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DEWAXING MINERAL OIL

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1

This invention relates to a process for the separation of petroleum into solid and liquid fractions. The process of the invention is particularly adaptable to the separation of crystalline and amorphous waxes from lubricating oil distillates and petroleum residues. It may be utilized in the treatment of any petroleum fraction from which it is desired to separate waxy material.

Many crude oils from which lubricating oil is produced contain wax. Wax is found associated with the lubricating oil fractions of paraffinic base crude oil and with the lubricating oil fractions produced from many of the so-called mixed base and asphaltic base crude oils. It is not only of doubtful lubricating value but limits the temperature at which lubricants containing it may be used. At low temperatures a wax-containing lubricating oil congeals to a semi-solid state. The temperature at which an oil congeals is commonly referred to as its pour-point. Therefore in the production of lubricating oil from petroleum fractions containing wax it is advantageous and customary to remove a substantial portion of the wax or wax-like substances present in the oil in order to lower the pour-point of the oil so that the lubricating oil may be effectively used at low temperatures.

Several methods well known in the art are employed at present for the production of low pour-point lubricating oil stock from petroleum fractions which contain wax. Briefly described these methods employ a liquid which is a solvent for all the liquid components of oil at the dewaxing temperature but which has almost no solubility for all the solid components thereof at the same temperature. The dewaxing temperature employed depends upon the desired pour-point of the lubricating oil or upon the amount of wax to be removed. For example, in conventional dewaxing processes, such as propane dewaxing or solvent dewaxing employing a mixture of methyl ethyl ketone, benzene and toluene, if it is desired to produce a lubricating oil having a pour-point of about —10° F., it is necessary to carry out the dewaxing operation at a temperature of about —45° F. to about —50° F. in a propane dewaxing process and at a temperature of about —25° F. in the above-mentioned solvent dewaxing process. If it is desired to produce a lubricating oil having a pour-point of about 0° F., the dewaxing temperature must usually be about —35° F. and about —10° F. for a propane dewaxing and a solvent dewaxing process respectively. Thus, the pour-point of a petroleum lubricating oil depends to a great extent upon the dewaxing temperature employed. As indicated, the temperature differential between the dewaxing temperature and the pour-point of the dewaxed oil in conventional commercial propane dewaxing operation is considerable, usually at least 30° F. While the temperature differential between the dewaxing temperature and the pour-point of the dewaxed oil in the conventional solvent dewaxing with MEK, benzene, and toluene is usually only 10 to 15° F., this solvent mixture requires external refrigeration which entails additional equipment, materials and expense.

2

It is an object of this invention to provide a method for obtaining a lubricating oil which has a pour-point substantially the same as the dewaxing temperature and to provide a method for obtaining a lubricating oil which has a pour-point appreciably lower than that obtained by conventional propane dewaxing and at least comparable to that obtained by methyl ethyl ketone, benzene and toluene solvent dewaxing at the same dewaxing temperature. It is another object of this invention to provide a method for dewaxing lubricating oil to yield lubricating oils of low pour-point at a relatively high dewaxing temperature and which permits rapid filtration and washing rates of the resulting wax cake. It is still another object of this invention to provide an economical method of producing a lubricating oil having a low pour-point. These and other objects of the invention will become apparent from the discussion of the invention as set forth hereinafter.

It has now been discovered that lubricating oil possessing a low pour-point, substantially the same as the dewaxing temperature employed, may be produced by a method which comprises dewaxing a wax-containing mineral oil fraction, such as a lubricating oil distillate or petroleum residue, with a liquid solvent mixture of a normally gaseous, readily liquefiable hydrocarbon, such as propane, or a liquid mixture of hydrocarbons containing the same, and an alkanone and/or an alkenone and/or an alkanol of 4 to 6 carbon atoms inclusive, and particularly methyl ethyl ketone and/or methyl isobutyl ketone. More particularly it has been discovered that raw (wax-containing) petroleum distillates and raw (wax-containing) petroleum residues, deasphalted if required, may be processed (dewaxed)

to produce a lubricating oil having the desired pour-point by a treatment which comprises: dissolving the wax-containing mineral oil fraction in a liquid solvent such as methyl ethyl ketone, mesityl oxide, and methyl isobutyl ketone, or a mixture thereof, at a suitable elevated temperature, usually within the range 100° F.–200° F., depending upon the volume ratio of the liquid solvent to the hydrocarbon material to be dewaxed; cooling the resulting solvent-oil solution to a selected dewaxing temperature and at the same time introducing into said solution an amount of liquid propane so that, at said selected dewaxing temperature, the proportion of liquid solvent to liquid propane is between about 1:9 by volume and about 4:1 by volume, said cooling being effected either by means of an external refrigerant or preferably by employing propane as an internal refrigerant.

For obvious reasons it is preferred that propane be employed as an internal refrigerant. This may conveniently and readily be accomplished (as is well known by those skilled in the art) by adjusting the feed rate and amount of the liquid propane to the solvent-oil solution and at the same time adjusting the rate and amount of gaseous propane vaporizing therefrom. During the cooling step, agitation of the resulting admixture may advantageously be employed. As required or desired, vaporization of the liquid propane may be carried out at subatmospheric or at atmospheric pressures. It is also possible to vaporize the liquid propane at a pressure greater than atmospheric, being limited of course by the vapor pressure of propane at the particular temperature.

With reference to the special solvent mixture of the invention, in accordance with a preferred embodiment thereof, it is preferred to employ a liquid solvent mixture of propane and methyl ethyl ketone when dewaxing a wax-containing petroleum distillate fraction. The use of a liquid solvent mixture of propane and methyl isobutyl ketone when dewaxing a wax-containing petroleum residue represents another preferred practice. In general the invention is particularly applicable to the dewaxing of a high viscosity index waxy oil, i. e., a petroleum fraction which does not contain an appreciable amount of monocyclic aromatic compounds. The invention, however, is applicable to both solvent extracted and unextracted oils. When the invention is applied to residual petroleum stocks, such as a waxy short residue, these stocks should advantageously be first deasphalted if necessary.

As indicated hereinbefore, in a conventional propane dewaxing process wherein liquid propane is employed both as an internal refrigerant and as the only solvent, the pour-point of the dewaxed oils is usually about 30–45° F. higher than the dewaxing (wax-filtering) temperature. Similarly in a dewaxing process employing the conventional solvent mixture of methyl ethyl ketone, benzene and toluene the pour-point of the resulting dewaxed oil is about 10–15° F. higher than the dewaxing temperature. Propane dewaxing however has an advantage in that propane may also be employed as an internal refrigerant whereas in a methyl ethyl ketone (hereinafter referred to as MEK)-benzene-toluene solvent dewaxing operation an external refrigerant must be employed. This is a disadvantage since additional equipment must be employed and the dewaxing operation is more expensive.

A dewaxing process employing a solvent mixture consisting of MEK, benzene and toluene and wherein propane is utilized as an internal refrigerant, does not afford a satisfactory method of producing low pour-point lubricating oils. The pour-point of a dewaxed lubricating oil produced by such solvent treatment is usually about 20–25° F. higher than the dewaxing temperature employed. For example, when employing a solvent mixture of MEK-benzene-toluene in the proportions by volume, 40–40–20, respectively, at dewaxing temperatures of −15° F. and −30° F. the dewaxed lubricating oils produced had a pour-point 20 and 25° F. higher, respectively, than the dewaxing temperature. These great differences between pour-point and dewaxing temperature were due to the fact that propane comprised approximately 10–20% by volume of the solvent mixture present in the filtrate. The resulting excessive solvent action of the propane in addition to the MEK-benzene-toluene retarded wax precipitation (increased its solubliity in the solvent-oil solution) and as a result gave pour-points 20–25° F. higher than the dewaxing temperature. Furthermore, it was not possible to remove all of the propane even when the dewaxing and propane removal (propane being used as an internal refrigerant) were carried out at relatively low pressures, in the order of 3–20 inches mercury absolute. Additionally it was found that lower dewaxing temperatures favored an increase in the amount of propane retained in the solvent-oil solution.

Oxygen-containing polar organic compounds such as methyl ethyl ketone (MEK), mesityl oxide (hereinafter referred to as MO) and methyl isobutyl ketone (hereinafter referred to as MIBK) reduce the solubility of wax-materials in mineral oil. These solvents however are also poor solvents for the liquid (non-wax) components of mineral oil. This is not surprising in view of the markedly similar chemical and physical properties of the normally solid (wax) and liquid (oil) components of mineral oil. The dewaxing solvent of the invention may if desired be modified by other solvents, especially the well known dewaxing solvents. Aromatic hydrocarbons such as benzene, toluene should not be included and are undesirable because of the relatively large solubility of waxes therein.

It is possible however by employing a polar material such as MEK, MO and MIBK or mixture of the same as a dewaxing solvent, to produce a lubricating oil having a pour-point identical to or substantially the same as, i. e., not greater than 10° F. above, the dewaxing temperature. Because of the poor solubility of petroleum fractions in these polar solvents a high solvent to oil ratio must be employed, at least 10, usually 30 volumes of the polar solvent (MEK, MO or MIBK) per volume of hydrocarbon material to be dewaxed. However, since the polar solvent in a commercial operation must be recovered and recycled, this method is not economically practical because of the excessive cost of the solvent recovery operations. Furthermore, at low temperatures and particularly at low solvent to hydrocarbon ratios, demixing usually occurs, resulting in the formation of three phases, a solid phase wax, a liquid polar solvent phase and a liquid hydrocarbon phase which contains a considerable amount of the undesired wax.

Solvent mixtures comprising a polar organic liquid, particularly MEK, MO or MIBK or mixtures of the same, and propane, wherein propane is employed not only as an active solvent but also

as an internal refrigerant are however excellent dewaxing solvents. Particularly effective solvent compositions comprise a liquid mixture of a polar solvent and propane wherein the volume ratio of the polar organic liquid to propane is between about 1:1 and about 4:1. An especially effective solvent composition comprises a liquid mixture of a polar solvent, such as MEK, MO and MIBK, and propane wherein the volume ratio of the polar solvent to the propane is about 7:3.

In the dewaxing operation according to the process of the invention, various ratios of solvent to the wax-containing mineral oil material may be employed, depending upon the desired pour-point of the lubricating oil to be recovered, the degree of dewaxing sought, the amount of waxy material present in the raw mineral oil fraction (distillate or residue) and upon the equipment available as well as sundry economic and practical considerations. In general a solvent to mineral oil volume ratio of from about 2:1 to about 10:1 is satisfactory, however, a volume ratio of from about 4:1 to about 6:1 is more preferred.

Advantages to be obtained by employing the process of the invention in a dewaxing operation, are illustrated by the results of a number of experiments which were carried out (1) wherein conventional dewaxing liquid mixtures of MEK-benzene-toluene were utilized as the dewaxing solvent, employing propane as an internal refrigerant, and (2) wherein a liquid mixture of MEK-propane was employed as the dewaxing solvent, and at the same time employing propane as an internal refrigerant. The experiments were carried out in the following manner.

Dewaxing equipment normally employed for standard HVI crude evaluations was used for the dewaxing operations. The equipment consisted of a 7½ gallon pressure vessel (bomb) and a separate externally chilled filter with a 0.66 sq. ft. filter area. A hot water bath was used for preliminary heating of the pressure vessel and its contents to the desired solution temperature. An insulating jacket was provided to enclose the vessel during the chilling and filtering periods.

The wax-containing lubricating oil distillate (wax content about 7.5% by weight and which after conventional furfural or phenol solvent extraction and dewaxing yields a raffinate having a viscosity of 250 S. S. U. at 100° F.), consequently termed a 250 distillate, from a West Texas Ellenburger (WTE) base stock and dewaxing solvent were charged to the dewaxing bomb. In the case of MEK-propane dewaxing the MEK was added at this point and the propane was added later, as described hereinafter. In a similar manner the solvent mixtures of MEK-benzene and toluene were added. The bomb was then immersed in the heating bath and heated to about 140° F. to assure complete solution of the oil and wax in the solvent. The bomb was then removed from the heating bath and the contents thoroughly mixed by end over end rotation of the bomb. After enclosing the bomb in the insulating jacket in a vertical position on a suitable platform scale, flexible hoses to propane feed and suction lines were connected and suitable valves opened to start the chilling cycle. The propane feed and suction line valves were regulated to maintain suitable chilling rate. In the case of the MEK-propane dewaxing experiments the amount of propane is additionally controlled in order to achieve the desired MEK-propane volume ratio at the dewaxing temperature.

When the desired dewaxing temperature was reached, suction was applied until a constant weight (in the case of the MEK-benzene-toluene solvent dewaxing) or a desired weight was reached (usually in the case of the MEK-propane solvent dewaxing). The propane lines were then disconnected and the pressure vessel connected to the chilled filter. An air line provided with a pressure gauge and a pressure regulating valve was attached to the inlet at the top of the bomb and the vent on the filter opened until the filter was full of liquid. After adjusting the pressure regulator to 10 p. s. i. g. and opening the discharge port of the filter, the filtration was timed to the point of pressure drop on the gauge. The solvent was then stripped from the dewaxed oil and wax and the resulting products weighed.

When external chilling was used instead of internal (propane) chilling, the same procedure of heating and mixing the bomb was used but the bomb was chilled in a kerosene bath refrigerated with Dry Ice, prior to attachment to the chilled filter.

The results of these experiments are set forth in Tables I and II.

TABLE I

MEK Dewaxing of WTE 250 Distillate

Run	A	B	C	D	E	F	G	H	J
Solvent Oil Ratio, by vol	2	[1] 3	4	4	[2] 4	4	4	[3] 4	[3] 4
Solvent Composition:									
MEK, percent v	40	40	40	60	40	40	40	40	40
Benzene, percent v	40	40	40	30	40	40	40	40	40
Toluene, percent v	20	20	20	10	20	20	20	20	20
Dewaxing Temp., °F	−15	−15	−15	−15	−15	−30	−30	−15	−30
Yield, Oil Recovery:									
Percent w	75.3	79.0	83.4	82.4	81.2	83.8	77.7	80.0	73.0
Percent v	75.5	79.0	83.4	82.3	81.1	83.8	77.6	69.7	72.8
Propane in Filtrate, percent v	------	14.2	------	11.8	------	24.2	16.9	4.8	17.2
Filter Rate, G. P. H./Sq. Ft.[4]	5	3	6	7	------	3	4	6	3
Oil Properties:									
API Gravity	26.0	26.4	26.5	26.2	26.2	26.4	26.2	25.8	26.1
S. U. Vis. at 100° F	294	284	308	273	297	301	308	299	312
S. U. Vis. at 210° F	52	51	53	51	52	52	53	52	53
Viscosity Index	95	96	94	95	95	94	94	94	94
Flash, °F	420	395	440	380	400	------	440	455	450
Pour-Point [5]	5	0	5	0	−5	−5	−5	3	−12
(PP-DWT)[6]	20	15	20	15	10	25	25	18	18

[1] Propane after chilling contained 0.10% v. MEK, 0.22% v. benzene and 0.03% v. toluene.
[2] External chilling with no agitation.
[3] Vacuum increased to 26 inches mercury during chilling.
[4] G. P. H./sq. ft.=gallons per hour per square foot of filter area.
[5] Average of three determinations.
[6] Pour-point minus the dewaxing temperature, °F.

TABLE II [1]

Propane-MEK Dewaxing of WTE 250 Distillate

Run No.	K	L	M	N	O
Solvent Oil Ratio, by vol.	4	4	4	4	4
Solvent Composition:					
MEK, percent v.	40	50	60	70	80
Propane, percent v.	60	50	40	30	20
Dewaxing Temp., °F.	−15	−15	−15	−15	−15
Yield, Recovery:					
Percent w.	77.3	68.9	76.5	80.5	77.3
Percent v.	77.0	68.8	76.2	80.2	76.7
Filter Rate, G. P. H./Sq. Ft.	2	1	17	37	34
Oil Properties:					
API Gravity	25.8	25.9	25.7	25.7	25.2
S. U. Vis. at 100° F.	318	333	287	328	359
S. U. Vis. at 210° F.	53	54	51	53	55
Viscosity Index	93	95	92	93	92
Flash, °F.	450	465		435	440
Pour-Point	−3	−7	−7	−13	−10
(PP–DWT)	12	8	8	2	5

[1] Designations are the same as in Table I.

The data of Table I demonstrate that a dewaxing operation, employing a solvent mixture of MEK-benzene-toluene and advantageously utilizing propane as an internal refrigerant, consistently yields a dewaxed lubricating oil having a pour-point considerably higher than the dewaxing temperature, at least 15° F. up to 25° F. higher. Furthermore the wax-filtration rates are low, consequently restricting production of both wax and dewaxed lubricating oil.

The data set forth in Table II, however, illustrate that when a liquid MEK-propane dewaxing solvent is employed the pour-point of the resulting dewaxed oil approaches the dewaxing temperature. For example when MEK and propane are employed in a volume ratio between about 1:1 and about 4:1 the pour-point of the dewaxed lubricating oil is not greater than 8° F. above the dewaxing temperature and at a MEK to propane volume ratio of 7:3 the temperature differential between the pour-point of the dewaxed oil and the dewaxing temperature amounts to only 2° F.

As indicated hereinbefore, the dewaxing temperature employed depends to a great extent upon the extent of wax-removal desired. As a general rule to obtain a relatively wax-free lubricating oil or petroleum fraction (e. g., a very low pour-point lubricating oil) relatively low dewaxing temperatures are required. In the practice of this invention it is preferred, however, to operate at a dewaxing temperature of between about 0° F. and about −40° F., the temperature range between about −15° F. and about −30° F. being preferred.

Another advantage of the invention, as illustrated by the data set forth in Table II is that the filtration rate of the wax-solvent-oil admixture at the dewaxing temperature is greatly increased. For example, at solvent ratios of MEK to propane of 1:1 and 3:2 the filter rates, expressed as gallons per hr. per sq. ft. of filtering area, at a temperature of −15° F., are 1 and 17, respectively. Whereas, at a solvent ratio of MEK to propane of 7:3 the filter rate is 37, increases of 1600% and about 120%, respectively.

A feature of the invention is that by the use of wax conditioners the filtration rate of the wax-solvent-oil admixture may be substantially increased. Added advantages accruing therefrom are that the yield of oil is increased by the use of a wax conditioner, filtration rate may be increased as much as several hundred per cent and the per cent yield of oil may be increased 4 to 5%. In general those which are well known in the art as pour-point depressants are also suitable as wax conditioners in the practice of the invention. These wax conditioners may be added in an amount up to about 1% by volume of the material to be dewaxed.

I claim as my invention:

1. The process of dewaxing a mineral lubricating oil distillate containing about 7.5% by weight of wax which comprises: cooling a liquid admixture of said wax-containing mineral oil distillate and a dewaxing solvent consisting essentially of a liquid mixture of methyl ethyl ketone and propane, the solvent to oil volume ratio being about 4:1 and the ketone to propane volume ratio being about 7:3, to precipitate solid wax from the oil, and separating the precipitated wax.

2. The process of dewaxing a substantially asphalt-free wax-containing mineral lubricating oil distillate which comprises: cooling a liquid admixture of said mineral oil distillate and a dewaxing solvent consisting essentially of methyl ethyl ketone and propane, the solvent to oil volume ratio being from about 4:1 to 6:1 and the ketone to propane volume ratio being from about 3:2 to 4:1, to precipitate solid wax from the oil, and separating the precipitated wax.

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