

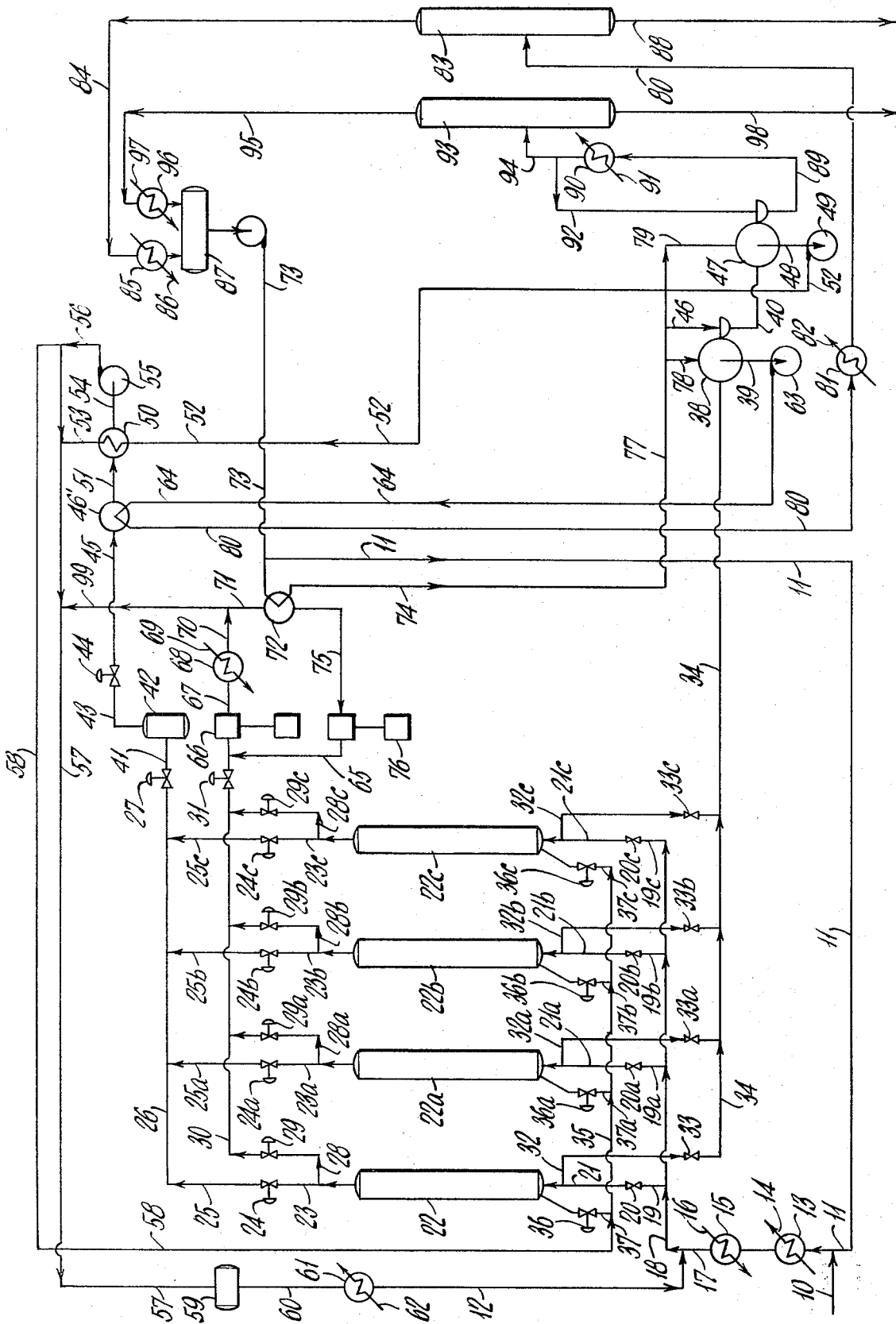
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## DEWAXING OF OILS

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### ABSTRACT OF THE DISCLOSURE

A process for dewaxing a petroleum oil stock with a liquid solvent and a normally gaseous liquid auto-refrigerant. The evaporated autorefrigerant is condensed by cooling prior to reuse by heat exchange with the dewaxed oil filtrate. Optionally, the dewaxed filter cake can be deoiled.

### FIELD OF THE INVENTION

This invention relates to oils such as lubricating oils. More particularly it relates to the dewaxing of oils including petroleum lubricating oils.

### BACKGROUND OF THE INVENTION

As is well known to those skilled in the art, many oils contain paraffin or waxy component which must be removed during processing. In the manufacture of lubricating oils for example from crude petroleum hydrocarbons, fractions containing the lubricating oil constituents are separated by distillation, usually by vacuum distillation. The raw lubricating oil distillate contains waxy constituents which cause the oil to have a high cloud point and high pour test. A common method of separating wax and waxy materials from hydrocarbon oil is by the solvent dewaxing process in which the waxy material is crystallized from a solvent-diluted mixture at a reduced temperature. The solvent dilutes the supernatant liquid and reduces its viscosity so that more complete and rapid separation of the supernatant liquid from crystallized wax may be effected. Solvents commonly used in solvent dewaxing include ketones, for example, acetone, methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, and their mixtures. The ketone solvent is modified by the addition of an aromatic hydrocarbon, for example, benzene or toluene.

### DESCRIPTION OF THE PRIOR ART

The prior art teaches that oils, typically petroleum lubricating oils, may be dewaxed either in heat exchangers wherein the mixture is indirectly cooled by refrigerant, or in vessels wherein cooling is effected by direct contact of the oil-solvent mixture with evaporating refrigerant-cooling being carried out by flashing of the liquid refrigerant. Typical of the prior art patents relating to this are U.S. Pats. 2,067,128; 2,164,773; U.S. Pat. 3,594,513; and U.S. Pat. 3,554,896.

As is well known to those skilled in the art, dewaxing (whether carried out by direct or indirect cooling) is characterized by use of steps carried out at very low temperature and by other steps conducted at elevated temperature. The refrigeration load needed to cool the system—even when using volatilizing refrigerant may be substantial; and the heat input required to heat up the various streams for distillation may also be substantial.

It is an object of this invention to provide a novel process particularly characterized by processing efficiencies which permits utilization of heat exchangeable streams. Other objects will be apparent to those skilled in the art.

### STATEMENT OF THE INVENTION

In accordance with certain of its aspects, the novel

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process of this invention for separating wax from a wax-bearing oil may comprise:

- (a) mixing said wax-bearing oil with a dewaxing solvent and a liquid refrigerant at an initial pressure at least sufficient to maintain said refrigerant in liquid phase;
- (b) reducing the pressure on the resulting oil-solvent-refrigerant mixture in a chilling operation, effecting evaporation of said refrigerant and concomitant cooling of said mixture to a temperature at which wax crystallizes forming a first slurry of wax in remaining oil-solvent mixture and a volatilized high pressure refrigerant vapor;
- (c) filtering said first slurry thereby forming (i) a first filter cake of slack wax containing wax crystals and occluded oil-solvent mixture and (ii) a first filtrate containing dewaxed oil and solvent;
- (d) cooling said volatilized high pressure refrigerant vapor in indirect heat exchange against said first filtrate thereby forming a cooled high pressure refrigerant;
- (e) condensing said cooled high pressure refrigerant thereby forming a liquid high pressure refrigerant;
- (f) passing said liquid high pressure refrigerant to said mixing step;
- (g) separating dewaxed oil from said first filter cake; and
- (h) separating deoiled wax from said first filter cake.

### DESCRIPTION OF THE INVENTION

The charge wax-bearing oils which may be treated in practice of this invention may include vegetable oils, typified by soy bean oils; or animal oils, typified by by-product oils recovered e.g. from various meat-processing operations; or mineral oils, typified by petroleum lubricating oil fractions.

The charge wax-bearing oil may typically contain wax in amount of 5%–25%. In the case of vegetable oils, the waxy component may contain saturated acids, whereas the oily component may include unsaturated acids. In the case of animal oils, the waxy component may include triglycerides whereas the oily component may include mono- and di-glycerides. In the case of petroleum oils, the waxy component may include high molecular weight paraffins while the oily component may include lower molecular weight hydrocarbons, unsaturates, aromatics, etc.

The preferred charge oil may be a petroleum oil, typically a refined vacuum distillate suitable for use in the manufacture of base oil for e.g. a SAE 20 motor oil. The wax-bearing charge oil may typically be characterized by the following properties:

TABLE

Property	Broad	Preferred	Typical
API gravity.....	28-34	30-31	30.6
Pour point, ° C.....	35-50	40-45	41
Wax content, wt. percent .....	5-30	8-12	10.2
Cloud point, ° C.....	45-60	50-55	50
Viscosity, cs. at 37.8° C.....	70-90	75-80	78

In practice of the process of this invention, 1 part of charge wax-bearing oil may be mixed with 1–7 parts, preferably 2–4 parts, say 3 parts of dewaxing solvent and 0–8 parts, preferably 2–4 parts, say 3 parts of liquid refrigerant. Additional liquid refrigerant may preferably be added during the chilling operation *infra* to permit attainment of the desired final temperature of the solvent mixture. Preferably about 75% of the refrigerant may be

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added with the charge; and 25% may be added to the chilling vessel after chilling has been initiated.

The dewaxing solvent may be methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, and mixtures thereof. The ketone solvent is preferably modified with an aromatic solvent such as benzene or toluene. The preferred solvent is a mixture of equal parts of methyl ethyl ketone and toluene.

The refrigerant may be a hydrocarbon such as ethane, ethylene, propane, butene, etc.; a Freon such as dichlorodifluoro methane; ammonia; etc. The preferred refrigerant may be a hydrocarbon, most preferably propane.

This charge mixture at temperature of 10° C.-80° C., preferably 25° C.-35° C., say 30° C. and 15-250 p.s.i.a., preferably 230-250 p.s.i.a., say 240 p.s.i.a. (which initial pressure is at least sufficient to maintain the refrigerant in liquid phase) may be heated to 25° C.-100° C., preferably 45° C.-55° C., say 50° C. thereby achieving complete solution of the charge oil, solvent, and refrigerant. The charge mixture in total amount of 2-16 parts, preferably 5-9 parts, say 7 parts may then be cooled to 20° C.-95° C., preferably 40° C.-50° C., say 45° C. at 65-250 p.s.i.a., preferably 230-250 p.s.i.a., say 240 p.s.i.a.—at which conditions the charge mixture is above the temperature at which wax precipitation begins.

The so-cooled oil-solvent-refrigerant mixture may be passed to an evaporative cooling operation, typically carried out in a vertically extending chiller vessel. The mixture may be subjected in a first chilling step to decreasing pressure over 3-100 minutes, preferably 25-75 minutes, say 55 minutes. The cooling rate may be controlled by adjusting a high pressure control valve on the outlet of the chiller vessel. During cooling, additional refrigerant (typically 25% of the total refrigerant) may be admitted directly to the chilling vessel wherein it produces further cooling as it volatilizes. As the pressure is reduced on the resulting oil-solvent-refrigerant mixture, evaporation of the refrigerant is effected with concomitant cooling of the mixture to a temperature at which wax crystallizes forming a first slurry of wax in remaining oil-solvent mixture and a volatilized high pressure refrigerant vapor.

Throttling control may permit maintenance of the cooling rate at 0.25-8.5° C./min., preferably 0.4-0.7° C./min., say 0.55° C./min. During the chilling period of 3-100 minutes, preferably 25-75 minutes, say 55 minutes, the temperature may drop to minus 5° C.-16° C., preferably 14° C.-16° C., say 15° C. as the pressure drops to 50-115 p.s.i.a., preferably 95-115 p.s.i.a., say 105 p.s.i.a. 50%-80%, preferably 66%-70% say 65% of the liquid refrigerant may vaporize or volatilize as a stream of high pressure refrigerant vapor in amount of 1.5-2.4 parts, preferably 1.8-2.1 parts, say 2 parts. Upon completion of this first chilling step, the high pressure control valve may be closed.

When the pressure in the chiller has dropped to the level noted supra, it is preferred to close the high pressure control valve and to direct the volatilizing liquid refrigerant into a low pressure receiving system. The oil-solvent refrigerant mixture may, during this second chilling step, be cooled further by passage through a low pressure control valve. Control of the low pressure control valve may permit a decreasing pressure over 3-100 minutes, preferably 40-75 minutes, say 60 minutes during which time, the pressure may drop to 15-55 p.s.i.a., preferably 30-40 p.s.i.a., say 35 p.s.i.a. The mixture may be cooled at a rate of 0.25-8.5° C./min., preferably 0.4-0.7° C./min., say 0.55° C./min. to a temperature of minus 40° C.-minus 7° C., preferably minus 20° C.-minus 15° C., say minus 18° C.

During the second chilling step, 45%-75%, preferably 55%-65%, say 50% of the liquid refrigerant (based upon the refrigerant initially charged to the first chilling step) may be volatilized as chilling is effected; and 1-4

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parts, preferably 1.4-3 parts, say 2 parts of volatilized low pressure refrigerant vapor may be withdrawn from the chiller.

During the preferably two-step chilling operation, the oil-solvent mixture is cooled to a point at which wax crystallizes and precipitates from the mixture to form a first slurry of wax in remaining oil-solvent mixture. The composition of the first slurry may be as follows:

TABLE

Component	Parts		
	Broad	Typical	Preferred
Wax.....	0.05-0.25	0.10-0.15	0.12
Oil.....	0.95-0.75	0.90-0.85	0.88
Solvent.....	1.00-7.00	2.00-4.00	3.00
Total.....	2.00-8.00	3.00-5.00	4.00

This first slurry may be withdrawn from the chilling operation upon completion of chilling and crystallizing (the low pressure control valve having been closed) and passed to a primary or first filtration operation. In the first filtration operation, wax may be separated as slack wax from the oil-solvent mixture. Typically 0.15-0.50 parts, preferably 0.20-0.30 parts say 0.25 parts of slack wax may be recovered containing 0.03-0.38 parts, preferably 0.08-0.18 parts, say 0.13 parts of occluded oil. First filtrate may be recovered at minus 40° C.-minus 7° C., preferably minus 20° C.-minus 15° C., say minus 18° C. at 15-50 p.s.i.a., preferably 15-20 p.s.i.a., say 15 p.s.i.a. (as withdrawn from the filter) in total amount of 2.0-6.0 parts, preferably 4.0-4.5 parts, say 4.25 parts. First filtrate may contain 0.50-0.85 parts, preferably 0.70-0.80 parts, say 0.75 parts of oil, 0.5-6.5 parts, preferably 3.0-5.0 parts, say 3.5 parts of solvents (including 1-2, preferably 1.25-1.75 parts, say 1.5 parts of wash solvent), and less than 0.05 parts, preferably 0.01-0.03 parts, say 0.01 parts of wax.

It is a feature of this invention that the volatilized high pressure refrigerant vapor may be cooled in indirect heat exchange against the first (or primary) filtrate thereby forming a cooled and at least partially condensed high pressure refrigerant. In typical practice of this aspect of the process of this invention, 1.5-2.4 parts, preferably 1.8-2.1 parts, say 2 parts of volatilized high pressure refrigerant vapor at 10° C.-50° C., preferably 20° C.-40° C., say 30° C. and 65-250 p.s.i.a. preferably 230-250 p.s.i.a., say 240 p.s.i.a. may be cooled to minus 5° C.-16° C., preferably 14° C.-16° C., say 15° C. In typical operation, a portion, preferably 5%-85%, more preferably 70%-80%, say 75% of of this refrigerant stream may be condensed against primary filtrate.

The slack wax recovered in the primary filtration operation may be mixed with 0.2-2.0 parts, preferably 0.50-1.50 parts, say 1.0 parts of dewaxing solvent at minus 40° C.-minus 7° C., preferably minus 20° C.-minus 15° C., say minus 18° C. to form a slurry of repulped wax which may be passed to a second (or secondary) filtration operation. Here it may be filtered at minus 37° C.-minus 4° C., preferably minus 18° C.-minus 12° C., say minus 15° C. to yield a second filter cake containing deoiled wax in amount of 0.15-0.20 parts, preferably 0.15-0.18 parts, say 0.18 parts. The secondary filtrate at minus 37° C.-minus 4° C., preferably minus 18° C.-minus 12° C., say minus 15° C. may be withdrawn in amount of 0.5-1.5 parts, preferably 0.75-1.25 parts, say 1.0 parts (including 0.3-0.7 parts, preferably 0.4-0.6 parts, say 0.5 parts of wash solvent).

It is a feature of the process of this invention according to certain of its aspects, that secondary filtrate may be heat exchanged in indirect heat exchange against the cooled partially condensed high pressure refrigerant (or alternatively against that portion of the high pressure re-

frigerant which is still in vapor phase. Typically the cooled partially condensed high pressure refrigerant in amount of 1.5–2.4 parts, preferably 1.8–2.1 parts, say 2 parts (of which 60%–80%, preferably 70%–80%, say 75% is in liquid phase) at minus 5° C.–16° C., preferably 14° C.–16° C., say 15° C. and 65–250 p.s.i.a., preferably 230–250 p.s.i.a., say 240 p.s.i.a., may be further condensed so that essentially 100% of the refrigerant may be condensed (ie. including that percentage condensed against primary filtrate). Preferably this condensate may be at its bubbling point—with a minimum of sub-cooling.

It is a feature of the process of this invention that the recycled high pressure refrigerant, in amount of 1.5–2.4 parts, preferably 1.8–2.1 parts, say 2 parts at minus 5° C.–16° C., preferably 14° C.–16° C., say 15° C. at 65–250 p.s.i.a., preferably 230–250 p.s.i.a., say 240 p.s.i.a. may be divided; one portion, typically 1 part, may be mixed with the secondary filtrate passing to the refrigerant collection drum and a second portion, typically 1 part, may be recycled to the chiller drums to provide additional cooling, preferably during the second chilling step.

Secondary filtrate in amount of 0.5–1.5 parts, preferably 0.75–1.25 parts, say 1.0 parts, when added to the cooled stream of high pressure refrigerant, forms a mixture containing 0.1–0.5 parts, preferably 0.2–0.4 parts, say 0.29 parts oil; 0.001–0.05 parts, preferably 0.005–0.02 parts, say 0.01 parts wax; 0.5–1.5 parts, preferably 0.6–0.8 parts, say 0.7 parts solvent; and 0.5–1.5 parts, preferably 0.75–1.25 parts say 1 part of refrigerant at minus 15° C. to 20° C., preferably 5° C.–15° C., say 10° C.

It is a feature of the process of this invention, in accordance with certain of its aspects, that volatilized low pressure refrigerant vapor at minus 25° C.–10° C., preferably minus 5° C.–0° C. say minus 1.5° C. and 15–55 p.s.i.a., preferably 30–40 p.s.i.a., say 35 p.s.i.a. may be admixed with 5–15 parts, preferably 8–12 parts, say 10 parts of circulating refrigerant at minus 10° C.–10° C., preferably minus 5° C.–5° C., say 0° C. and 15–55 p.s.i.a., preferably 30–40 p.s.i.a., say 35 p.s.i.a.

The mixed refrigerant streams may be compressed to 15–275 p.s.i.a., preferably 230–260 p.s.i.a., say 250 p.s.i.a. and 20° C.–80° C., preferably 60° C.–70° C., say 65° C., and then cooled if necessary and condensed to 40° C.–70° C., say 45° C.

1–4 parts, preferably 1.4–3 parts, say 2 parts of cooled refrigerant may be added to the compressed high pressure refrigerant stream passing to the refrigerant collection drum. 5–15 parts, preferably 8–12 parts, say 10 parts of a drawn-off side stream of cooled refrigerant may be passed to solvent cooler wherein it may cool solvent. As it passes through the solvent cooler, it may be heated to minus 40° C.–0° C., preferably minus 40° C.–minus 15° C., say minus 35° C. as it volatilizes at 15–30 p.s.i.a., preferably 15–20 p.s.i.a., say 15 p.s.i.a.

The volatilized drawn-off refrigerant may be compressed to 15–55 p.s.i.a., preferably 30–40 p.s.i.a., say 35 p.s.i.a. and minus 10° C.–10° C., preferably minus 5° C.–5° C., say 0° C. and then blended into the stream of volatilized low pressure refrigerant passing from the chiller vessels.

In practice of the process of this invention the first or primary filtrate, after it has been heated to minus 5° C.–45° C., preferably minus 15° C.–20° C., say 17° C. by heat exchange against volatilized high pressure refrigerant, may be further heated typically to 150° C. and passed to a dewaxed oil stripping operation. Stripping of solvent from dewaxed oil may be carried out at 15–20 p.s.i.a., say 18.5 p.s.i.a. in a dewaxed oil stripping column to yield as overhead (at 90° C.–120° C., preferably 100° C.–110° C. say 104° C.), 0.5–6.5 parts, preferably 1.5–3.5 parts, say 3.5 parts of solvent which may be condensed against water and passed to a solvent receiver.

0.55–0.90 parts, preferably 0.7–0.8 parts, say 0.75 parts of stripped dewaxed oil may be reboiled and withdrawn

from the dewaxed oil stripping operation. Typical dewaxed oil may have the following properties:

TABLE

Property	Broad	Preferred	Typical
API gravity.....	28 to 34.....	30 to 31.....	30.4
Pour point, °C.....	–40 to 0.....	–20 to –10.....	–15
Wax content, wt. percent.....	0.005 to 1.0.....	0.01 to 0.03.....	0.01
Cloud point, °C.....	–35 to 5.....	–15 to –5.....	–10
Viscosity, cs. at 37.8° C.....	65 to 85.....	70 to 75.....	75

The secondary filtrate containing 0.25–1.5 parts, preferably 0.5–1.0 parts, say 0.7 parts of solvent and 0.1–0.5 parts, preferably 0.2–0.4 parts, say 0.3 parts of oil at minus 18° C.–minus 12° C., say minus 15° C. may be heat exchanged against the cooled high pressure refrigerant and thereby warmed to minus 10° C.–15° C., preferably 0° C.–10° C., say 5° C.; and it may then be combined with the cooled stream of high pressure refrigerant.

The wax recovered as second filter cake from secondary filtration (in amount of 0.1–2 parts, preferably 1.0–1.5 parts, say 1.25 parts and containing 0.5–2.0 parts, preferably 0.8–1.2 parts, say 1.0 parts of solvent) may be sluiced with 0.5–2.0 parts, preferably 0.75–1.5 parts, say 1.25 parts of hot wax-solvent mixture at 75° C.–175° C., preferably 100° C.–150° C., say 120° C. The sluiced mixture in total amount of 1.0–4.0 parts, preferably 2–3 parts, say 2.5 parts may be heated to 75° C.–175° C., preferably 100° C.–150° C., say 120° C. and 30%–70%, preferably 40%–60%, say 50% of this heated mixture may be used as sluicing liquid.

The net molten filter cake may be heated, typically to about 150° C. and passed to wax stripping operation at 5–50 p.s.i.a., preferably 15–20 p.s.i.a., say 18.5 p.s.i.a. 0.15–0.20 parts, preferably 0.15–0.18 parts, say 0.15 parts of deoiled wax may be withdrawn as stripped bottoms at 190° C.–200° C., say 195° C. Stripped solvent overhead, in amount of 0.5–1.5 parts preferably 0.8–1.2 parts, say 1.0 parts at 90° C.–120° C., preferably 100° C.–110° C., say 104° C. may be withdrawn as overhead, condensed in indirect heat exchange with water, and passed to a solvent receiver.

0.5–50 parts, preferably 1–3 parts, say 2 parts of solvent may be withdrawn from the solvent receiver at 10° C.–60° C., preferably 20° C.–50° C., say 45° C. and mixed with the waxy feed to provide dilution. 1.0–5.0 parts, preferably 2.0–3.0 parts, say 2.5 parts of solvent may be withdrawn from the solvent receiver at 10° C.–60° C., preferably 20° C.–50° C., say 45° C. and passed into indirect heat exchange with the drawn off side stream of cooled refrigerant from the low pressure refrigerant stream. The solvent may be cooled to minus 40° C.–minus 7° C., preferably minus 20° C.–minus 15° C., say minus 18° C.

A first portion for the cooled solvent (1.0–3.0 parts, preferably 1.5–2.0 parts, say 1.5 parts) may be passed to the primary filtration operation as wash solvent, a second portion (0.1–1.0 parts, preferably 0.3–0.7 parts, say 0.5 parts) to the primary filter for repulping the slack wax, and a third portion (0.1–1.0 parts, preferably 0.3–0.7 parts, said 0.5 parts) to the secondary filtration operation as wash liquor.

It will be apparent to those skilled in the art from the above description that substantial operating economies may be obtained by the use of the instant invention. It is particularly significant that the improved refrigeration heat exchange circuit permits reduction of refrigeration capacity by as much as 50% or more in illustrative embodiments. This means that the compressor requirements may be cut in half—and either smaller compressors or a smaller number may be used with attendant decrease in compressor horsepower. This decrease in operating costs and capital costs permits recovery of dewaxed oil with sub-

stantial savings. In common design, the net effect may be to eliminate one substantial compressor and to reduce the total compressor horsepower to less than one half that otherwise required.

The novel process of this invention permits replacement of expensive vapor compressors with liquid pumps; and the savings attendant on this substitution may decrease capital costs to 0.03%–0.1% based upon the costs incurred with vapor compressors.

#### DESCRIPTION OF A PREFERRED EMBODIMENT

Practice of the process of this invention may be apparent to those skilled in the art from inspection of the following description wherein, as elsewhere in this specification, all parts are parts by weight unless otherwise stated.

A preferred embodiment of this invention may be illustrated by reference to the accompanying drawing wherein, as will be apparent to those skilled in the art, major pieces of apparatus are shown; other equipment including pumps, heat exchangers, holding vessels, etc. may be provided as necessary.

In practice of the novel process of this invention according to a specific embodiment, the charge wax-bearing petroleum oil may be a solvent refined vacuum distillate suitable for use in the manufacture of base oil for SAE 20 motor oil. It has an API° gravity of 30.6, a pour point of 41° C., a cloud point of 50° C., a viscosity at 37.8° C. of 78 cs., and contains 10.2% wax.

This wax-bearing petroleum oil, in amount of 1 part at 30° C., is admitted through line 10 and passed to line 11 wherein it is contacted with 2 parts of solvent at 30° C. Dewaxing solvent includes 50% methyl ethyl ketone and 50% toluene. This charge mixture, at 30° C. and 250 p.s.i.a., is passed to heat exchanger 13 (heated by steam in line 14) wherein it is heated to 55° C. and 245 p.s.i.a. at which point, intimate mixing and complete solution is achieved.

Charge mixture is passed to head exchanger 15, cooled by cooling water in line 16. Charge mixture leaves heat exchanger 15 at 43° C. and 235 p.s.i.a. through line 17. There is admitted to line 17 through line 12, 4.1 parts of propane refrigerant and secondary filtrate at 6° C. and 235 p.s.i.a., which pressure is at least sufficient to maintain the propane refrigerant in liquid phase. Mixing the propane refrigerant and oil-solvent solution occurs at the junction of lines 12 and 17 and throughout manifold 18.

The resulting cooled mixture of oil-solvent-refrigerant is then passed to the chilling operation through manifold 18. The chilling operation may include in this embodiment, a group of four chillers arranged in parallel. Each chiller includes chiller feed line 19 (for the first chiller; for the other chillers 19a, 19b, and 19c), chiller inlet valve 20 (for the first chiller; for the other chiller inlet valves 20a, 20b, and 20c), and chiller inlet line 21 (for the first chiller; for the other chillers 21a, 21b, and 21c). The chiller 22 (for the first chiller; for the others 22a, 22b, and 22c) is fitted with volatilized high pressure refrigerant vapor line 23 (for the first chiller; for the other chillers 23a, 23b, and 23c) and a high pressure chiller outlet back pressure control valve 24 (for the first chiller; for the other chillers 24a, 24b, and 24c). The high pressure chiller outlet valve 24 feeds through a high pressure outlet line 25 (for the first chiller; for the other chillers, 25a, 25b, and 25c) in to high pressure manifold 26 bearing high pressure, back pressure valve 27.

Each of the chillers is also fitted with volatilized low pressure refrigerant vapor line 28 (for the first chiller; for the other chillers 28a, 28b, and 28c) including low pressure chiller outlet (back pressure) valve 29 (for the first chiller; for the other chillers 29a, 29b, and 29c) which control passage of volatilized low pressure refrigerant vapor to manifold 30. Manifold 30 includes low pressure back pressure control valve 31.

Each of the chillers bears charge slurry outlet line 32 (for the first chiller; for the other chillers 32a, 32b, and 32c), and slurry outlet valves 33 (for the first chiller; for the others 33a, 33b, and 33c) which permit control of the slurry passing to slurry manifold 34. Manifold 35 bears additional refrigerant valves 36 (for chiller 22; for the others, 36a, 36b, and 36c) which permit passage of refrigerant through line 37 (for chiller 22; for the others 37a, 37b, and 37c) during the chilling.

In practice of the process as hereinafter set forth, it will be apparent that the chillers 22, 22a, 22b, and 22c are operated on a sequential program including (i) filling, (ii) chilling in a first chilling step with evolution of high pressure refrigerant, (iii) chilling in a second chilling step with evolution of low pressure refrigerant, and (iv) emptying. At a given time, each chiller is in one stage or mode of the program; and the inlet and outlet valves (e.g. valves 20, 24, 29, and 33 in the case of chiller 22) are opened or closed to permit passage of materials in accordance with the mode of the program being followed by the particular chiller.

The cooled oil-solvent-refrigerant mixture in line 18 at 43° and 235 p.s.i.a. (containing 1 part of wax-bearing oil charge, 3 parts of propane refrigerant, 1.1 parts of secondary filtrate, and 2 parts of dewaxing solvent) is passed through manifold 18 into chiller feed line 19 through open chiller inlet valve 20 and chiller inlet line 21 into chiller 22. At this time, during the filling stage of the cyclic operation, valves 36, 33, 24, and 29 are closed. It will be apparent to those skilled in the art that chillers 22a, 22b, and 22c (or other chillers which may be employed, the four shown being merely illustrative of the number) may be operating in different modes of the cycle during the time in which chiller 22 is filling. Thus chiller 22a for example may be in the first chilling mode, chiller 22b in the second chilling mode, and chiller 22c may be in the emptying mode. For purpose of convenience, the entire cycle will be described with reference to chiller 22.

When chiller 22 is filled, valve 20 is closed, valve 24 is opened and propane refrigerant is permitted to evaporate until the pressure in the chiller 22 drops from initial pressure of 230 p.s.i.a. to final pressure of 105 p.s.i.a. As this occurs, the temperature in chiller 22 drops to 15° C. and 50% of the wax contained in the charge precipitates and forms a slurry.

The rate of cooling in chiller 22 is preferably maintained at about 0.55° C./min. by controllably opening high pressure, back pressure valve 27. During this first or high pressure chilling step, 2 parts of high pressure propane refrigerant is passed through valve 27.

At the termination of the first chilling operation, the pressure in the chiller is 105 p.s.i.a. and the temperature is 15° C. this state being arrived at after about 55 minutes. 1 part of additional refrigerant is admitted to chiller 22 from manifold 35 through line 37 and valve 36 (which is now opened).

Valve 24 is then closed. Low pressure chiller outlet valve 29 is then opened; and the second chilling operation is initiated under the control of low pressure, back pressure valve 31. The cooling rate is controlled to be 0.55° C./min. and as the pressure drops from 105 p.s.i.a. to 35 p.s.i.a. over 60 minutes, the temperature falls from 15° C. to minus 18° C. During this time, 50% more wax precipitates; and the resultant first slurry contains 0.25 parts of wax and 3.85 parts of liquid.

At the conclusion of the chilling operation, the first slurry is withdrawn from chiller 22 over 30 minutes (at this point valves 20, 24, 29 and 36 are closed and valve 33 is open) through valve 33 and passes through manifold 34 to primary filter 38. Filtration at minus 18° C. and 15 p.s.i.a. yields 4.25 parts of first filtrate withdrawn through line 39 containing 0.75 parts of dewaxed-oil and 3.5 parts of solvent. The first filter cake, withdrawn through line 40 contains slack wax.

In practice of the process of this invention, the 2 parts of volatilized high pressure refrigerant leaving valve 27 at an average temperature of 30° C. and 105 p.s.i.a. are passed through line 41 to collector 42 and thence through line 43 and valve 44 and line 45 first high pressure refrigerant cooler and partial condenser 46' wherein it is heat exchanged against primary filtrate at minus 18° C. and 250 p.s.i.a. During heat exchange, the primary filtrate passed from line 39, pump 63 and line 64, is heated to 17° C. and the refrigerant is cooled to 15° C. at 95 p.s.i.a. and is partially (75%) condensed.

The slack wax (1.35 parts) recovered in primary filtration operation 38 is mixed with 0.5 parts of dewaxing solvent at minus 18° C. admitted through line 46, to form a slurry of repulped wax which passes through line 40 to secondary filter 47. Filtration of the repulped wax yields 1.25 parts of deoiled wax filter cake which contains dewaxing solvent and 1.1 parts of secondary filtrate at minus 15° C. which also contains dewaxing solvent. Second filtrate is passed through line 48 at minus 15° C. through pump 49 to heat exchanger 50 wherein it is heat exchanged against the cooled high pressure refrigerant leaving heat exchanger 46 through line 51.

Secondary filtrate at minus 15° C. in line 52 is heated as it passes through heat exchanger 50; and it leaves through line 53 at 5° C. in liquid phase at 250 p.s.i.a. During its passage through heat exchanger 50, the remaining high pressure refrigerant vapor is condensed to a liquid in line 54 and passed through pump 55 and thence into line 56 and to manifold 57.

1 part of refrigerant liquid in line 56 at 15° C. is pumped through line 58 to line 35 and thence to chiller 22 to which it is introduced prior to the second chilling step. 1 part of liquid in line 56 is passed through manifold 57 and mixed with secondary filtrate at 5° C. from line 53, the mixture being at 12° C.

In an alternative embodiment, it may be desirable to pass the refrigerant in line 51 into direct contact with the stream in line 52 thereby eliminating line 53 and replacing heat exchanger 50 with, e.g. an absorption vessel, the net total liquid being passed through line 54. The combined secondary filtrate and condensed high pressure refrigerant is joined in manifold 57 by recycle low pressure refrigerant liquid in amount of 2 parts at 43° C. and 250 p.s.i.a. from line 99; and the total mixture in amount of 4.1 parts at 16° C. and 250 p.s.i.a. is passed through manifold 57 to recycle refrigerant drum 59; refrigerant in drum 59 is passed through line 60 and heat exchanger 61 wherein it is heated to 43° C. by steam from line 62 and passed through line 12.

The 2 parts of volatilized low pressure refrigerant vapor at minus 1.5° C. and 35 p.s.i.a. withdrawn from chiller 22 through line 28, valve 29 and manifold 30 (and from chillers 22a, 22b, and 22c, through lines 28a, 28b, and 28c, and valves 29a, 29b, and 29c) under the control of valve 31, are combined with refrigerant in amount of 10 parts from line 65 at a point down stream of low pressure valve 31; the mixture is compressed in compressor 66 to 55° C. and 260 p.s.i.a. and passed through line 67 to condenser 68 cooled by cooling water in line 69. Condensed low pressure refrigerant at 43° C. and 250 p.s.i.a. in line 70 may be passed in first portion of 2 parts through line 99 into manifold 57 and in second portion in amount of 10 parts through line 71 to heat exchanger 72.

In heat exchanger 72, the second portion of low pressure refrigerant at 43° C. and 250 p.s.i.a. from line 71 may be volatilized to minus 40° C. and 15 p.s.i.a. as it cools the stream of dewaxing solvent in line 73 to minus 18° C. at 250 p.s.i.a. in line 74. The volatilized refrigerant in line 75 may be compressed in compressor 76 to 0° C. and 35 p.s.i.a. and passed through line 65 to the inlet of compressor 66 at manifold 30. Compressed refrigerant may be passed through line 65 to manifold 30.

2.5 parts of the dewaxing solvent in line 74 are passed to manifold 77; and of this amount, 1.5 parts are passed through line 78 as wash for the filter cake of primary filtration operation 38. 0.5 parts are passed from manifold 77 through line 46 to repulp slack wax and a third part (0.5 parts) is passed through line 79 to be used as wash for the filter cake from secondary filtration operation 47.

The first or primary filtrate which has been passed through line 39, pump 63, and line 64 into heat exchange against volatilized high pressure refrigerant in heat exchanger 46' is then passed in amount of 4.25 parts at 17° C. and 240 p.s.i.a. through line 80 to heat exchanger 81, heated by steam from line 82 and passed to dewaxed-oil stripping operation 83. Overhead at 104° C. and 18.5 p.s.i.a., containing 1.75 parts of toluene and 1.75 parts of methyl ethyl ketone is passed through line 84 to condenser 85 cooled by water in line 86 and passed to dewaxing solvent collection drum 87.

Dewaxed oil bottoms at 205° C. and 220 p.s.i.a. are recovered in line 88 in amount of 0.75 parts. The dewaxed oil is characterized by API gravity of 30.4, pour point of minus 15° C., cloud point of minus 10° C., viscosity at 37.8° C. of 75 cs., and a wax content of 0.01%.

The wax (0.15 parts) recovered from secondary filtration in amount of 1.25 parts is sluiced with 1.25 parts of recycled wax-solvent mixture at 120° C. to form a sluiced mixture at 60° C. containing 0.30 parts of wax and 2.2 parts of solvent in line 89 and is heated to 120° C. at 100 p.s.i.a. in heat exchanger 90 heated by steam in line 91. 1.25 parts of the so-heated mixture are withdrawn and passed through line 92 to the sluicing operation in secondary filtration operation 47. 1.25 parts of the so-heated mixture are passed to wax-stripping operation 93 through line 94.

Overhead at 104° C. and 18.5 p.s.i.a., 1.0 parts of dewaxing solvent mixture is withdrawn through line 95 and condensed in heat exchanger 96 cooled by water in line 97. Condensate is passed to dewaxing solvent collection drum 87. Deoiled wax, in amount of 0.15 parts at 195° C. and 20 p.s.i.a. is withdrawn through line 98.

It will be apparent to those skilled in the art that the novel process of this invention permits attainment of unexpected and unobvious economies in the dewaxing of wax-bearing oils. By use of this novel process, it is possible to decrease operating and capital costs by substantial amount. In the preferred embodiment disclosed herein, the novel process permits decrease in the compression load (for compressing high pressure refrigerant) by about 50%; and specifically in practice this may mean that the number of compressors may be cut in half. In terms of investment costs, this may decrease the cost of the equipment required for dewaxing by 20%.

Although this invention has been illustrated by reference to specific embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made which clearly fall within the scope of this invention.

I claim:

1. The method of separating wax from a wax-bearing oil which comprises:

- (a) mixing said wax-bearing oil with a dewaxing solvent and a liquid refrigerant at an initial pressure at least sufficient to maintain said refrigerant in liquid phase;
- (b) reducing the pressure on the resulting oil-solvent-refrigerant mixture in a chilling operation effecting evaporation of said refrigerant and concomitant cooling of said mixture to a temperature at which wax crystallizes forming a first slurry of wax in remaining oil-solvent mixture and a volatilized high pressure refrigerant vapor;
- (c) further reducing the pressure on said resulting oil-solvent-refrigerant mixture effecting further evaporation of a second portion of said refrigerant at a low pressure and concomitant further cooling of said

mixture to a temperature at which additional wax crystallizes in said first slurry forming a volatilized low pressure refrigerant vapor;

- (d) filtering said first slurry from step (c) thereby forming (i) a first filter cake of slack wax containing wax crystals and occluded oil-solvent mixture and (ii) a first filtrate containing dewaxed oil and solvent;
- (e) cooling said volatilized high pressure refrigerant vapor, at a pressure no higher than the pressure of its evaporation, in indirect heat exchange against said first filtrate thereby forming a cooled high pressure refrigerant;
- (f) condensing said cooled high pressure refrigerant thereby forming a liquid high pressure refrigerant;
- (g) passing said liquid high pressure refrigerant to said mixing step;
- (h) separating dewaxed oil from said first filter cake; and
- (i) separating deoiled wax from said first filter cake.

2. The method of separating wax from a wax-bearing oil as claimed in Claim 1 wherein a portion of said volatilized high pressure refrigerant is condensed in indirect heat exchange against said first filtrate.

3. The method of separating wax from a wax-bearing oil as claimed in Claim 1 wherein 5%-85% of said volatilized high pressure refrigerant is condensed in indirect heat exchange against said first filtrate.

4. The method of separating wax from a wax-bearing petroleum oil which comprises:

- (a) mixing said wax-bearing petroleum oil with a dewaxing solvent and a liquid refrigerant at an initial pressure at least sufficient to maintain said refrigerant in liquid phase;
- (b) reducing the pressure on the resulting oil-solvent-refrigerant mixture in a chilling operation, effecting evaporation of said refrigerant and concomitant cooling of said mixture to a temperature at which wax crystallizes forming a first slurry of wax in remaining oil-solvent mixture and a volatilized high pressure refrigerant vapor;
- (c) further reducing the pressure on said resulting oil-solvent-refrigerant mixture effecting further evaporation of a second portion of said refrigerant at a low pressure and concomitant further cooling of said mixture to a temperature at which additional wax crystallizes in said first slurry forming a volatilized low pressure refrigerant vapor;
- (d) filtering said first slurry from step (c) thereby forming (i) a first filter cake of slack wax containing wax crystals and occluded oil-solvent mixture and (ii) a first filtrate containing dewaxed oil and solvent;
- (e) cooling said volatilized high pressure refrigerant vapor, at a pressure no higher than the pressure of its evaporation, in indirect heat exchange against said first filtrate thereby condensing 5%-85% of said high pressure refrigerant;
- (f) condensing said cooled high pressure refrigerant thereby forming a liquid high pressure refrigerant;
- (g) passing said liquid high pressure refrigerant to said mixing step;
- (h) separating dewaxed oil from said first filter cake; and
- (i) separating deoiled wax from said first filter cake.

5. The method of separating wax from a wax-bearing petroleum oil which comprises:

- (a) mixing said wax-bearing oil with a dewaxing solvent and a liquid refrigerant at an initial pressure at least sufficient to maintain said refrigerant in liquid phase;
- (b) reducing the pressure on the resulting oil-solvent-refrigerant mixture effecting evaporation of said refrigerant and concomitant cooling of said mixture to a temperature at which wax crystallizes forming a first slurry of wax in remaining oil-solvent mixture and a volatilized high pressure refrigerant vapor;

(c) further reducing the pressure on said resulting oil-solvent-refrigerant mixture effecting further evaporation of a second portion of said refrigerant at a low pressure and concomitant further cooling of said mixture to a temperature at which additional wax crystallizes in said first slurry forming a volatilized low pressure refrigerant vapor;

- (d) filtering said first slurry from step (c) thereby forming (i) a first filter cake of slack wax containing wax crystals and occluded oil-solvent mixture and (ii) a first filtrate containing dewaxed oil and solvent;
- (e) contacting said slack wax with additional solvent forming a second slurry;
- (f) filtering said second slurry thereby forming (i) a second filter cake containing deoiled wax and (ii) a second filtrate containing oil and solvent;
- (g) cooling said volatilized high pressure refrigerant vapor, at a pressure no higher than the pressure of its evaporation, in indirect heat exchange against said first filtrate thereby forming a cooled high pressure refrigerant;
- (h) further cooling said cooled high pressure refrigerant in indirect heat exchange against said second filtrate;
- (i) condensing said cooled high pressure refrigerant thereby forming a liquid high pressure refrigerant;
- (j) passing said liquid high pressure refrigerant to said mixing step;
- (k) separating dewaxed oil from said first filter cake; and
- (l) separating deoiled wax from said first filter cake.

6. The method of separating wax from a wax-bearing petroleum oil as claimed in Claim 5 wherein said second filtrate which is used to condense said cooled high pressure refrigerant is combined with said liquid high pressure refrigerant.

7. The method of separating wax from a wax-bearing petroleum oil as claimed in Claim 5 wherein at least a portion of said liquid high pressure refrigerant is passed directly to said chilling operation.

8. The method of separating wax from a wax-bearing petroleum oil which comprises:

- (a) mixing said wax-bearing oil with a dewaxing solvent and a liquid refrigerant at an initial pressure at least sufficient to maintain said refrigerant in liquid phase;
- (b) reducing the pressure on the resulting oil-solvent-refrigerant mixture in a chilling operation effecting evaporation of a first portion of said refrigerant at a high pressure and concomitant cooling of said mixture to a temperature at which wax crystallizes forming a first slurry of wax in remaining dewaxed oil-solvent mixture and a volatilized high pressure refrigerant vapor;
- (c) further reducing the pressure on said resulting oil-solvent-refrigerant mixture effecting evaporation of a second portion of said refrigerant at a low pressure and concomitant further cooling of said mixture to a temperature at which additional wax crystallizes in said first slurry forming a volatilized low pressure refrigerant vapor;
- (d) filtering said first slurry from step (c) thereby forming (i) a first filter cake of slack wax containing wax crystals and occluded oil-solvent mixture and (ii) a first filtrate containing dewaxed oil and solvent;
- (e) cooling said volatilized high pressure refrigerant vapor, at a pressure no higher than the pressure of its evaporation, in indirect heat exchange against said first filtrate thereby forming a cooled high pressure refrigerant;
- (f) condensing said cooled high pressure refrigerant thereby forming a liquid high pressure refrigerant;
- (g) passing at least a portion of said liquid high pressure refrigerant to said mixing step;
- (h) compressing said volatilized low pressure refrigerant vapor;

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(i) condensing said compressed low pressure refrigerant vapor; and

(j) recycling at least a portion of said condensed low pressure refrigerant vapor to said chilling operation.

9. The method of separating wax from a wax-bearing petroleum oil as claimed in Claim 8 wherein a second portion of said condensed low pressure refrigerant vapor is passed into indirect heat exchange with solvent admitted to said filtration operation as wash solvent.

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