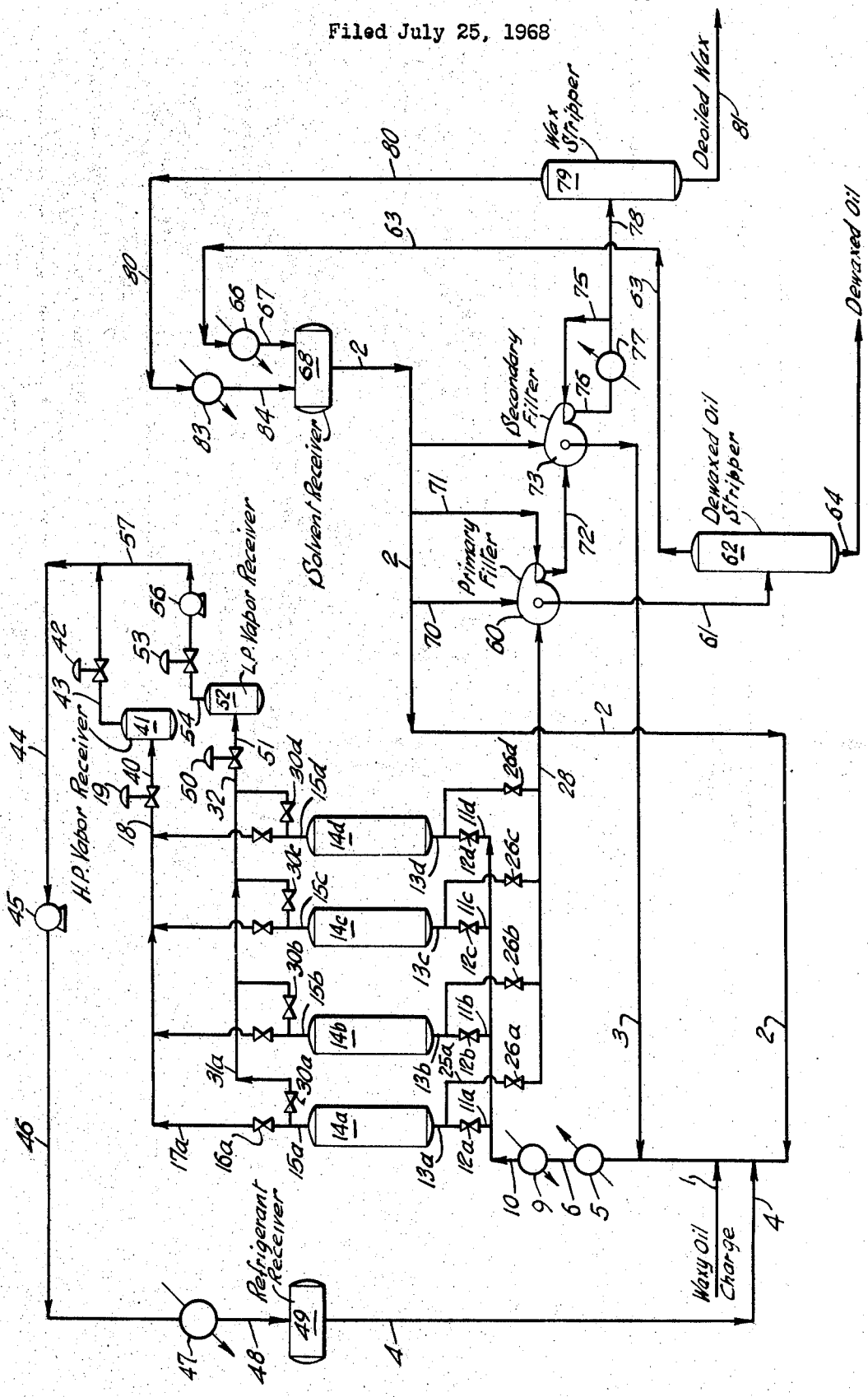
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SOLVENT DEWAXING AND DEOILING PROCESS

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SOLVENT DEWAXING AND DEOILING PROCESS

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ABSTRACT OF THE DISCLOSURE

This invention relates to a method of separating wax from a wax bearing mineral oil employing a mixture of an aromatic hydrocarbon and a ketone as a dewaxing solvent and chilling of the oil-solvent mixture by direct heat exchange with a liquid refrigerant. Cooling to dewaxing temperature is effected by admixing liquid refrigerant with the oil-solvent mixture at an elevated pressure and reducing the pressure effecting evaporation of refrigerant and concomitant cooling. Wax crystals formed at the dewaxing temperature are separated from oil-solvent mixture and repulped with additional solvent and dewaxed oil product is separated from the oil-solvent mixture. Repulped wax is separated from the repulping solvent mixture forming wax of low oil content. Repulping solvent containing oil washed from the wax crystals is recycled to the initial dewaxing step to achieve high yields of dewaxed oil.

BACKGROUND OF THE INVENTION

(1) Field of the invention

In the manufacture of lubricating oils 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.

(2) Description of the prior art

In accordance with the dewaxing processes of the prior art, the oil-solvent mixture is usually chilled by indirect heat exchange. As wax crystals separate from the oil-solvent mixture, wax accumulates on the heat exchange surface reducing the heat transfer coefficient and the cooling capacity of the exchanger. It is, therefore, customary to employ double pipe heat exchange equipment with provision for scraping the heat exchange surface upon which the wax tends to form. The use of mechanical scrapers causes mechanical shearing of the wax crystals. The extent of this shearing in turn affects the filtration rate which may be achieved in separating the wax crystals from the supernatant oil-solvent mixture. Attempts have

been made to effect cooling of an aromatic-ketone-oil mixture by direct contact with evaporating refrigerant by instantaneous flashing of the liquid refrigerant as described in U.S. Pats. 2,067,128 and 2,164,773. However, the wax crystals formed in such highly turbulent flash vaporization systems appear to be subjected to high shearing which results in poor filtration rates.

It has also been known that oils may be dewaxed employing a refrigerant as solvent and evaporating a part of the solvent to effect chilling. Such a process, known as the propane dewaxing process, is described by Kalichevsky, "Modern Methods of Refining Lubricating Oils," Reinhold (1938), page 56. As described therein, propane is employed as solvent and chilling of the oil-propane mixture is effected by evaporation of part of the propane. However, a major disadvantage of the propane dewaxing process is the large temperature differential found between the filtering temperature in the dewaxing operation and the pour point of the product oil. This dewaxing differential of approximately 40° F. for propane dewaxing requires considerably more costly refrigeration than is needed when employing ketone-aromatic solvent mixtures for dewaxing which are characterized by a small dewaxing differential of from 0 to about 10° F.

SUMMARY OF THE INVENTION

In accordance with this invention, the economy of direct heat exchange with evaporating refrigerant is achieved under circumstances producing wax crystals of high filterability achieving high filter rates and concomitantly producing dewaxed oil in high yield and product wax of low oil content. Wax bearing mineral oil is diluted with an aromatic-ketone solvent in admixture with liquid refrigerant and chilling is effected by controlled evaporating of the refrigerant by reducing the pressure at a rate such that the cooling rate is maintained within the range of about 1 to 30° F. per minute and preferably within the range of about 1.5 to 15° F. per minute.

Wax crystals formed in cooling the oil-solvent mixture are filtered separating a first filter cake comprising a slack wax composed of wax crystals and occluded oil-solvent mixture and a first filtrate comprising dewaxed oil and solvent. The slack wax is repulped with additional dewaxing solvent and the repulped wax is filtered separating a second filter cake comprising deoiled wax and a filtrate comprising oil washed from the slack wax and solvent. Solvent is stripped from the first filtrate to separate dewaxed oil product and solvent is stripped from the deoiled wax to produce wax product. Filtrate from the repulping operation is recycled in admixture with the oil-solvent mixture passed to the first filtration step.

Pressure reduction in the wax crystallization step is controlled at a rate such that the cooling of the oil-solvent mixture is maintained within the range of about 1.5 to 15° F. per minute. Dewaxing temperatures within the range of about −40 to +20° F. depending upon the desired pour point of the product oil are used. Suitable liquid refrigerants which may be used for direct chilling include ammonia, normally gaseous hydrocarbons such as propane, and chlorofluorocarbons such as Freon. Refrigerant evaporated in chilling the oil-solvent mixture is recompressed and condensed to form liquid refrigerant which is recycled for reuse.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying flow diagram is illustrative of the process of this invention. Although the flow diagram il-

lustrates a particular arrangement of apparatus and is described with reference to particular materials which may be used in practice of this invention, it is not intended to limit the invention to the particular apparatus, conditions, or materials described.

Waxy oil charge at a rate of 11,000 barrels per day is introduced through line **1**. The waxy oil charge is a solvent refined vacuum distillate suitable for use in the manufacture of base oil for SAE 20 motor oil. The waxy oil charge has a gravity of 30.6° API, a pour point of 105° F., and a wax content of 10.2 weight percent. To the waxy oil feed is added 13,950 barrels per day of solvent from line **2**. The solvent employed is a mixture of 50 percent methyl ethyl ketone and 50 percent toluene. Also added to the waxy oil and solvent mixture is second stage filtrate from line **3** added at a rate of 22,200 barrels per day and liquid propane from line **4** added at a rate of 6.77 million pounds per day at a pressure of 300 pounds per square inch absolute (p.s.i.a.). The combined stream of oil, solvent, and refrigerant is heated in exchanger **5** to a temperature of 130° F. to achieve complete solution of the oil, solvent, and refrigerant. The mixture is then passed through line **6** to cooler **9** which is a conventional liquid-liquid heat exchanger used to cool the combined stream to 110° F. With all connecting valves closed except valve **12***a*, the cooled mixture of oil, solvent, and refrigerant is passed through lines **10**, **11***a*, valve **12***a*, and line **13***a* into crystallizer **14***a*. Upon completion of the filling of crystallizer **14***a*, the temperature of the contents is 110° F. and the pressure is 245 p.s.i.a. Valve **12***a* is then closed and valve **16***a* opened. Throttle valve **19** is then opened gradually in response to the temperature in crystallizer **14***a* to maintain a cooling rate of about 1 to 30° F. per minute. As throttle valve **19** opens, the pressure in crystallizer **14***a* falls with concomitant vaporization of refrigerant and cooling of the contents. The pressure is then reduced from 245 p.s.i.a. to 90 p.s.i.a. over a period of 36 minutes during which time the temperature of the crystallizer drops from 110 to 55° F. The evaporated refrigerant passes through throttle valve **19** and line **40** into high pressure vapor receiver **41**. A pressure of 90 p.s.i.a. is maintained on high pressure vapor receiver **41** by pressure control valve **42** in line **43**. Refrigerant vapor at 90 p.s.i.a. is then passed through line **44** to compressor **45**. Compressed vapors are passed through line **46** to cooler **47**. In cooler **47**, the refrigerant is condensed and liquid refrigerant passed through line **48** to receiver **49**.

When the pressure in crystallizer **14***a* has fallen to 90 p.s.i.a., valve **16***a* is closed and valve **30***a* opened. With valve **30***a* open, pressure is maintained by venting vapors through lines **31***a* and **32** to throttle valve **50**. Throttle **50** gradually opens reducing the pressure of crystallizer **14***a* from 90 p.s.i.a. to 15 p.s.i.a. over a period of 36 minutes. The resulting reduction in pressure effects evaporation of remaining refrigerant reducing the temperature of the contents of crystallizer **14***a* from 55 to 0° F. The refrigerant vapors pass through line **51** to vapor receiver **52** maintained at a pressure of 15 p.s.i.a. by pressure control valve **53** in line **54**. Vapors in line **54** are compressed from 15 p.s.i.a. by compressor **56** to a pressure of 90 p.s.i.a. and discharged through line **57** to line **44** where they are combined with the vapors from high pressure receiver **41** for further compression and condensation.

Upon completion of chilling the contents of crystallizer **14***a* to 0° F., valve **30***a* is closed. Cold oil-solvent mixture and crystallized wax is then withdrawn through line **25***a* by opening valve **26***a* and the resulting slurry of wax in cold oil and solvent is passed through line **28** to primary filter **60**. In filter **60**, slack wax is separated from oil-solvent filtrate which filtrate is discharged through line **61** to dewaxed oil stripper **62**. In dewaxed oil stripper **62**, methyl ethyl ketone-toluene solvent mixture is separated as distillate withdrawn through line **63**

and dewaxed oil product is withdrawn through line **64** at a rate of 9,130 barrels per day. Solvent distillate in line **63** is cooled in condenser **66** and the condensed solvent passed through line **67** to solvent receiver **68**.

The filter cake in primary filter **60** is washed with solvent from line **70** and repulped with solvent from line **71**. The repulped filter cake is passed through line **72** to secondary filter **73**. The repulped wax is filtered in filter **73**, washed with solvent from line **74** and the resulting filtrate withdrawn through line **3**. Wax from secondary filter **73** is sluiced with hot wax-solvent mixture at a temperature of about 140° F. from line **75** and is passed through line **76**, heater **77** and line **78** to wax stripper **79**. In wax stripper **79**, solvent is withdrawn as distillate through line **80** and deoiled wax is withdrawn at a rate of 1,870 barrels per day through line **81**. Solvent vapor in line **80** is condensed in cooler **83** and the resulting condensed solvent passed through line **84** to solvent receiver **68**.

Crystallizer **14***a* is one of four crystallizers arranged so that the functions of filling, first stage cooling, second stage cooling, and emptying may be carried out continuously by switching the corresponding valves and employing the corresponding lines, valves, and vessels lettered *a*, *b*, *c* and *d*. In the course of cooling from 110 to 55° F. about one-half of the liquid propane is evaporated with the pressure not falling below 90 p.s.i.a. This operation significantly reduces compressor horsepower from that which would be required if all propane were vaporized to atmospheric pressure.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The higher filtration rates which may be obtained in the controlled evaporation of refrigerant in direct heat exchange may be used in a two-stage dewaxing-deoiling process to achieve a higher filter rate employing the same solvent ratios or a lower solvent ratio may be employed at the same filtration rates. The advantage of employing lower dilution in direct contact chilling as compared with conventional scraped wall heat exchange, both at a yield of 83 volume percent wax free oil when dewaxing a solvent refined vacuum distillate used in the manufacture of SAE 20 grade motor oil, is shown in Table I following:

TABLE I

	Direct contact refrigerant	Scraped wall double pipe heat exchangers
Total solvent ratio, solvent:chg	3.6	3.1
Chilling rate, ° F./min	1.5	1.5
Overall filter cycle rate, gal./ft.²/hr	4.4	2.2
Primary filter data:		
Temperature, ° F	4	0
Dilution, solvent:chg. oil, volume	1.3:1.0	0.5:1.0
Wash, solvent:chg. oil, volume	1.4:1.0	0.9:1.0
Cycle rate, gal./ft.²/hr	23	5.0
Secondary filter data:		
Temperature, ° F	0	0
Dilution, solvent:chg. oil, volume	0.5:1.0	1.2:1.0
Wash, solvent:chg. oil, volume	0.5:1.0	0.5:1.0
Cycle rate, gal./ft.²/hr	2.1	0.6

When operating as shown in Table I, direct contact chilling requires about 50 percent less filter area than is required in conventional scraped wall heat exchange equipment.

The higher filter rates obtainable in the direct contact cooling method of this invention may alternatively be used to reduce the solvent dilution employed so that less refrigeration and solvent stripping is required. A comparison of the direct contact chilling and conventional scraped wall operation at the same yield of 83 volume percent wax free oil and the same overall filter cycle rate with the same SAE 20 grade waxy oil feed is shown in Table II following.

TABLE II

	Direct contact refrigerant	Scraped wall double pipe heat exchangers
Total solvent ratio, solvent:chg.	2.7	3.1
Chilling rate, ° F. min.	1.5	1.5
Overall filter cycle rate, gal./ft.²/hr.	2.2	2.2
Primary filter data:		
Temperature, ° F.	0	0
Dilution, solvent:chg. oil, volume	1.0:1.0	0.5:1.0
Wash, solvent:chg. oil, volume	1.4:1.0	0.9:1.0
Cycle rate, gal., ft.²/hr.	3.2	5.0
Secondary filter data:		
Temperature, ° F.	0	0
Dilution, solvent:chg. oil, volume	0.9:1.0	1.2:1.0
Wash, solvent:chg. oil, volume	0.5:1.0	0.5:1.0
Cycle rate, gal./ft.²/hr.	2.1	0.6

These data show that the process of this invention employing controlled direct contact refrigerant evaporation permits a reduction of solvent dilution so that about 8% less refrigeration is required and 11% less solvent stripping is required than with conventional scraped wall chillers when employing the same overall filter surface.

We claim:

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

mixing said wax-bearing mineral oil with an aromatic-ketone dewaxing solvent and a liquid refrigerant at an initial pressure at least sufficient to maintain said refrigerant in the liquid phase,

reducing the pressure on the resultant oil-solvent-refrigerant mixture effecting evaporation of said refrigerant and concomitant cooling of said oil and solvent to a temperature at which said wax crystallizes forming a first slurry of wax in remaining oil-solvent mixture,

filtering said first slurry separating a first filter cake comprising a slack wax of wax crystals and occluded oil-solvent mixture and a first filtrate comprising dewaxed oil and solvent,

contacting said slack wax with additional dewaxing solvent forming a second slurry,

filtering said second slurry separating a second filter cake comprising deoiled wax and a second filtrate comprising said occluded oil and solvent and recycling said second filtrate to said mixing,

separating dewaxed oil from said first filtrate,

separating deoiled wax from said second filter cake,

the dewaxing temperature being in the range of −40 to +20° F.,

the cooling rate of said oil-solvent mixture being in the range of about 1.5 to 15° F. per minute,

and wherein the evaporated refrigerant is compressed to a pressure at least about as high as said initial pressure and condensed to form said liquid refrigerant which is recycled to said mixing.

2. The method of claim 1 wherein said refrigerant is a liquefied normally gaseous hydrocarbon.

3. The method of claim 1 wherein said refrigerant is liquid propane.

4. The method of claim 1 wherein said refrigerant is liquid ammonia.

5. The method of claim 1 wherein said refrigerant is a liquid chlorofluorocarbon.

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