United States Patent Office 2,786,015 Patented Mar. 19, 1957

2,786,015

MANUFACTURE OF LUBRICATING OILS

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No Drawing. Application January 16, 1952, Serial No. 266,789

8 Claims. (Cl. 196—18)

This invention relates to the preparation of lubricating oils, particularly to those exhibiting low pour-points. In one aspect this invention relates to the manufacture of Arctic oils, i. e. lubricating oils employed in internal combustion engines under extremely low atmospheric temperature conditions. In another aspect this invention relates to a process for solvent dewaxing an oil, employing a normally liquid ketone in conjunction with propane as an internal refrigerant, which process has the internal refrigeration advantage of propane dewaxing, and the advantage of the narrow differential between chilling temperature and pour-point, characteristic of dewaxing processes employing a normally liquid dewaxing solvent. In still another aspect this invention relates to a method for dewaxing a partially dewaxed oil, employing urea as a final dewaxing agent. In still another aspect this invention relates to a process for producing oils of very low pour-point, e. g. Arctic oils, without the need for extremely low solvent dewaxing temperatures required heretofore. In one aspect this invention relates to the production of low pour-point oils from a wax containing lubricating oil stock, dewaxing such a stock employing methyl isobutyl ketone together with propane as an internal refrigerant, as a dewaxing solvent, and then further dewaxing a resulting partially dewaxed and solvent-free oil, employing urea as the dewaxing agent.

In propane dewaxing of oils a solution of propane and a waxy oil is chilled, for example by vaporization of a portion of the propane, to cause precipitation of the amount of wax necessary to impart the desired pour-point to the recovered lubricating oil. The wax may be separated from the propane-oil solution, for example by filtration or settling. The propane is vaporized from the oil for recovery of the finished dewaxed oil. One undesirable feature of the propane dewaxing process is the necessity for chilling the propane-oil solution to a temperature well below the desired pour-point of the finished oil. For example, it may be necessary to chill a propane-oil solution to —40° F. to —60° F. in order to dewax a lubricating oil to a pour-point of 0° F. This large differential between chilling temperature and pour-point of the dewaxed oil militates against the use of propane as a dewaxing solvent in the production of oils having low pour-point. The spread between chilling temperature and pour-point is substantially unchanged for chilling temperatures as low as —100° F. A second difficulty of the propane dewaxing process is the tendency of a propane-oil solution to supercool with the attendant inconvenience in having to induce crystallization of the wax.

In ordinary solvent dewaxing, the oil is mixed with a normally liquid solvent, for example methyl isobutyl ketone, and the mixture is subsequently chilled to a temperature at which sufficient wax precipitates to yield an oil which, when separated from the precipitated wax and the solvent, has the desired pour-point. The temperature to which the solvent-oil solution must be cooled is approximately the desired pour-point temperature of the finished oil. Straight ketone dewaxing has the disadvantage of a lower heat transfer coefficient through the exchanger surface because of a wax layer, and has the further disadvantage that cooling to the dewaxing temperature cannot be effected by evaporation of the solvent.

In accordance with my invention, I have provided for the manufacture of low pour-point oils from wax-containing lubricating oil stocks, by partially dewaxing the said oil stock and then further dewaxing the resulting partially dewaxed oil, employing urea as a dewaxing agent. The partial dewaxing step is preferably effected employing as a dewaxing solvent a normally liquid ketone in conjunction with propane as an internal refrigerant, or if desired, employing a normally liquid dewaxing solvent, such as for example ketone-type solvents such as methyl isobutyl ketone, acetone-benzol mixtures, ester-type solvents such as butyl acetate, amyl acetate or the like, and a blend of such acetates with dichlorethyl ether, and the like. Depending on the desired ultimate pour-point of the oil to be treated, the wax-containing oil stock can be treated with a normally liquid ketone in conjunction with propane as an internal refrigerant as a dewaxing solvent, without the added treatment with urea, although I have found that, when employing urea in this manner, pour-points of from 10 to at least 20° F. lower are obtained, without the necessity of employing the low dewaxing temperatures ordinarily required when producing oils of comparably low pour-point by solvent dewaxing. My invention is accordingly applied advantageously to the production of Arctic-type lubricating oils, particularly when incorporating pour-point depressant agents with the final low pour-point oil product.

In accordance with one embodiment of this invention, a lubricating oil crude is distilled into a gas oil fraction, which is then distilled to produce a distillate lube-oil base stock. This latter stock is then solvent extracted employing a solvent such as for example phenol, furfural, or the like, from which extraction a solvent-free wax-containing raffinate is recovered. The said raffinate is then mixed with a normally liquid ketone, preferably methyl isobutyl ketone, generally in a volume ratio to the ketone within the limits of 0.25:1 to 1:1 although ratios outside this range are advantageously employed, as for example as low as 0.20:1 or lower and up to about 4:1 or higher, together with liquid propane generally in a volume ratio of propane to the ketone within the limits of 1:1 to 5:1. The desired dewaxing temperature is effected by vaporizing propane in the resulting admixture to provide the necessary chilling to that temperature. Chilling temperatures can be at 0° F. to —60° F. dependent on the desired extent of dewaxing. For preparation of low pour-point oils this latter dewaxing temperature may be within the limits of —20 to —40° F. or lower if desired. The resulting chilled oil admixture, contains precipitated wax and is filtered and the dewaxed oil is freed of solvent. The resulting dewaxed solvent-free oil has a pour-point generally from about —25 to about —45° F., often from —30 to —40° F.

In accordance with another embodiment, a partially dewaxed oil, such as the —25 to —45° F. pour-point oil above described, is treated by dewaxing with urea as a dewaxing agent, whereby the pour-point is reduced by an additional 10–20° F., without the necessity for employing a lowered dewaxing temperature. The temperature employed during the last said treatment, i. e. while employing urea as the dewaxing agent, is above the existing pour-point of the oil to be further treated, and can be as high as 100° F. if desired. Preferred temperatures employed during treatment with urea, as described, are from about 0° F. to about 70° F. In carrying out this embodiment, the weight ratio of urea to the partially dewaxed oil being treated is generally from 0.1:1 to 3:1,

In another embodiment, a wax containing raffinate as described above, as for example recovered from phenol extraction, is partially dewaxed employing a normally liquid dewaxing solvent followed by removal of resulting precipitated wax and solvent from the oil, and treatment of the partially dewaxed solvent-free oil with urea in the manner already described to improve the pour-point of that oil, i. e. to lower it to form the desired low pour-point oil.

Typical specifications of an Arctic oil are as follows:

Viscosity at 210° F. of 45 SUS (minimum)
Viscosity at —40° F. of 39,500 SUS (maximum)
Stable pour-point of —65° F.

Such oils have heretofore been prepared by blending substantial proportions of synthetic diester oils with a mineral oil base with subsequent addition of viscosity index improvers and pour-point depressants.

In treating the partially dewaxed oil with urea, higher temperatures, due to the instability of the urea-hydrocarbon complex, usually give lower yields while lower temperatures also give lower yields due to lower rates of reaction. To compensate for the lower rate of reaction at lower temperatures, it may be advisable to use an excess of urea in order to increase the rate of formation of addition compounds, or to increase the length of contact time, or both. For the production of automotive lubricants complete removal of the n-paraffins is not necessary and usually is even undesirable, so reasonable rates of complex formation are usually attainable by the use of an excess of urea.

The presence of an activator increases the rate of urea-hydrocarbon complex formation to a marked degree. The amount of activator used may vary over a relatively large range of concentration. However, excessive amounts of activator should be avoided. The urea and the activator may be added to the oil to be dewaxed as a saturated solution of urea in activator, as an activator-urea slurry or as solid urea merely wet with the activator. An excessive amount of activator is not desirable. Since the activators are solvents for urea, large amounts will decompose the addition product by dissolving the urea. Materials which may be used as such activators are such as methanol, ethanol, acetone, methyl ethyl ketone and low molecular weight ethers, such as dimethyl ether, diethyl ether, or methyl ethyl ether.

In carrying out one specific embodiment of this invention, the following sequence of operations is employed in order to arrive at an all-petroleum oil. (1) a solvent extracted raffinate derived from a distillate fraction segregated from the gas-oil fraction of a lubricating oil crude is dewaxed to obtain a low pour-point oil by dissolving one volume of oil in from 1 to 5 volumes of methyl isobutyl ketone or other suitable dewaxing solvent and 1 to 2 volumes of propane. The oil-solvent mixture is chilled in a conventional propane dewaxing plant by internal refrigeration and filtered with continuous rotary filters. The solvent-free dewaxed oil will have a pour-point of —30 to —50° F. depending on the filtration temperature. This compares with pour-points of 0 to —10° F. from conventional propane dewaxing. (2) Since it is necessary to produce a base stock with a pour-point well below —40° F., the oil from step (1) is treated with urea in the presence of a suitable activator solvent system such as methanol or methyl-isobutyl ketone-water. Since the dewaxing in step (1) is non-selective, straight chain paraffins still remain in the oil and can be removed with urea at room temperature. This treatment will further lower the pour-point of the oil from 15 to 20° F. resulting in base stocks of —45 to —70° F. pour-point. Exhaustive urea treatment of the original waxy stocks can reduce the pour-point only to about —30° F. (3) The base stock from (2) is adjusted with respect to viscosity with a V. I. improver such as Acryloid 150 [1].

[1] Polymerized cetyl or lauryl methacrylate.

This invention is illustrated by way of the following examples:

EXAMPLE I

Several wax-containing oil stocks were dewaxed to produce low pour-point oils, employing methyl isobutyl ketone in conjunction with propane as an internal refrigerant, as summarized in the following tabulation (Table I).

Table I

Oil Charge	Filtration Temp., ° F.	Ketone[4]/Oil, Volume ratio	Propane/Oil (Cold), Volume	Wax Yield, Wt. Percent	Pour-Point Dewaxed Oil, ° F.	Pour-Point of Oil Charge, ° F.
A[1]	—53	2.0	1.69	17.0	—30	65
B[2]	—10	2.0	0.71	32.4	—5	>75
C[3]	—10	2.0	4.3	10.1	+15	70

[1] Close cut Mid-Continent solvent extracted raffinate, 36.7 SUS @ 210.
[2] Mid-Continent solvent extracted raffinate, 100 SUS @ 210 F.
[3] Mid-Continent solvent extracted raffinate, 42 SUS @ 210 F.
[4] Methyl isobutyl ketone.

EXAMPLE II

375 pounds of a gas oil obtained from a Mid-Continent crude oil was vacuum distilled to produce overhead distillate fractions 1–19, each roughly 4 volume per cent of the charge. Fractions 16–19 and bottoms product, recovered from the vacuum distillation are characterized by the following tabulated data (Table II).

Table II

Fraction No.	Weight, Lbs.	Vol. Percent of Gas Oil Charge	Viscosity at 100° F., SUS	Specific Gravity 60/60 F.
16	13.92	3.7	57.51	0.8692
17	14.24	3.8	59.64	0.8697
18	14.28	3.8	61.04	0.8697
19	0.98	0.3	60.69	0.8686
Bottoms	118.52	31.2	86.21	0.8751

These fractions (16–19 and bottoms) were blended to produce a "base oil," as indicated in the following tabulation (Table III).

Table III

Fraction No.:	Pounds added to blend
16	9.28
17	9.50
18	9.52
19	0.65
Bottoms	79.00

The base oil of Table III was phenol-water extracted in a counter-current flow extraction column. Extraction conditions employed and raffinate inspection data are tabulated as follows (Table IV).

Table IV

OPERATING CONDITIONS

Temperatures: (° F.)	
Top column	182
Phenol outlet	185
Bottom separator	158
Oil inlet	170
Water inlet	102
Duration of run, hours	9.667

Feed rates: (gals./hr.)

Phenol at 140° F	3.515
Oil at 60° F	1.168
Water at 60° F	0.292
Total feed	4.975
Phenol to oil ratio (volume)	3.01
Water to phenol ratio (volume)	0.083

INSPECTION DATA

Raffinate oil:

Gravity, API	36.7
Specific gravity 60/60 F	0.8415
Viscosity at 100 F., SUS	68.71
Viscosity at 210 F., SUS	36.51
Viscosity index, kinematic	112
Viscosity gravity constant at 210 F	0.797
Refractive index at 70 C	1.4450
Pour point, F	65

EXAMPLE III

Various samples of the raffinate oil of Table IV were partially dewaxed, employing methyl isobutyl ketone as a dewaxing solvent, in conjunction with propane as an internal refrigerant. The resulting solvent-free partially dewaxed oil was then treated with urea, i. e. "urea-dewaxed." Data pertinent to these dewaxing steps are tabulated as follows (Table V).

Table V

Volumes of MIBK [2] Per Volume of Oil	Volumes of Propane Per Volume of Oil	Filtration temperature, F [3]	Pour Point of Dewaxed Oil, F	Pour Point of Urea Treated [1] Dewaxed Oil, F
4.0	1.3	−53	−30	−45
4.0	2.7	−53	−25	−40
2.0	3.6	−53	−25	−40
1.0	—	−65	−45	−60
2.0	1.7	−53	−30	−45

[1] Activator was 5 ml. of methanol per gram of oil. Urea to oil ratio was 2.0 by weight. Urea treatment was effected with constant agitation at 70° F. for 1 hour.
[2] Methyl isobutyl ketone.
[3] Estimated.

EXAMPLE IV

Two samples of the raffinate oil of Table IV, were partially dewaxed employing methyl isobutyl ketone as a dewaxing solvent. The resulting solvent-free partially dewaxed oil was then treated with urea, i. e. "urea dewaxed." Data pertinent to these dewaxing steps are tabulated as follows (Table VI).

Table VI

Volumes of MIBK [1] Per Volume of Oil	Filtration Temperature, F.	Pour Point of Dewaxed Oil	Pour Point of Urea Treated [2] Dewaxed Oil
4	−80	−70	
4	−60	−45	−65
4	−50	−35	−55

[1] Methyl isobutyl ketone.
[2] Activator was 5 ml. of methanol per gram of oil. Urea to oil ratio by weight was 2. Urea treatment effected with constant agitation at 70° F. for 1 hour.

Reasonable variation and modification are possible within the scope of the foregoing disclosure and the appended claims to the invention, the essence of which is a method for producing low pour-point oils, e. g. Arctic oils, by dewaxing a wax-containing oil, employing a ketone-propane mixture, preferably methyl isobutyl ketone-propane, thereby providing a process having the internal refrigeration advantage of propane dewaxing and as a further advantage the narrow differential between chilling temperature and the pour-point characteristic of dewaxing processes employing normally liquid solvents; or by dewaxing a wax-containing lubricating oil stock employing as a dewaxing solvent a normally liquid solvent, such as a ketone, preferably methyl isobutyl ketone, in conjunction with propane as an internal refrigerant, so as to provide a partially dewaxed oil, followed by further treating a resulting solvent-free dewaxed oil with urea at a temperature not lower than the pour-point of the oil treated and as high as 100° F. if desired, thereby further reducing the pour-point by about 10–20° F. The low pour-point oils of the process of this invention can be incorporated with selected pour-point depressants, when desired, and/or with selected viscosity improvers.

I claim:

1. In a dewaxing process in which a lubricating oil stock is partially dewaxed in a first dewaxing step and then the partially dewaxed oils is dewaxed in a second dewaxing step comprising admixing the partially dewaxed oil with urea at a temperature in the range of 0 to 100° F. to form a precipitated urea-hydrocarbon complex, separating said complex from the last said admixture and recovering an oil having a low pour-point, the improvement which comprises conducting said first dewaxing step by forming an admixture of said lubricating oil stock with methyl isobutyl ketone and with liquid propane, said admixture having a volume ratio of said oil stock to said ketone within the limits of 0.20:1 to 1:1 and a volume ratio of said propane to said ketone within the limits of 1:1 to 5:1, chilling the resulting admixture to a subatmospheric temperature within the range of 0 to −60° F. by vaporizing propane therefrom so as to thereby precipitate wax from the oil component to partially dewax said oil, and separating the precipitated wax from said admixture.

2. In a process for producing an Arctic-type oil comprising the steps of solvent extracting lubricating oil to remove naphthenic components therefrom in the extract, partially dewaxing the resulting wax-containing raffinate in a first dewaxing step, and dewaxing the resulting partially dewaxed raffinate in a second dewaxing step comprising admixing the said partially dewaxed raffinate with urea in a weight ratio of 0.1:1 to 3:1, maintaining the last said admixture at a temperature in the range of 0 to 100° F. whereby urea forms a complex with wax components in said raffinate contacted therewith, separating said complex from the last said admixture, and recovering an Arctic oil having a low pour-point, the improvement which comprises conducting said first dewaxing step by forming an admixture of said wax-containing raffinate with methyl isobutyl ketone and with liquid propane, said admixture having a volume ratio of said oil stock to said ketone within the limits of 0.20:1 to 1:1 and a volume ratio of said propane to said ketone within the limits of 1:1 to 5:1, chilling the resulting admixture to a subatmospheric temperature within the range of 0 to −60° F. by vaporizing propane therefrom so as to thereby precipitate wax from the oil component to partially dewax said oil, and separating the precipitated wax from said admixture.

3. The process of claim 2 wherein a liquid activator is employed in conjunction with said urea to increase the rate of urea-hydrocarbon complex formation.

4. The process of claim 3 wherein said activator contains said urea in solution therewith.

5. The process of claim 3 wherein said urea is initially associated with said activator as an activator-urea slurry.

6. The process of claim 3 wherein said urea is wet with said activator.

7. The process of claim 2 wherein, subsequent to separating the said complex from the said admixture containing same, a pour point depressant is added to the said oil in an amount sufficient to further reduce the pour point of said oil.

8. The process of claim 2 wherein, subsequent to separating the said complex from said admixture containing same, a viscosity improvement agent is added to the said

oil in an amount sufficient to further decrease the viscosity of said oil.

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