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METHOD FOR PRODUCING VERY LOW POUR OILS FROM WAXY OILS HAVING BOILING RANGES OF 680°-750° F. BY DISTILLING OFF FRACTIONS AND SOLVENTS DEWAXING EACH FRACTION

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The present invention relates to an improved hydrocarbon oil. More particularly, it pertains to the art of producing low pour point oils from waxy crudes.

Paraffinic oils are an excellent source of lubricating oil and hydraulic fluids because paraffins have a high resistance to oxidation and superior viscosity-temperature characteristics. On the other hand, they have the disadvantage of solidifying at lower temperatures. This has been attributed to the crystallization of wax as the temperature decreases. Various methods are known in the art for separating wax from oil, thereby rendering it satisfactory for use in cold areas. One such method, for instance, is chilling the waxy oil and filtering off the solid wax. One of the most popular ways of dewaxing paraffinic oils is known as solvent dewaxing. This comprises diluting the oil with a solvent, heating until complete solution is obtained, and then chilling until the desired amount of wax has crystallized out. The selection of the solvent is primarily based on its ability to give a clean separation between wax and oil. Depending upon the solvent used, the dewaxed oil will have a pour point from 5° to 40° F. above the dewaxing temperature.

The pour point of a waxy oil is defined as being 5° F. above the temperature at which the oil is a solid in a chilled glass tube of standard dimensions. The lowest temperature at which an oil pours is a reasonably good indication of the temperature below which the oil would not flow in an engine or pump. A satisfactory motor oil must have a pour point at least as low as the lowest temperature at which it is to be used.

Conventional methods of dewaxing have not been successful in producing an oil which pours at very low temperatures, and therefore it has been necessary to resort to the use of pour depressant additives. It is thought that these additives prevent solidification in cold weather by inhibiting wax crystal growth. It is common practice to employ both dewaxing procedures and pour depressants in winter oils. The addition of a pour depressant to a normally dewaxed oil does not prevent the formation of wax crystals which may interfere with the flow properties of the oil. Oils containing pour depressants often show a phenomenon known as "pour reversion" when subjected to a series of alternately very cold and mild temperatures. When this occurs the oil becomes solid at temperatures well above the original depressed pour point. The addition of a pour depressant to a moderately dewaxed paraffinic oil generally lowers the pour point to about —30° F. But this is not adequate in extremely cold areas which require very low pour point oils.

In order to produce oils that pour at extremely low temperatures it is necessary to add upwards to 75 volume percent naphthenic oils. These oils have very low pour points, but have the disadvantage of having a relatively low viscosity index. Viscosity index is a viscosity-temperature relationship of oils and is defined on pages 75 and 76 in Petroleum Refining Engineering by W. L. Nelson, 1936. Since low temperature fluidity is a function of both ability to flow and viscosity, the latter is an important factor. The most satisfatcory lubricants for cold weather use are those having not only low pour points, but high viscosity indices and therefore low viscosities at low temperatures.

An object of this invention is to disclose a method for producing paraffinic oils having extremely low pour points. This is accomplished without the necessity of adding naphthenic oils and, in some cases, pour depressants. Where pour depressants are used an even lower pour point is obtained than would be had by adding the same amount of additive to a conventional oil.

A further object of this invention is to permit dewaxing at higher than normal temperatures to obtain oils with normal pour points.

These objects are achieved by dewaxing selected narrow cuts of paraffinic oil distillate under the conditions hereafter described. The selection of the cut for a particular oil should be such that it results in a lubricating oil having a pour point at least about 10° F. below the dewaxing temperature. The dewaxing temperature chosen should substantially remove all the normal paraffin waxes and leave only a small quantity of isoparaffins of a narrow molecular weight range.

The fractionation of the waxy mixture is most advantageously effected by an efficient fractional distillation carried out in such a manner so as to produce a relatively sharp separation between the fractions, for example, a 15-plate column operating at a 5:1 reflux ratio. These waxy distillates are then dewaxed with a suitable solvent, such as methyl ethyl ketone, propane, methyl propyl ketone, diethyl ketone, methyl isobutyl ketone, acetone, toluene and many other dewaxing solvents and mixtures thereof.

The following experiment was carried out to demonstrate the effect of the width of the cut of a distillate boiling in its critical range, on the pour point of dewaxed oil. Leduc and Redwater (Western Canadian) crude oils were distilled under good fractionation conditions and a series of distillate oils were recovered having a viscosity of 95 seconds at 100° F. in the Saybolt Universal Viscosimeter. This series of samples having a variety of boiling ranges but about the same viscosity and mid-boiling point, were dewaxed at 0° F. with a solvent consisting of 60% diethyl ketone and 40% methyl propyl ketone, in the ratio of about one and one-half parts of solvent to one part of oil. The pour points of the resultant oils were compared.

TABLE I

Sample	A	B	C	D	E
Source of crude	Leduc	Leduc	Leduc	Redwater	Leduc.
Distillation:					
5% (° F. at atmospheric pressure).	607	675	705	720	741.
95%	870	810	810	765	753.
Range 5–95%, ° F	263	135	105	45	12.
Pour point, ° F	10	0	—10	—20	—30.

As the boiling range of the distillate is decreased, the pour point of the dewaxed oil likewise decreases. These data bring out the significance of the relationship of the boiling point range and the pour point of paraffinic oils in the critical boiling point range which for these oils is between 680° F. and 750° F. at atmospheric pressure. Thus in this range a dewaxed oil having a 5% to 95% range of less than about 45° F. has the desirable property of excellent fluidity at very low temperatures. Distillates having a boiling range of about 20° F. or less are preferred and those having a range of 10° F. or less are especially desirable. The basis for these preferences will be seen in the subsequent tables.

Another experiment was carried out to find which narrow cut distillate fractions would yield the lowest pour point oils. A wide boiling range distillate from Leduc crude oil, having a viscosity of 95 seconds at 100° F. in the Saybolt Universal Viscosimeter, was carefully fractionated into 10% distillation cuts in a 15 plate distillation column operating at a reflux ratio of 5:1. Each fraction was dewaxed at 0° F. with the same solvent and solvent to oil ratio used in the previous experiment.

TABLE II

	Distillate cut, percent	Fraction, ° F.	Δ,[1] ° F.	Viscosity of dewaxed oil at 100° F., sec.	Pour point, ° F.
(1)	0–10	675–685	10	58.4	−25
(2)	10–20	685–701	16	68.3	−50
(3)	20–30	701–711	10	79.0	<−50
(4)	30–40	711–729	18	85.0	−20
(5)	40–50	729–741	12	100.0	−30
(6)	50–60	741–753	12	112.8	−35
(7)	60–70	753–768	15	130.7	+3
(8)	70–80	768–779	11	156.0	−6
(9)	80–90	779–797	18	202.6	+5

[1] Refers to difference between the high and low figure in the fraction.

The same distillation and dewaxing procedures were repeated using a less viscous Leduc oil (50 seconds at 100° F.). The results are presented in the following table:

TABLE III

	Distillate cut, percent	Fraction, ° F.	Δ,[1] ° F.	Viscosity of dewaxed oil at 100° F., sec.	Pour point, ° F.
(1)	20–30	583–625	42	45.1	+5
(2)	30–40	625–656	31	52.6	+5
(3)	40–50	656–682	26	60.0	+5
(4)	50–60	682–704	19	73.6	−50
(5)	60–70	704–720	16	87.1	−30
(6)	70–80	720–749	29	109.8	−10

[1] See footnote to Table II.

These data demonstrate that dewaxing carefully fractionated, narrow boiling range paraffin oil distillates, for example having a Δ° F. of about 10° to 20° F. and boiling between about 680° to about 750° F., results in very low pour point oils that are quite suitable for use in cold areas. This unexpected decrease in pour point seems to occur in the greatest degree between about 685° and 710° F. in the case of Leduc crude oil. For this reason this boiling range is preferred for this crude. A boiling point between 701° and 711° F. is especially preferred, because this is the range the lowest pour point lube oil was obtained. The critical boiling range may be wider or narrower for other crudes but will always occur in the same temperature region as observed with Leduc and Redwater distillates. The preferred cut can only be found by dewaxing various narrow cuts to remove substantially all waxes and determining the pour points of the respective dewaxed oil fractions.

The following is a preferred embodiment of the invention. It will give a better understanding of the practice of the invention and indicate the correlations between the various operations.

Example 1

Leduc paraffinic oil having a viscosity of 95 seconds at 100° F. in a Saybolt Universal Viscosimeter was distilled, and the fraction boiling between 701° and 711° F. at atmospheric pressure was isolated. The distillate was then solvent dewaxed by conventional means at 0° F. using a 1.5 to 1 ratio of solvent to oil. The solvent consisted of 60% diethyl ketone and 40% methyl propyl ketone. The oil obtained poured at −50° F. without the addition of pour depressants or naphthenic oils.

Example 2

An oil distillate in the critical boiling range having a viscosity of 95 seconds was fractionated in a 15 plate column operating at a 5:1 reflux ratio into narrow cuts, phenol treated and dewaxed at 0° F. with 40% methyl propyl ketone and 60% diethyl ketone. Two volume percent of a methacrylate ester polymer having a molecular weight between 15,000 to 25,000 was added to some of the dewaxed fractions. The methylacrylate ester polymer is conventionally used as a pour depressant and viscosity index improver. The results obtained are set forth in the following table.

TABLE IV

Fraction, ° F.	Δ, ° F.	Viscosity of dewaxed oil at 100° F., sec.	Pour point, ° F.	Depressed pour point, ° F.
(1) 650–670	20	54.1	+1	−30
(2) 670–685	15	65.3	−25	−50
(3) 685–700	15	67.1	−45	−60
(4) 700–705	5	74.3	−30	----------
(5) 705–715	10	75.3	−43	----------
(6) 715–720	5	80.1	−40	−50
(7) 720–730	10	88.5	−40	----------
(8) 730–739	9	90.1	−30	----------
(9) 739–740	1	96.9	−25	−60
(10) 740–745	5	101.6	−20	----------

The preceding experiment demonstrates the beneficial effect obtained when a combination pour depressant and viscosity index improver was added to the narrow cut lube oil disclosed in this invention.

A sample of distillate (1) in Table IV, boiling between 650° to 670° F. at atmospheric pressure was dewaxed at −10° F. with the same solvent and solvent to oil ratio used in Table IV. Instead of having a pour point of +1° F. as it did when dewaxed at 0° F., its pour point was −30° F. Another distillate boiling between 760° and 770° F., with a viscosity at 100° F. of 152.7 seconds and a pour point of +5° F. when dewaxed at 0° F., was dewaxed at +30 F. with the same solvent. Its pour point was +10° F. which is 20° F. below its dewaxing temperature. These results indicate that when the boiling points of narrow fractions are extended outside the critical range and the pour point advantage disappears for 0° F. dewaxing, there is still some advantage to be obtained by dewaxing the higher or lower boiling fractions at higher or lower temperatures respectively.

Furthermore, it has been found that blending these narrow cut distillates after phenol treating and dewaxing results in an oil with a lower pour point than the oil obtained when the same fractions are blended before phenol treating and dewaxing.

Table IV illustrates that lower pour points can be obtained with an equivalent amount of depressant when a specially dewaxed narrow cut oil having a critical boiling range is used intsead of conventional oil.

Other pour depressants and/or viscosity index improvers may be added in amounts up to about 3% by volume. For example, wax alkylated naphthalene, wax alkylated phenol, fumaric acid-vinyl ester copolymer and maleic acid-vinyl ester copolymer may be used.

It is understood that the ratio of solvent to oil may be varied over relatively wide ranges for the various operations, depending on the nature of the solvent, the types of waxes in the oil being treated and other factors. In general, for a given separation step, the ratio of solvent to oil may range from about 1:1 to 5:1.

Various modifications of the hereinabove described techniques that are known in the art may be utilized in the practice of the invention. Thus, the separation of wax from oil may be effected by pressure filtration, vacuum filtration and centrifugation.

What is claimed is:

1. A process for producing a low pour point oil which comprises distilling a wax-containing petroleum oil, recovering a fraction having a boiling range of less than about 20° F. and having initial and final boiling points within the range between about 680° F. and about 750° F. at atmospheric pressure, dewaxing said fraction at a temperature between about −10° F. and about +30° F. in the presence of a ketone dewaxing solvent, and recovering a dewaxed oil having a pour point at least about 20° F. below the dewaxing temperature.

2. A process as defined by claim 1 wherein said fraction has a boiling range less than about 10° F.

3. A process as defined by claim 1 wherein the initial and final boiling points of said fraction lie in the range between about 685° F. and about 710° F.

4. A process for producing a low pour point lubricating oil which comprises distilling a wax-containing petroleum

oil, recovering a plurality of distillate fractions having boiling ranges of less than about 20° F. and having initial and final boiling points within the range between about 680° F. and about 750° F. at atmospheric pressure, separately dewaxing each of said fractions at a temperature between about −10° F. and +30° F. in the presence of from 1 to 5 volumes of a ketone dewaxing solvent, and recovering dewaxed oil fractions having pour points at least about 20° F. below the dewaxing temperature.

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