Solvent Dewaxing Process with Cooling by Direct Contact with Evaporating Refrigerant

Robert A. Woodle, Nederland, Tex., assignor to Texaco Inc., New York, N.Y., a corporation of Delaware
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ABSTRACT OF THE DISCLOSURE

In solvent dewaxing a mineral oil, the oil is mixed with an aromatic-ketone dewaxing solvent and the mixture is chilled to dewaxing temperature by direct contact with evaporating refrigerant. The rate of cooling is controlled by reducing the pressure on the mixture of oil, solvent, and refrigerant at a controlled rate such that the cooling rate of the oil-solvent mixture is maintained within the range of about 1 to 30°F per minute. The solvent mixture may compromise methyl ethyl ketone and toluene and the refrigerant may be a liquefied normally gaseous hydrocarbon such as propane, liquid ammonia, or a chlorofluorocarbon such as Freon. In one embodiment the refrigerant is expanded in two stages of pressure reduction and refrigerant evaporated in the lower pressure stage is separately compressed to a pressure at least as high as the terminal pressure of the first expansion zone.

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 point. 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. Pat. 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 Kaliachkov, "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 vaporization 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 so that high filter rates are achieved. Wax bearing mineral oil is diluted with an aromatic-ketone solvent in admixture with liquid refrigerant and chilling is effected by controlled evaporation of the refrigerant by reducing the pressure at a rate such that the refrigerant evaporates at a controlled rate. Controlled evaporation is achieved by mixing the oil, solvent and refrigerant at an initial pressure at least sufficient to maintain the refrigerant in liquid phase and then 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 1.5 to 15°F per minute. The initial pressure may be within the range of about 100 to 300 pounds per square inch absolute and the final pressure may be within the range of about 14.7 to 60 pounds per square inch absolute.

The dewaxing temperature or temperature at which the wax is filtered from the oil-solvent mixture is within the range of about —40 to +20°F depending upon the desired pour point of the product oil. Vaporized refrigerant is separated from the chilled oil-solvent mixture and compressed and condensed for reuse. In one embodiment of this invention, cooling is effected in two stages of pressure reduction. In this case the pressure is reduced from the initial pressure to an intermediate pressure in the first stage of evaporation and from the intermediate pressure to the terminal pressure in a second stage of evaporation and the cooling rate in each stage is maintained within the range of about 1 to 30°F per minute and preferably within the range of 1.5 to 15°F per minute. Advantageously, vapors produced in the first stage are compressed from said intermediate pressure to a pressure at least as high as the initial pressure and vapors from the second stage are compressed from said terminal pressure to a pressure at least as high as said intermediate pressure. In this way, vapors from the second stage of evaporation may be compressed and combined with vapors from the first stage of evaporation and the combined vapor stream then compressed to the initial pressure so that only a part of the vapors need be compressed from the terminal pressure to the initial pressure.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying flow diagram is illustrative of the process of this invention. Although the flow diagram illustrates a particular arrangement of apparatus is described with reference to particular materials which
may be used in the practice of this invention, it is not intended to limit the invention to the particular apparatus or materials described.

Waxy oil feed in line 1 is combined with ketone-atic solvent mixture from line 2 and passed to cooler 3. Cooler 3 may be a conventional shell and tube heat exchanger and is employed to cool the combined oil-solvent stream to a temperature of about the cloud point of the oil-solvent mixture. Under these conditions no wax forms on the exchanger surfaces to reduce heat transfer and it is not necessary to employ scraped wall exchangers. The cooled oil-solvent mixture in line 4 is combined with liquid refrigerant from line 6 and the resulting oil-solvent-refrigerant mixture is passed through line 7a, valve 8a and line 9a to crystallizer 12a.

Four crystallizers designated 12a, 12b, 12c, and 12d are manifolded by correspondingly designated piping and valves to permit four sequential steps of filling, first stage cooling, second stage cooling, and emptying on a continuous or batch basis, as desired. The crystallizers are in connection with the four steps as they are performed in a single crystallizer but it will be understood that continuous operation is maintained by employing each of the crystallizers serially to perform one of the steps described. While filling crystallizer 12a, valves 13a, 14a, and 22a are closed. Crystallizer 12a is filled maintaining the pressure above the vapor pressure of the refrigerant to maintain the refrigerant in liquid phase.

Upon completion of the filling step, valve 8a is closed and valve 14a opened to initiate the second step which is the first stage of cooling. In the first stage of cooling, control valve 17a opens at a controlled rate to reduce the pressure causing the liquid refrigerant to evaporate and to cool the oil-solvent mixture by the resulting expansion. Refrigerant vapors are discharged through line 18a valves 14a and 17a and line 20 to intermediate pressure vapor receiver 21. Valve 17a is opened to reduce the pressure in crystallizer 12a from the initial pressure to an intermediate pressure at a rate such that the rate of cooling of the oil-solvent mixture in crystallizer 12a is maintained within the range of about 1 to 30° F. per minute. When the pressure on crystallizer 12a falls to the pressure of intermediate pressure vapor receiver 21, valve 14a is closed ending the second step and valve 22a is opened initiating the third step which is the second stage of cooling.

Control valve 24a is opened permitting vapors from crystallizer 12a to flow through lines 18a, valves 22a and control valve 24a and line 25 to low pressure vapor receiver 26. Valve 24a is then opened at a rate to lower the pressure at a rate to maintain the cooling rate in crystallizer 12a at 30° F. per minute. Vapor from low pressure vapor receiver 26 is withdrawn through line 30 and compressed by compressor 31 to a pressure at least as high as the intermediate pressure of receiver 21 and discharged through line 32 to receiver 21. Vapor from intermediate pressure vapor receiver 21 is withdrawn through lines 25, 36, and 37 and passed through line 37 to cooler 38. In cooler 38, the refrigerant vapors are cooled condensing the refrigerant to liquid. Liquid refrigerant is discharged through line 39 to liquid refrigerant receiver 40 to provide the supply of liquid refrigerant passed through line 6.

When all liquid refrigerant from crystallizer 12a has been evaporated and the oil-solvent mixture cooled to the desired dewaxing temperature, valve 22a is closed and the third step of second stage cooling is initiated by opening valve 13a and discharging the chilled oil-solvent mixture through atmospheric pressure receiver 45a, valve 13a and line 46 to filter feed drum 47. Upon completion of emptying crystallizer 12a, the fourth step is completed and valve 13a closed. Crystallizer 12a is then ready to repeat the cycle as described above.

Oil-solvent mixture and wax crystals separated as a result of the cooling effected in crystallizer 12a is withdrawn from feed drum 47 through line 48 and passed to filter 50. In filter 50 the wax crystals are separated from filtrate as a wax cake. The wax cake is washed with solvent from line 77 and then slurried with solvent from line 53. The slurry of wax in solvent is then passed through line 52 to wax stripper 54. In wax stripper 54, the aromatic-ketone solvent mixture is distilled and removed through line 55. Slack wax product stripped of solvent is withdrawn as bottoms through line 56. Solvent vapors in line 55 are condensed in cooler 60 and the resulting condensed solvent vapor is withdrawn through line 61 to solvent receiver 62. Filtrate from filter 50 in line 65 is passed to oil stripper 66. Solvent vapors separated as distillate from stripper 66 are passed through line 67 to cooler 68 where the solvent is condensed to liquid. The condensed solvent is then passed through line 69 to solvent receiver 62. Dewaxed oil product stripped of solvent is withdrawn from stripper 66 through line 75. Solvent from receiver 62 is withdrawn through line 76 to supply the solvent recycled through line 2, the wash solvent in line 77 and the slurring solvent in line 53.

**DESCRIPTION OF THE PREFERRED EMBODIMENT**

In an example of the process of this invention, a waxy, solvent refined vacuum distillate is dewaxed to produce a base stock for SAE 40 grade motor oil. The feed stock has the following characteristics:

- Gravity, °API—29.2.
- Flash, COC, °F.—510.
- Fire, OC, °F.—585.
- Visc., SUS at 100°F.—5.3.
- Vis., SUS at 140°F.—7.9.
- Visc., SUS at 210°F.—64.1.
- Viscosity index—100.5.
- Pour, °F.—115.
- Wax, weight percent—12.9.

The charge stock is admixed with 4 parts by volume of a solvent mixture comprising 60 percent methyl ethyl ketone and 40 percent toluene. The oil-solvent mixture is then heated to 150° F. to effect complete solution of the wax and oil in the solvent. Liquid propane is then added to the solvent-oil mixture at a pressure of 375 pounds per square inch absolute. The pressure is then gradually reduced to atmospheric pressure at a rate controlled to maintain a uniform cooling rate of 1.5° F. per minute so that after a period of 100 minutes the temperature of the oil-solvent mixture is 0° F. Cooling precipitates wax from the oil-solvent mixture and the resulting mixture is filtered maintaining a cake thickness of 0.25 inch. The filtration rate is found to be 14.58 gallons per square foot per hour.

In a comparison test, the same waxy feed stock diluted with the same solvent at the same solvent dilution ratio is cooled from 150 to 0° F. at a cooling rate of 1.5° F. per minute in a scraped wall exchanger. The resulting slurry of wax particles in oil-solvent mixture is filtered in the same filtration equipment with a filter cake thickness of 0.25 inch and the filtration rate found to be 4.57 gallons per square foot per hour.

In a second comparative test, the same oil-solvent mixture is cooled by admitting liquid propane to the mixture and the mixture cooled by rapid release of pressure. The resulting wax crystals separated on filtration have a moisture content of 0.5%.

I claim:

1. A method of separating wax from a waxy mineral oil wherein said mineral oil is mixed with an aromatic-ketone dewaxing solvent, the resulting oil-solvent mixture is chilled to a dewaxing temperature effecting crystallization of at least a portion of the wax therein...
5 and the crystallized wax is separated from the oil-solvent mixture, the improved method of chilling said mixture to said dewaxing temperature and recovering the chilling agent which comprises:

mixing a liquid refrigerant with said oil-solvent mixture at an initial pressure at least sufficient to maintain said refrigerant in the liquid phase, and reducing the pressure on the oil-solvent-refrigerant mixture in at least two stages from said initial pressure to an intermediate pressure thence to a final pressure effecting vaporization of said refrigerant and concomitant cooling of said oil-solvent mixture to said dewaxing temperature, the pressure being reduced at a rate such that the cooling rate of said oil-solvent mixture is maintained within the range of about 1 to 30°F per minute,

recovering the evaporated refrigerant and recycling said liquid refrigerant to said mixing, said recovery comprising compressing the portion of said refrigerant evaporated in reducing pressure from said intermediate pressure to said final pressure to said intermediate pressure, combining the recompressed portion with that portion of said refrigerant evaporated in reducing the pressure from said initial pressure to said intermediate pressure and compressing the resultant combined stream to said initial pressure.

2. The method of claim 1 wherein said dewaxing temperature is within the range of -40 to +20°F.

3. The method of claim 1 wherein said cooling rate of said oil-solvent mixture is maintained within the range of about 1.5 to 15°F per minute.

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

5. The method of claim 4 wherein said refrigerant is liquid propane.

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

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

8. The process of claim 1 wherein said initial pressure is within the range of about 100 to 300 pounds per square inch absolute and said final pressure is within the range of about 14.7 to 60.0 pounds per square inch absolute.

References Cited

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HERBERT LEVINE, Primary Examiner

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