concentrated or fuming sulfuric acid before extraction. If desired, the oil may be mixed with the propane before acid treating and the chlorex introduced afterward.

The mixture from mixer 4 is delivered through valve 9 into chiller 10 with or without reduction of pressure, depending on the method of operation adapted. In one method of operation the chiller 10 is substantially filled with the mixture whereupon the incoming supply is shut off and the pressure is reduced by opening valve 11 leading from the vapor line 12 in the top of the chiller. As the propane is withdrawn in this manner the mixture of extraction solvent and oil separates into two phases. Where the extraction solvent is heavier than the oil, as in the case of "Chlorex", the solvent forms a separate layer at the bottom of the chiller. This layer, containing the naphthenic fractions of the oil and other undesirable impurities, may be drawn off at intervals during the chilling operation, line 13 and pump 14 being provided for this purpose. If desired, however, the entire charge may be chilled down to the minimum temperature em-

ployed in the process before any separation of solvent phase is made.

The solvent or extract phase which is drawn off by pump 14 is conducted by line 15 to stripper 16 where the propane which it contains is removed by raising the temperature of the extract by means of heating coil 17. The propane vapors from the heated mixture are led by line 18 and valve 19 to condenser 20 where they are reliquefied under pressure and the liquid is returned to storage tank 1. When the pressure of the vapors is insufficient for proper liquefaction, the vapors may be conducted by valve 21 and line 22 to compressor 23 which delivers them to the condenser under sufficient pressure for liquefaction.

After the removal of propane from the extract it is conducted by line 24 and pump 25 to still 26 for reclaiming the extraction solvent. Heat is supplied to the still and the solvent is vaporized from the oil, the vapors being led by line 27 to condenser 28 where they are condensed and the recovered solvent is collected in receiver 29 from which it flows by line 30 to pump 31 and is returned by line 32 to the solvent storage tank 5. The oil freed from solvent is removed from the still by line 26a to cooler 26b and line 26c to extract storage 26d.

In order to facilitate the recovery of extraction solvent from the naphthenic oil and reduce decomposition which would result from the use of high temperatures, a stripping gas is introduced into the still 26 by line 33. This gas may suitably be propane vapor withdrawn from the propane storage reservoir 1 by line 34, as illustrated. The propane which is carried over with the solvent vapors collects in receiver 29 and is withdrawn by line 35 and returned to the propane system by a line not shown.

After the extract layer is withdrawn from chiller 10 the oil or raffinate layer, which may suitably be at a low temperature, for example, zero to -50° F., is transferred by pump 14 and valved line 36 to filter press 37, valved line 15 being closed. To obtain lower viscosity and lower temperatures for the filtering operation, I may add additional propane to chiller 10 via line 3, mixer 4 and valve 9. The filter press 37 removes any crystallized wax from the raffinate fraction, the wax being transferred by line 38 to stripper 39 where it is heated by steam coil 40 to melt it and remove propane therefrom. The propane vapors are led by line 41 back to the propane vapor line 22 and compressor 23, and the wax fraction is discharged from the stripper by line 42. Liquid propane from storage tank 1 may be led by valved line 43 to the filter for the purpose of washing the filter press cake and recovering the maximum quantity of oil therefrom.

The filtrate, containing a large quantity of propane and some extraction solvent, is led by line 44 and pump 45 to stripper 46 where it is heated by coil 47, the propane being thereby expelled from the mixture. The propane vapors are led by lines 48 and 41 to the condenser 20 or the compressor 23 as desired, depending on the pressure. When the pressure of the vapors is sufficient for condensation they are led by valved line 49 directly to the condenser, otherwise they are recompressed by compressor 23.

The extract fraction now freed from propane is withdrawn from stripper 46 by line 50, pump 51 and line 51a to settler 52 equipped with coil 53 which may be employed for cooling if necessary. Here the raffinate fraction will ordinarily

separate into two layers due to the removal of the liquefied hydrocarbon gas. When heavy solvents are used, such as "Chlorex" and nitrobenzene, the lower layer will consist principally of solvent containing some oil in solution. This oil is more naphthenic in character than the oil remaining in the upper layer and it is therefore ordinarily desirable to make a separation between these two fractions. Accordingly, the lower layer may be withdrawn to tank 54 and the upper layer may be charged directly to still 55 for recovery of solvent. This may be done by controlling valves 60 and 60a, permitting the lower layer to pass through line 59 to tank 54 and thereafter diverting the upper layer to pump 61 and still 55. The solvent fraction in tank 54 may be returned directly to the process for re-extraction, line 56, pump 57 and line 58 being used for this purpose. When desired, however, this fraction may likewise be charged to still 55 for recovery of solvent as hereafter described.

The upper layer in separator 52 which is comprised largely of raffinate containing some solvent in solution is conducted by line 59 and valve 60 to pump 61 and still 55. This still, like still 26, may also be equipped with a supply of stripping gas introduced by valve 62 from line 34. The extraction solvent is vaporized and stripped from the oil and carried by vapor line 63 to condenser coil 64 where it is condensed and conducted to receiver 65. The propane gas collecting in this receiver may be returned by valved line 66 to line 41 and thence to compressor 23, as previously described. The recovered solvent is withdrawn from the receiver by valved line 67 leading to pump 31 and line 32, leading it to storage tank 5. The raffinate oil remaining in still 55 is withdrawn by line 68 to cooler 69, thence by line 70 and valve 71 to raffinate storage reservoir 72.

When it is desired to recover the solvent from the intermediate extract contained in tank 54 this material may be led by line 73 and valve 74 to still 55 where the extract is vaporized in a manner similar to that just described. The intermediate oil freed from extract may be withdrawn through cooler 69, line 70 and valved line 75 to storage tank 76. This intermediate oil fraction may be discharged from the system or may be reprocessed by returning it through line 77, pump 57 and line 58 to the solvent extraction system.

When it is not desired to make a separation of the intermediate oil fraction just described, the raffinate contained in stripper 46 may be led directly by line 50, pump 51 and line 78 to still 55 for recovery of solvent, as previously described.

The process just described is semi-continuous in nature and it should be understood that various units of the equipment may be employed in multiple when necessary to obtain a balanced working of the plant. Thus, for example, chiller 10 and filter press 37 may suitably be in duplicate and the charge to these units may be controlled by suitable manifolds not described but well understood in the art. In certain cases where the oil treated forms a mixture with the solvent which rapidly separates into two layers, I may operate the chiller 10 in a continuous fashion by reducing the pressure of the charge flowing through valve 9. In this way I maintain a low pressure and correspondingly low temperature within the chiller 10 which results in a continuous separation of the charge into two layers. The bottom layer may be continuously with-

drawn by line 13 and pump 14 to line 15 and stripper 16, as previously described. The upper layer may likewise be continuously withdrawn by line 19 and pump 80 leading to filter press 37.

One of the principal advantages of this method of operation is that a continuous supply of hydrocarbon gas is available for compression and for other operations, such as stripping the solvent in stills 26 and 55 in which case the gas for this purpose may be led directly from line 22 to line 34 by a connection not shown. Another advantage of continuous operation is the possibility of employing smaller quantities of extraction solvent in the system and thus reducing the inventory on this expensive material.

One of the important advantages of my combination solvent extraction process is that the dewaxing and extraction operations may be carried out simultaneously without the necessity of making a careful separation of extraction solvent and dewaxing diluent, in this case a liquefied hydrocarbon gas.

Another and still more important advantage is that the separation of wax from the oil and the diluent is greatly facilitated by the presence of the extraction solvent which, as previously indicated, acts as a wax antisolvent. The raffinate layer which is charged to the filter is saturated with the extraction solvent which possesses a very low solubility for wax. By subjecting this material to filtration at the separation temperature or critical solution temperature the maximum amount of wax is removed from the oil, thus producing an oil which is substantially entirely wax-free. In my preferred embodiment I filter the wax from the raffinate layer at the temperature of separation. At higher temperatures a part of the wax passes into solution in the oil and cannot be removed in the filter press. At lower temperatures a still further separation of solvent occurs and produces a second liquid phase which interferes with the filtration process.

Another advantage of my combination process of extraction and dewaxing lies in the diluting effect of the liquefied hydrocarbon gas on the oil. Many of the oils which it is desired to treat have very high viscosities and are difficult to separate from extraction solvents. The presence of the liquefied hydrocarbon gas in the oil reduces its viscosity to a very low value and permits solvent extraction at temperatures far below those heretofore available. As a result I am enabled to use oils and employ solvents which heretofore could not be handled, or which could only be separated by expensive centrifugal apparatus. The ready separation obtained by the use of diluents in my solvent extraction process enables it to be carried out without the use of centrifugal machines although such machines may be used in place of or in conjunction with gravity separation when desired.

In this specification I have referred specifically to propane as my preferred light hydrocarbon diluent. It should be understood, however, that I may use other light hydrocarbons, such as ethane, butane, pentane, hexane, iso-butane, isopentane, butylene, propylene, ethylene, etc. Also the diluent may contain or consist of substituted light hydrocarbons, particularly low boiling ethers and halogenated compounds, such as methyl chloride, dichlor-difluor methane, etc. Although I prefer to use those hydrocarbons which are normally gaseous in order to obtain conveniently the refrigeration necessary, it will

be understood that certain advantages of the process may be obtained by using even heavy diluents, such as light naphtha. With heavier diluents whose volatility is insufficient to provide self-refrigeration by evaporation, I may add a portion of a lighter solvent, e. g. propane, or I may supply indirect cooling to effect separation when necessary.

The extraction solvents which I may use all belong to the class of organic liquids which are incompletely miscible with petroleum lubricating oils at ordinary temperature, e. g. 70° F. These solvents, when mixed with a lubricating oil and allowed to separate, extract from it certain constituents undesired in the finished oil and which impart to the oil a high viscosity temperature coefficient or low viscosity index as defined by Dean and Davis in Chemical & Metallurgical Engineering, 1929 volume 36, page 618-619. The extraction solvents vary a great deal among themselves in their efficiency and those which I prefer to use belong chiefly to the class of ketones, phenols, ethers, esters, nitro and chloro compounds and amines. Examples of those I may employ in addition to "Chlorex" and nitrobenzene, hereinbefore mentioned, are phenol, furfural, aniline, pyridine, ethyl chlor acetate, cresol, xylydine, alpha naphthol, acetone, ethylene diamine, glycol, diacetate, cellosolve acetate, benzonitrile or mixtures of these.

Although the advantages of my process are most apparent when treating a wax-containing oil, it can also be applied to a wax-free oil or one which has been previously dewaxed. The light hydrocarbon diluent reduces the viscosity and the specific gravity of the mixture, permitting ready separation of the extract, particularly as the diluent remains chiefly in the oil or raffinate layer. Also the diluent facilitates mixing as previously described and in the case of the liquefied hydrocarbon gases, the diluent aids in cooling the mixture below the miscibility temperature.

As an example of the results which may be obtained by my process, a mid-continent lubricating distillate having a viscosity of 122 seconds at 210° F. and 2682 seconds at 100° F. was mixed under pressure with two volumes of "Chlorex" and three volumes of liquid propane. The mixture was cooled to 15° F. and was allowed to separate into two layers. The lower layer contains the non-paraffinoid components and the upper layer contains the paraffinoid components. The lower layer was removed and the upper layer was freed from solvent and propane as it was not necessary to dewax for the reason that the initial lubricating distillate had already been subjected to a dewaxing operation. The resulting oil was obtained in a yield of 84% and had a viscosity of 95 seconds at 210° F. and 1350 seconds at 100° F. equivalent to a viscosity index of 79. The viscosity index of the original oil was 55.5, showing the improvement obtained in the process. The extract fraction after removal of solvent and diluent was a dark colored, heavy tar valuable as a fuel oil, impregnating or paving oil. It is characterized by a high fluidity when heated, a high specific gravity and freedom from paraffin wax.

In another example of the advantages obtained by the use of liquefied hydrocarbon gases in solvent extraction of lubricating oils, the same mid-continent lubricating distillate described above was treated with three volumes of "Chlorex" and

two volumes of propane to one volume of oil. The mixture was separated at a temperature of minus 18° F. giving a yield of 79% of raffinate, having a viscosity of 97 at 210° F. and 1310 at 100° F. The viscosity index was 86.8 and the A. P. I. gravity was 25.3. After percolation through clay the viscosity index rose to 90.7.

In comparison with this result another sample of oil was extracted with three volumes of "Chlorex", without propane. The separation was made at a temperature of 100° F. and the resulting oil had a viscosity index of 87.7, almost identical with that obtained when propane was used and the separation was made at minus 18° F. In this case, however, the yield was only 58.2%, a loss of over 20% compared with the yield obtained when propane was used. In another example, the same mixture without propane was separated at 10° F. in which case a yield of 80.4% was obtained, practically the same as that obtained previously with propane. However the viscosity index was only 82.3 in comparison with 86.8 previously obtained when propane was used.

The finished oil may be given a treatment with acid and finally with clay to improve its color stability and its anti-sludging qualities. Any acid treatment, however, will be slight, preferably less than ½ pound of concentrated acid per gallon. If desired, the acid treatment may be applied before the solvent extraction process as previously mentioned.

In the above description I have not gone into detail or described the most desirable arrangement of heat exchangers, etc. and I have not attempted to provide a working drawing with respect to valves, pipe fittings, storage means, etc. All of these features will be well known to those skilled in the art and they form no part of the present invention. I have given a complete description of a preferred embodiment of this invention which will enable those skilled in the art to practice it. I do not limit myself to these particular details and it should be understood that many modifications are possible, for instance, I may separate the raffinate and wax from the "Chlorate" extract by means of settlers or centrifuges. Likewise I may partially dewax at an intermediate point in the process and then complete the extraction and dewaxing thereafter. In either case, the diluent serves to reduce the viscosity in both stages, acts as a refrigerant and serves the important function of stripping the solvent from the oil in the final distillation step. I may also conduct the process in stages, first extracting the propane-oil mixture with "Chlorex" to remove undesired low viscosity index constituents, then further cooling the raffinate fraction to separate a wax-free oil extract of intermediate grade after which the remaining raffinate fraction may be dewaxed in the manner previously described.

I claim:

1. A process of producing lubricating oil from oil containing paraffinoid and non-paraffinoid components which comprises mixing liquid pro-

pane and dichlorethyl ether with said oil and separating the solution of non-paraffinoid components in said dichlorethyl ether from the solution of paraffinoid components in said liquid propane.

2. A process of producing lubricating oil from oil containing paraffinoid and non-paraffinoid components which comprises mixing liquid propane and dichlorethyl ether with said oil, separating the solution of non-paraffinoid components in said dichlorethyl ether from the solution of paraffinoid components in said liquid propane and separating the dichlorethyl ether and propane from their respective solutions.

3. A process of producing lubricating oil from oil containing paraffinoid and non-paraffinoid components which comprises mixing liquid propane and dichlorethyl ether with said oil, reducing the viscosity of said mixture by heating the same and separating the solution of non-paraffinoid components in said dichlorethyl ether from the solution of paraffinoid components in said liquid propane.

4. In a process of separating mineral oil containing paraffinic and naphthenic constituents into fractions, respectively, more paraffinic and more naphthenic than the original oil, the steps comprising mixing the oil with beta beta' dichlorethylether and a liquid diluent selected from the group consisting of propane, butane, pentane, and hexane, cooling the admixture to effect a two-layer liquid system, separating the upper layer which contains the paraffinic constituents from the lower layer which contains the naphthenic constituents, and separating the beta beta' dichlorethylether and diluent from the respective layers.

5. In the process of refining mineral lubricating oils containing naphthenic oils, paraffinic oils, and wax, the steps comprising diluting said mineral oil under pressure with liquid propane, mixing the diluted oil with beta beta' dichlorethylether, cooling the admixture by flashing a portion of the propane and thereby forming a two-layer solvent system, and separating the upper layer from the lower layer.

6. The method of refining mineral lubricating oils containing naphthenic compounds, paraffinic compounds and wax, which comprises diluting said oil with liquid propane, admixing the diluted oil with beta beta' dichlorethylether, cooling the diluted mixture by vaporization of a portion of the propane whereby an extract phase containing the naphthenic compounds separates from a raffinate phase which contains the paraffinic compounds, separating said raffinate phase from said extract phase, precipitating wax from the raffinate phase in the presence of the liquid propane and beta beta' dichlorethylether, mechanically separating the precipitated wax from the oil solution, and recovering the propane and beta beta' dichlorethylether from said raffinate phase.

WILLIAM HERBERT BAHLKE.