Oct. 19, 1948. S. W. FERRIS 2,451,545

DEWAXING OF HYDROCARBON OILS

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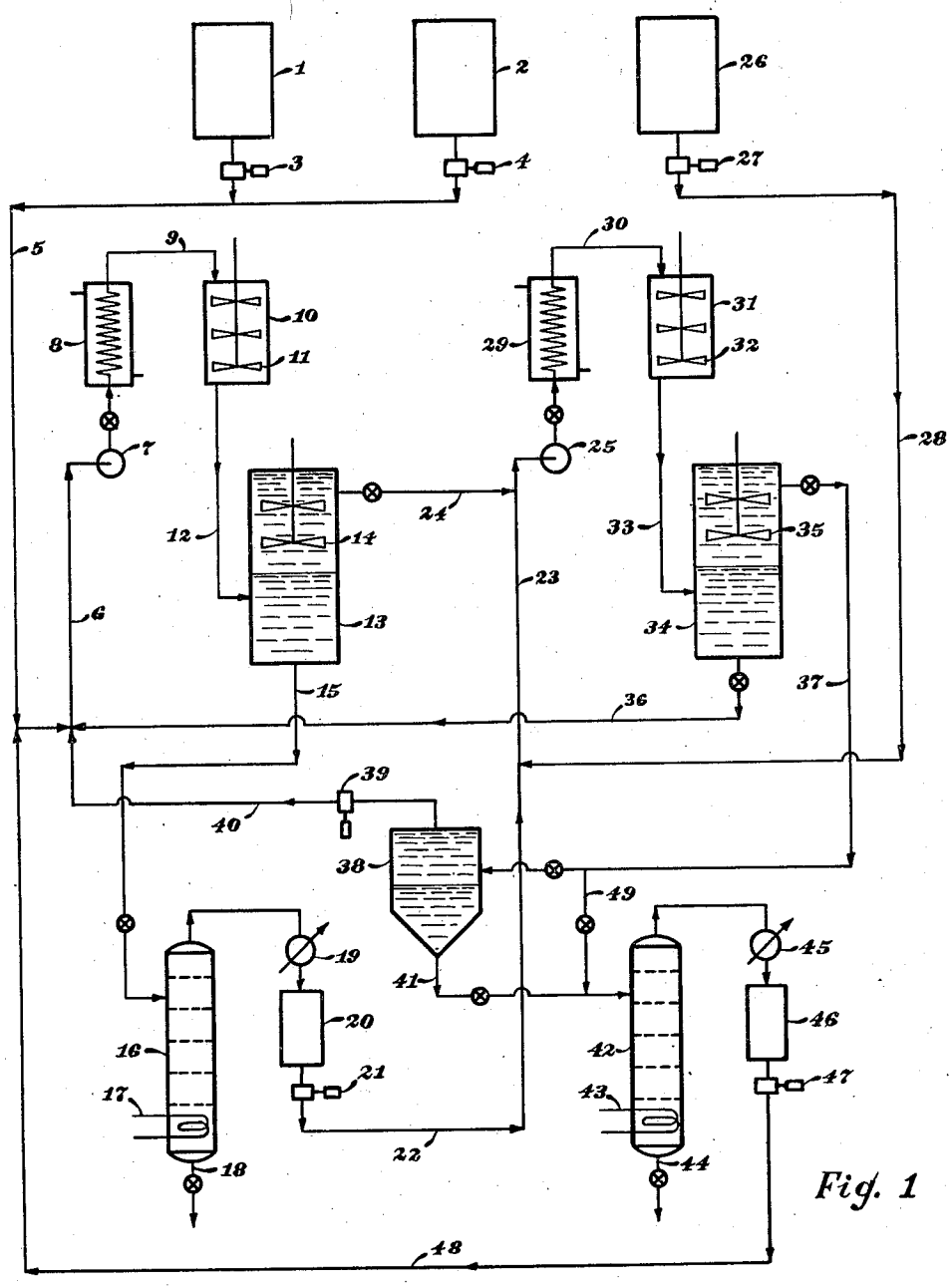


Fig. 1

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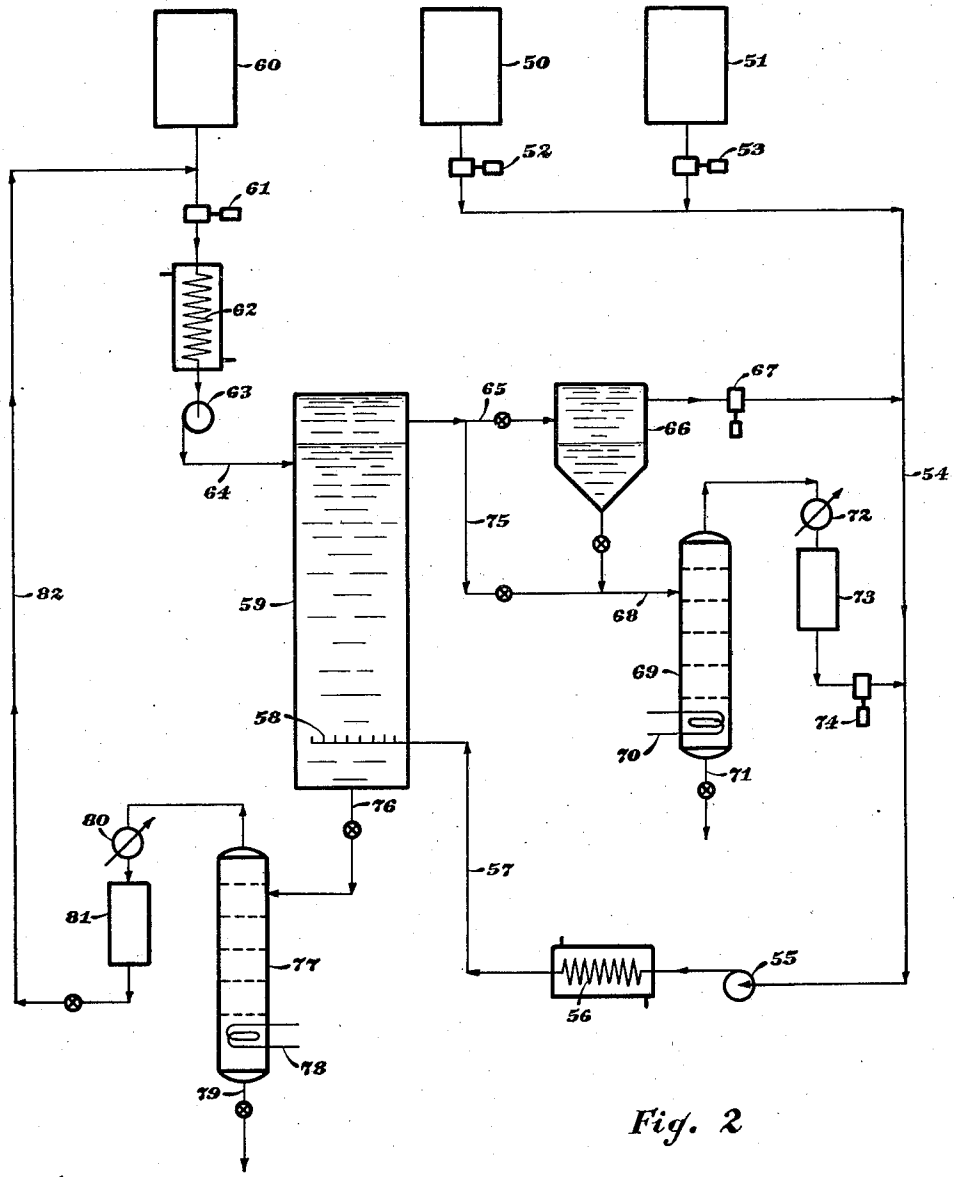


Fig. 2

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UNITED STATES PATENT OFFICE

2,451,545

DEWAXING OF HYDROCARBON OILS

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Application December 23, 1944, Serial No. 569,603

2 Claims. (Cl. 196—18)

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The present invention relates to the separation of oil-wax mixtures into solid and liquid components, and relates more particularly to the separation of wax from hydrocarbon oil-wax mixtures by means of a solvent or solvent mixture and a cerophile, i. e., an agent capable of preferentially wetting the wax.

In accordance with the present invention, I provide a process for separating solid wax from liquid hydrocarbon oil by transferring the solid wax from the oil into a liquid cerophile, thus forming a suspension of the solid wax in the cerophile, such transfer being effected in the presence of a solvent having a high solvent power for oil and a low solvent power for the cerophile and for the wax at the dewaxing temperature.

I have found that when an oil containing wax is diluted with a solvent having a high solvent power for oil and a low solvent power for wax, and the resulting mixture is commingled with a relatively immiscible cerophile at a temperature such that the wax is solidified, said cerophile being liquid at such temperature and having a preferential wetting power for the wax, the solid wax passes from the solvent-diluted oil into the cerophile substantially completely and forms a suspension therein which may be separated with the cerophile from the diluted oil, for example, by decantation or other means. The process of the present invention therefore involves the separation of two liquid phases, one of which contains the solid wax, which operation is far simpler and less expensive than the separation of solid wax from a liquid phase by filtration as in the commonly used acetone-benzol or propane dewaxing process.

Herein and in the appended claims, the term "solvent" is to be understood to comprehend a liquid which has a high solvent power for oil and a low solvent power for wax at the dewaxing temperature and which is capable of retaining in solution at such temperature the constituents of the oil-wax mixture other than wax, be they liquid paraffinic or naphthenic constituents, or asphaltic material. Such solvent is further characterized, in general, in having a higher specific gravity than the cerophile and in having a low solvent power for the cerophile and the solid wax at the dewaxing temperature. In other words, the solvent must preferentially dissolve the oil but not the wax at the dewaxing temperature, and the resulting oil-solvent solution must be relatively immiscible with the cerophile and the wax, and therefore separable therefrom by decantation or other means.

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Likewise, herein and in the appended claims, the term "cerophile" is to be understood to comprehend a liquid which preferentially wets the solid wax and permits it to pass from the oil-solvent phase into said liquid to form a suspension of solid particles therein. Such cerophile is further characterized, in general, in having a specific gravity lower than that of the solvent, and in having a low solvent power for both wax and oil in the presence of said solvent, and in being relatively immiscible with the oil-solvent solution at the dewaxing temperature, and therefore separable therefrom by decantation or other means.

In accordance with the present invention, an oil-wax mixture is commingled with a solvent and a cerophile, the temperature of the mixture is adjusted to cause crystallization or solidification of the wax if the wax is not already solidified, and the mixture is permitted to settle and stratify whereby two liquid phases or layers are formed, the lighter phase comprising the cerophile and solidified wax suspended therein, and the heavier phase comprising the solvent and oil substantially free of solidified wax. The phases are separated from one another by decantation or other means, and the solvent and cerophile are recovered from the respective phases by vaporization or fractional distillation. In many cases the solidified wax in the lighter phase will be found to have settled within the phase, in which case it is preferable to further decant the cerophile from the concentrated wax slurry prior to distillation of the slurry for the removal of the cerophile therefrom. The final products produced by this process are oil substantially free of solid wax, and wax substantially free of oil or containing a controlled amount of oil. Depending upon the choice of solvents and cerophiles, operating temperatures, and mode of operation, there may be produced oils of desired pour point varying, for example, from −50° F. to +50° F., and waxes which may be substantially free of oil or containing oil in desired amounts, for example, of from 1% to 10% or more. In the preferred method of operation, I employ a multi-stage batch countercurrent system, or alternatively, a single stage continuous countercurrent system, as will be described in detail hereinafter.

In carrying out my process, I may employ various ratios of solvent to oil-wax mixture within the range of 0.5:1 to 4:1, depending upon the nature of the oil-wax stock, the nature of the cerophile, and the operating temperature. The solvent may comprise a single compound or a

mixture of two or more compounds, and usually consists of a mixture of a polar compound and a non-polar compound in such a ratio that the resulting solvent will have a relatively high specific gravity, a relatively low freezing point, a high solvent power for oil and a low solvent power for wax at the dewaxing temperature, and will be relatively immiscible with the cerophile. The polar compounds, i. e., those having a dipole moment greater than 1×10^{-18} e. s. u., may be exemplified by nitrobenzene, o-nitrotoluene, nitrocumene, quinoline, o-chloraniline, β,β'-dichlordiethyl ether (Chlorex), ethylene dichloride, furfural, methyl aniline, toluidine, xylidine, o-chlorphenol, benzonitrile, benzaldehyde, nicotine, and pyridine. The non-polar compounds may be represented by benzene, toluene, xylene, carbon tetrachloride, methyl chloride, chloroform, diethyl ether, and carbon disulfide. The ratio of non-polar compound to polar compound may vary from 0 to 1.5:1, no non-polar compound being utilized if the polar compound, per se, fulfills the requirements with respect to gravity, solvent power, freezing point, etc., as described above with respect to the solvent.

In conjunction with the solvent or solvents mentioned above, a cerophile is employed, the ratio of cerophile to oil-wax mixture being within the range of 0.5:1 to 10:1. The cerophiles, which are substantially non-polar may be exemplified by liquefied ethane, ethylene, propane, propylene, n-butane, isobutane, isobutylene, butene-1, butene-2, the pentanes including neopentane, the hexanes including neohexane, and the higher homologues of the paraffin and olefin series which are liquid at dewaxing temperatures. All of these cerophiles have boiling points below that of the wax, and may be recovered by distillation from the wax. On the other hand, it is also possible to employ relatively paraffinic oils having a boiling point above that of the wax, in which case the wax is recovered by distilling it from the high boiling cerophile. Such high boiling paraffinic oils include the selective solvent raffinates (dewaxed) from lubricating oil stocks, lubricating distillates or residuum from paraffin base crude oils such as from Pennsylvania, hydrocarbon polymers, and the like. In the dewaxing of heavy oil stocks, such as waxy residuums, it is preferable to employ a relatively light cerophile such as liquefied ethane, propane, or propylene, or mixtures of two or more thereof. With intermediate waxy stocks, the butanes, pentanes, or hexanes are preferred. And with very light waxy stocks, the heavier or high boiling cerophiles are most satisfactory, particularly a dewaxed selective solvent raffinate of relatively high paraffinicity derived from a lubricating oil stock.

In dewaxing hydrocarbon oils to obtain 0° F. pour point oils, using the technique of the present invention, a dewaxing temperature of 0° F. to −10° F. is satisfactory. In the event that oils of higher or lower pour point are to be made, the dewaxing temperatures may be increased or decreased correspondingly. For the production of low melting point waxes, temperatures considerably below 0° F. may be employed, whereas for the production of high melting point waxes, for example, those of 140° F. to 175° F. melting point, temperatures approaching ordinary room temperature may be utilized.

My invention may be further understood with reference to the accompanying drawing, in which Figure 1 illustrates a 2-stage batch countercurrent system and Figure 2 a single stage continuous countercurrent system suitable for carrying out my process.

Referring to Figure 1, oil to be dewaxed is supplied from tank 1 and cerophile is supplied from tank 2 by means of proportioning pumps 3 and 4, respectively, and the mixture is passed through pipes 5 and 6 to circulating pump 7. Simultaneously, the solvent containing oil dissolved therein is delivered through pipe 36 and pipe 6 to pump 7. The mixture of waxy oil, solvent, and cerophile is forced by pump 7 through the cooler 8 wherein the mixture is brought to the dewaxing temperature, for example, 0° F. and the wax is caused to solidify as fine crystals. The cooled mixture is then delivered by pipe 9 to mixer 10 provided with stirring means 11, and the components of the mixture are vigorously agitated to insure thorough contacting thereof. The mixture is then passed by means of pipe 12 into settling vessel 13 provided in its upper section with stirring means 14. Settling and stratification of the mixture results in the formation of two immiscible phases or layers, the upper and lighter phase comprising the cerophile with substantially all of the finely divided solidified wax suspended therein, and the lower and heavier phase comprising the solvent and oil substantially free of solidified wax. It will be understood, of course, that while the phases are substantially immiscible, a small amount of solvent and oil will be dissolved or entrained in the lighter phase, and a small amount of cerophile from the lighter phase will be dissolved or entrained in the heavier phase. The heavier phase comprising essentially solvent and oil is withdrawn from the bottom of settling vessel 13 and passed through pipe 15 into fractionating tower 16 provided with heating means such as steam coil 17. In tower 16 the solvent is vaporized and stripped from the oil, and the dewaxed oil substantially free of solvent is withdrawn from the bottom of the tower through pipe 18 and passed to storage not shown. The solvent which has been vaporized from the oil is removed from the top of the tower, condensed by condenser 19 and collected in receiver 20, from whence it is delivered by pump 21 and pipe 22 into pipe 23 for further use, as will be described in detail hereinafter.

Referring again to settling vessel 13, the lighter phase comprising the cerophile and solid wax dispersed therein is withdrawn through pipe 24 and delivered by pipe 23 to circulating pump 25 together with recovered solvent from pipe 22, fresh solvent being supplied from tank 26 by proportioning pump 27 and pipe 28 as needed. Since there is a tendency for the solidified wax particles to settle in the cerophile it may be necessary to apply slow agitation to the lighter phase in settling vessel 13 by means of stirring means 14, thus providing a uniform dispersion of wax in the cerophile for withdrawal through pipe 24. Pump 25 forces the mixture of solvent, cerophile and wax containing minor amounts of oil through cooler 29 wherein the temperature is again adjusted if necessary, for example, to 0° F., and the cooled mixture is passed through pipe 30 into mixing vessel 31 provided with stirring means 32. Herein the mixture is thoroughly agitated to effect intimate contact between the relatively immiscible solvent, cerophile, and wax. The mixture is then delivered by pipe 33 to settling vessel 34 provided with stirring means 35, and is permitted to settle and stratify, whereby there are formed two immiscible liquid phases or layers,

the upper and lighter phase comprising the cerophile and solidified wax particles relatively free of oil, and the lower and heavier phase comprising the solvent containing the residual oil but substantially no solid wax. The heavier phase is drawn from the bottom of vessel 34 and passed by means of pipe 36 into pipe 6 for further use in the treatment of the original oil-wax mixture in mixer 10 and settler 13. To prevent settling of the wax particles in the cerophile, the upper phase or layer may be slowly agitated by the stirring means 35, and the cerophile and suspended wax is withdrawn from the vessel 34 by means of pipe 37 and delivered to an auxiliary settling vessel 38, in which the wax particles, by virtue of their higher specific gravity, settle through the cerophile and accumulate as a wax slurry in the lower section of the settler 38. From the upper section of this settler, cerophile substantially free of wax particles is withdrawn and passed by pump 39 and pipe 40 into pipe 6 for recycling to the initial oil-wax mixture to be treated in mixer 10 and settler 13. The slurry comprising wax particles and cerophile is withdrawn from the bottom of settler 38 and passed by pipe 41 into the fractionating tower 42 provided with heating means such as steam coil 43. In this tower the cerophile is distilled or stripped from the wax, the wax being withdrawn from the tower by means of pipe 44 and passed to storage not shown. The vaporized cerophile is passed from the top of tower 42, condensed in condenser 45 and delivered from receiver 46 by pump 47 through pipe 48 to pipe 6 for reuse in the treatment of additional quantities of the initial oil-wax mixture. The auxiliary separator 38 affords a simple means for separating the bulk of the cerophile from the wax, and simultaneously reduces both the load upon the fractionating tower 42 and the content of oil which would normally appear in the wax had the entire stream from pipe 37 been charged directly to tower 42. In the event that it is desired to fractionally distill the entire stream from pipe 37, proper manipulation of the valves in pipes 37, 41, and 49 will permit the entire stream to enter the tower 42 via pipe 49.

While the above batch countercurrent operation has been described with reference to only two stages, it is obvious that the number of stages may be increased by inserting between the first and last stages, the desired number of additional coolers, mixers, and settlers to give a total of 3, 4, 5, or 6, or more stages. In any case, regardless of the number of stages, the operation is carried out in a continuous manner, employing the well-known countercurrent contacting principles.

The process of the present invention may also be carried out in a single stage continuous countercurrent system such as that illustrated in Figure 2 of the drawing.

Referring to Figure 2, oil to be dewaxed is supplied from tank 50 and cerophile is supplied from tank 51 by means of proportioning pumps 52 and 53, respectively, and the mixture is passed through pipe 54 to circulating pump 55, which forces it through cooler 56, wherein the mixture is brought to the dewaxing temperature, for example, —10° F., and the wax is caused to solidify as fine crystals. The cooled mixture is then delivered by pipe 57 to the spray head 58 disposed in the lower section of contacting tower 59, and is thence sprayed into the body of cooled solvent contained in the tower. The tower may be provided with packing, if desired. Such solvent is supplied from solvent tank 60 by means of proportioning pump 61, cooled to the dewaxing temperature, for example, of —10° F., in cooler 62, and passed by circulating pump 63 and pipe 64 into tower 59 at a point somewhat below the top of the tower. The finely divided mixture of wax, oil, and cerophile from the spray head 58, being of lower specific gravity than the solvent, rises through the solvent contained in the tower, and during the intimate countercurrent contact with the solvent, the oil is dissolved from the wax and the cerophile, with the result that there accumulates above the solvent phase in the tower, a second immiscible phase comprising cerophile containing a suspension of finely divided solid wax particles substantially free of oil, or containing a controlled amount of oil. This lighter phase containing the cerophile and solid wax with traces of dissolved or entrained oil is withdrawn from the top of tower 59 by means of pipe 65 and delivered to an auxiliary settling vessel 66, in which the wax particles, by virtue of their higher specific gravity, settle through the cerophile and accumulate as a wax slurry in the lower section of the settler. From the upper section of this settler, cerophile substantially free of solid wax particles is withdrawn and passed by pump 67 into pipe 54 for recycling to the initial oil-wax mixture to be treated in contacting tower 59. The slurry comprising wax particles and cerophile is withdrawn from the bottom of settler 66 and passed by pipe 68 into the fractionating tower 69 provided with heating means such as steam coil 70. In this tower the cerophile is distilled or stripped from the wax, the wax being withdrawn from the tower by means of pipe 71 and passed to storage not shown. The vaporized cerophile is passed from the top of tower 69, condensed in condenser 72 and delivered from receiver 73 by pump 74 to pipe 54 for reuse in the treatment of additional quantities of the initial oil-wax mixture. In the event that it is desired to fractionally distill the entire light phase comprising cerophile and wax withdrawn from the top of contacting tower 59, proper manipulation of the valves in pipes 65, 68, and 75 will permit the entire stream to enter fractionating tower 69 via pipe 75.

Referring again to contacting tower 59, the heavier phase comprising solvent and oil substantially free of solid wax, is withdrawn from the bottom of such tower and introduced by pipe 76 into fractionating tower 77 provided with heating means such as steam coil 78. In this tower the solvent is fractionally distilled from the oil, the oil being withdrawn from the bottom of the tower through pipe 79 and passed to storage not shown. The vaporized solvent is passed from the top of the tower, condensed in condenser 80, and delivered from receiver 81 by pipe 82 to pump 61 for reuse in the treatment of additional quantities of the initial oil-wax mixture.

The dewaxing systems described with reference to Figures 1 and 2 are designed for operation with solvents and cerophiles, both of which have boiling points lower than those of the oil and wax. In the event that the solvent or the cerophile or both, are higher boiling than the oil and the wax, the fractionating equipment and recirculation system must be suitably modified to take overhead the wax and the oil, and to leave as distillation residues, the solvent and the cerophile. When the solvent is lower boiling and the cerophile is higher boiling than the oil and wax, the solvent is taken overhead, and the cerophile is taken as a residue. Such modifications are ob-

viously within the skill of those familiar with the art, and require no further elaboration.

The following examples are illustrative of the results which may be obtained in the practice of the present invention, but are not to be construed as limiting the scope thereof.

1. The hydrocarbon oil stock to be dewaxed was a distillate from a wax-bearing crude, such distillate having the following properties and containing approximately 10% of crystallizable paraffin hydrocarbons.

Pour point	°F.	30
S. U. vis., 100° F.	seconds	42
A. P. I. gravity	degrees	35.4
Boiling range (10 mm. pressure)	°F.	138–448

The cerophile employed was prepared from a dewaxed, solvent extracted vacuum still overhead from a crude residuum, such overhead fraction having the following properties:

Pour point	°F.	5
S. U. vis., 100° F.	seconds	815
A. P. I. gravity	degrees	27.9

This overhead fraction was mixed with an equal volume of ethylene dichloride and the mixture was cooled to +5° F., at which temperature two liquid phases were formed and permitted to stratify into layers. The lower layer comprising a major portion of the ethylene dichloride and the more naphthenic constituents of the oil dissolved therein was separated from the upper layer comprising that portion of the oil insoluble in the ethylene dichloride and containing an equilibrium amount of ethylene dichloride dissolved therein. This upper layer constituted the cerophile.

In carrying out the present invention, 120 volumes of hydrocarbon oil stock first described was admixed with 120 volumes of the cerophile and 480 volumes of solvent consisting of ethylene dichloride, the temperature being about 75° F. This mixture was then cooled, with agitation, to 0° F., during which step a portion of the crystallizable paraffinic constituents of the oil stock crystallized in the form of small, solid particles and two liquid phases formed. Agitation was stopped, and the mixture was permitted to settle. Two immiscible layers were formed, the upper layer comprising the cerophile containing a suspension of solid crystals, and the lower layer comprising the solvent, i. e., ethylene dichloride, containing the oil dissolved therein. The layers were separated from one another, and the ethylene dichloride was removed by vaporization. There was obtained from the lower layer 54% of the non-crystallizable constituents of the original oil stock, while the crystallizable constituents were concentrated in the remaining 46% of the oil stock contained in the cerophile. By employing multi-stage batch or continuous countercurrent operation, in lieu of the single stage batch separation above described, the quantity of oil associated with the crystallizable constituents contained in the cerophile could be markedly reduced, and if desired, such crystallizable constituents could be obtained substantially oil-free. The crystallizable constituents may be separated from the cerophile by distillation, preferably at reduced pressure.

2. In this example, the oil stock to be dewaxed comprised a solvent extracted wax-bearing paraffinic oil containing approximately 12% of wax, and having a pour point of +80° F., a Saybolt Universal viscosity of 44 seconds at 210° F., and an A. P. I. gravity of 31.3°. The oil solvent comprised a mixture of 47% by volume of o-nitrotoluene, 38.5% by volume of nitrobenzene, and 14.5% by volume of toluene. The cerophile comprised commercial liquid propane having the mole percent composition of 82.3% propane, 13.5% propene, 3.2% ethane, 0.6% isobutane, and 0.3% n-butane.

182 volumes of the oil stock, 636 volumes of the oil solvent, and 182 volumes of the cerophile were thoroughly mixed at −20° F. for 30 minutes, under sufficient pressure to maintain the mixture in the liquid phase. At this temperature the wax crystallized in the form of solid particles. The agitation was then stopped, and the mixture was permitted to settle and stratify into two liquid layers. The upper layer comprising the cerophile containing a suspension of crystallized wax and a small amount of solvent and oil in solution was separated from the lower layer comprising the oil solvent containing the major portion of the oil in solution and a minor amount of cerophile, but no crystallized wax. The cerophile layer then thoroughly mixed with 550 volumes of fresh oil solvent comprising 51% by volume of o-nitrotoluene, 41.6% by volume of nitrobenzene, and 7.4% by volume of toluene, the temperature being held at −20° F. under pressure sufficient to maintain the mixture in the liquid phase. The mixture was permitted to settle and stratify into two liquid layers, the upper layer comprising the cerophile and crystallized wax, and the lower layer comprising the oil solvent containing a small amount of dissolved oil but no solid wax, and the layers were separated. The lower layers from the two treatments above described were combined and subjected to distillation at reduced pressure to remove the oil solvent and traces of cerophile. The distillation residue comprising a dewaxed oil having a pour point of −5° F., a Saybolt Universal viscosity of 46 seconds at 210° F., and an A. P. I. gravity of 28.1°. The cerophile layer from the second treatment, after removal of the cerophile by vaporization, comprised a hydrocarbon wax of low oil content.

3. The oil stock to be dewaxed was the same as that employed in Example 1, the solvent was ethylene dichloride, and the cerophile was a dewaxed, solvent extracted vacuum still overhead from a crude residuum, such overhead having an A. P. I. gravity of 27.9° and a Saybold Universal viscosity of 815 seconds at 100° F.

Equal volumes of the oil stock and the cerophile were mixed, and the mixture was treated with the solvent in a 3-stage batch countercurrent system similar to that illustrated in Figure 1 of the drawing, the cerophile-oil stock mixture being charged at the rate of 1 volume to every 4 volumes of solvent used, the temperature of separation of the crystallizable constituents of the oil stock being maintained at 0, F. After the system had reached equilibrium, the solvent phase was found to contain 95% of the oil constituents of the stock, whereas the crystallizable constituents or "wax" was concentrated in the remaining 5% contained in the cerophile. The "wax" recovered from the cerophile by distillation had a melting point of 61° F.

Other combinations of solvents and cerophiles which may be suitably employed in accordance with this invention are exemplified by the following, it being understood that the ratio of the components of the solvent, as well as the ratio of solvent to cerophile may be varied considerably from the values given below. The parts of

solvent and cerophile are given per 100 parts of oil stock.

Solvent	Parts	Cerophile	Parts
nitrocumene	200	liquid propane	300
anisole	100	do	300
o-nitrotoluene	100		
α-picoline	90	do	300
quinoline	110		
toluene	60	liquid ethane	150
nitrobenzene	106		
o-nitrotoluene	127		
toluene	30	do	150
quinoline	210		
toluene	200	liquid propane	250
aniline	350		
toluene	60	do	150
β,β' dichlordiethyl ether	200		

The process of the present invention is applicable not only to the separation of crystallizable hydrocarbons usually referred to as "wax" and having melting points above 110° F., but is likewise adapted for the separation of crystallizable hydrocarbons having melting points lower than those usually associated with wax. For example, in accordance with the present invention, it is possible to separate from hydrocarbon oils, crystallizable hydrocarbons having melting points below 100° F., i. e., the so-called "liquid waxes." Furthermore, by operating at very low temperatures, for example, —50° F. to —150° F. it is possible to separate from a "dewaxed" oil, certain fractions which at ordinary temperatures appear as viscous liquid hydrocarbons. The present invention is also adapted to the separation or purification of various materials other than hydrocarbon wax. For example, animal and vegetable fats and waxes may be refined by my process, as may be rosin, stearic acid, crystallizable coal tar derivatives such as naphthalene, anthracene, and carbazole, and many other substances comprising mixtures of crystallizable and non-crystallizable compounds.

Hydrocarbon oils which may be subjected to treatment in accordance with the present invention include paraffinic oils, paraffin distillate, intermediate distillate, residuums, oils from the destructive hydrogenation of carbonaceous materials, cracked tars, polymers, and the like. The wax-bearing oils which also contain asphaltic material may be subjected to a premilinary treatment for the removal of asphalt, for example, by precipitation with liquefied normally gaseous hydrocarbons, or by treatment with chemical agents such as sulfuric acid, aluminum chloride, or other refining agents.

Furthermore, the waxy oils may be dewaxed by my method and the dewaxed oil then separated into liquid fractions respectively more paraffinic and more naphthenic than the original oil. This may be accomplished in a relatively simple manner by modifying the solvent power of the solvent in the oil-solvent phase resulting from my dewaxing operation. For example, a wax-bearing oil is dewaxed by treatment with a cerophile such as liquid propane and a solvent which has a high solvent power for oil but not for wax, e. g., a mixture of nitrobenzene, o-nitrotoluene, and toluene. The cerophile-wax phase is separated from the oil-solvent phase, and the toluene is removed from the later phase by distillation. Upon removal of the toluene, the remainder of the solvent, i. e., nitrobenzene and o-nitrotoluene becomes selective as to the liquid constituents of the dewaxed oil, and as a result of this selectivity, a separation of the oil-solvent mixture into two immiscible liquid phases or layers is effected. One phase comprises the major portion of the more paraffinic oil constituents in which is dissolved a minor portion of the solvent, and the other phase comprises the major portion of the solvent in which is dissolved the more naphthenic oil constituents. Upon separation of the phases and removal of the solvent from each, there is obtained a liquid paraffinic oil fraction and a liquid naphthenic oil fraction.

It is, of course, possible to reverse the order of these operations, namely, to effect the selective solvent separation of the oil into paraffinic and naphthenic oil fractions, and then dewax the paraffinic oil fraction by the method of the present invention. For example, the wax-bearing oil stock may be treated first with nitrobenzene or a mixture of nitrobenzene and o-nitrotoluene, or any other conventional selective solvent, whereby there is obtained a phase comprising wax, paraffinic oil constituents, and a minor amount of solvent. and a second phase comprising the major portion of the solvent and the naphthenic oil constituents. After separation of the phases, the wax-containing phase is admixed with a cerophile such as liquid propane and the mixture is treated with an oil solvent such as a mixture of nitrobenzene, o-nitrotoluene, and toluene, whereby two immiscible liquid phases are formed, one comprising the cerophile and the wax, and the other comprising the solvent containing the dissolved paraffinic oil. The phases, after separation and removal of cerophile and solvent, yield wax and dewaxed paraffinic oil, respectively. If desired, the initial selective solvent extraction of the waxy oil stock may be carried out in the presence of liquid propane or other low boiling, relatively paraffinic hydrocarbons.

The oils or waxes separated in accordance with this invention may be subjected to subsequent refining operations, such as sulfuric acid treatment, aluminum chloride treatment, or treatment with adsorbents such as fuller's earth, bauxite, or the like. In the dewaxing of crude residuums in accordance with the present invention, it has been found that any inorganic salts which may be present are removed together with the wax. It appears that the salt particles, particularly sodium chloride associated with crude residuums from certain sources, are coated or enveloped with a wax film, and that such salt particles, therefore, act as wax, and are incidentally removed during the dewaxing operation.

From the description of my process and the various modifications thereof given herein, it will be evident that the successful operation thereof depends upon the use of a polar oil solvent and a non-polar cerophile, the oil solvent being of such composition as to be relatively immiscible with the wax and the cerophile at the dewaxing temperature, and the cerophile being relatively immiscible with the solvent, the oil, and the wax at such temperature, the cerophile being further characterized in its ability to preferentially wet the wax in the presence of the oil and solvent and to transfer the wax from the oil and solvent, and thus make possible the separation of two immiscible liquid phases, one comprising the serophile and suspended solid wax, and the other comprising the solvent and the oil substantially free of solid wax. Thus the process of the present invention differs from the conventional solvent dewaxing processes in which the oil and solvent forms one liquid phase from which the solid wax is filtered, and likewise differs from the conventional selective solvent extraction

processes in which the oil is separated into two liquid fractions, one being relatively more naphthenic and the other relatively more paraffinic than the original oil, any wax content of the original oil being concentrated in the more paraffinic liquid oil fraction which must subsequently be dewaxed by the present process or by the conventional dewaxing methods known to the art.

Herein, the particular solvent or solvent combination has generally been referred to as being polar, i. e., having a dipole moment greater than 1×10^{-18} e. s. u., while the cerophile or cerophile combinations have generally been referred to as being non-polar, i. e., having a dipole moment less than 1×10^{-18} e. s. u. It is to be understood, however, that such definition is arbitrary, and that the oil solvents are relatively polar with respect to the cerophiles. For example, nitrobenzene has a dipole moment of 3.9, o-nitrotoluene 3.7, furfural 3.57, pyridine 2.1, and ethylene dichloride 1.8, such compounds representing the oil solvents or components of the oil solvents. The cerophiles are generally less polar than the oil solvents, and compared with the oil solvents, have lower dipole moments, for example, the liquefied normally gaseous hydrocarbons and the liquid paraffinic hydrocarbons have dipole moments of 0.

I claim:

1. The method of dewaxing an oil-wax mixture which comprises commingling the oil-wax mixture with a solvent and a cerophile at a temperature at which the wax is solidified, said solvent comprising a mixture of toluene, nitrobenzene, and o-nitrotoluene, and said cerophile comprising a liquid paraffinic hydrocarbon, forming

two immiscible liquid phases of different specific gravities of which the lighter one comprises the cerophile and the solidified wax suspended therein, and the heavier one comprises the solvent and oil substantially free of solidified wax, separating the lighter phase from the heavier phase, and removing the wax from the lighter phase and the solvent from the heavier phase.

2. The method of dewaxing an oil-wax mixture which comprises commingling the oil-wax mixture with a solvent and a cerophile at a temperature at which the wax is solidified, said solvent comprising a mixture of toluene, nitrobenzene, and o-nitrotoluene, and said cerophile comprising a liquid paraffinic hydrocarbon, forming two immiscible liquid phases of different specific gravities of which the lighter one comprises the cerophile and the solidified wax suspended therein, and the heavier one comprises the solvent and oil substantially free of solidified wax, and separating the lighter phase from the heavier phase.

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