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DEWAXING SOLVENT

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ABSTRACT OF THE DISCLOSURE

The invention relates to the dewaxing of lubricating oils. More particularly, it relates to the formation of low pour point lube oils which may be utilized in cold climates. These lube oils are produced when wax is removed from the lube oil by means of an autorefrigerative dewaxing solvent combining an olefin and a polar electron acceptor. The removal of waxes by means of these compounds results in the creation of a lube oil which has a low pour point.

DESCRIPTION OF THE PRIOR ART

Two types of crude oils are normally utilized in the manufacture of lubes and specially oils, namely, paraffinic crudes and naphthenic crudes. Paraffinic crudes are generally used in the production of high quality motor oils, aviation oils, turbine oils and hydraulic oils. The paraffinic crudes produce lubricating oils with a relatively high viscosity index. However, the waxy constituents present in these crudes confer upon the libricating oil products excessively high pour points and cloud points. It is essential that these waxy constituents are removed in order to improve the pour point and cloud point of the oil. When utilizing paraffinic lubricating oil particularly in cold climates, such as those found in Canada and the northern sections of the United States and Europe, it is essential to reduce the pour point so that the lubricating oil may flow freely and perform the function for which it is intended, i.e., friction reduction. Low cloud points which generally go along with low pour points are required to gain customer acceptance of the oil although cloud point is not usually a critical performance characteristic of the oil.

Naphthenic crudes are generally used to make a variety of industrial and process oils which do not require high viscosity indices. These oils are used for such purposes as diesel engine lubricants, transformer oils and spray oils. The natural pour point of these oils is low enough so that dewaxing is not generally required. However, the higher viscosity naphthenic lubes usually require treatment in a dewaxing plant to reduce cloud point to acceptable levels.

Traditionally, the waxy oil and the solvent are heated to a temperature sufficiently high to secure a single phase of substantially completely miscible ingredients. The waxy mixture is then chilled in order to precipitate wax particles or crystals from the solution. The chilled mass is filtered in order to segregate the wax particles and further treated to recover the dewaxing solvent. This process has generally been effective to the extent that it is capable of producing lube oils which have a lower pour point. However, conventional propane dewaxing, which is one of the most widely used dewaxing processes, is limited in that safety hazards prevent the production of lube oils having a pour point lower than about 10° F. In recent years, there has been an increasing demand for lube oils which pour at or below 0° F. As mentioned previously, the main limiting factor determining the resulting pour point after a dewaxing step is the filtration temperature at which the lube oil is dewaxed. When utilizing conventional autorefrigerative propane dewaxing, the minimum chiller temperature which may be utilized is —44° F. which is the normal boiling point of propane. Filtration temperatures are usually 2°–4° F. higher than the chiller temperature, so that the minimum practical filtration temperature is about —40° F. Product pour points are usually about 50° F. higher than filtration temperatures. This means that conventional propane dewaxing is substantially limited to a minimum product pour point of about 10° F. It was thought to utilize lower chilling temperatures which can be obtained by operating at subatmospheric pressure to reduce the boiling point of propane. However, this type of low pressure operation is extremely hazardous since air leakage into the vacuum system containing puopane vapor can produce an explosive mixture. Consequently, there has been little or no use of this technique because of the accompanying danger.

Propane is widely used as a dewaxing solvent since it also may be used as an autorefrigerant. That is to say, propane has a dual function; acting as an oil solvent or diluent and chilling the lube oil mixture. Typical of many U.S. patents disclosing this propane dewaxing technique is U.S. 3,291,718. Indicative of those patents which make use of ketone as a dewaxing solvent is U.S. 3,192,125.

BRIEF SUMMARY OF THE INVENTION

According to this invention, the problems associated with obtaining low pour point oils have been solved. It has unexpectedly been discovered that by combining a designated olefin and polar electron acceptor, lubricating oils and specialty oils may be dewaxed to a point where they will pour readily at temperatures of below 0° F., i.e. —5° to —20° F. Additionally, higher filter temperatures than those traditionally associated with propane dewaxing may effectively be utilized with this mixture. Other advantages of this technique include substantially higher filter rates than with propane alone, also reduced refrigeration compression since the filter temperature for a given pour point is higher than for propane.

Lubricating and specialty oils which boil in the range of about 400° to 900° F. initially and 600° to 1050+° F. finally, may effectively be treated with the process of the instant invention. The purpose of the olefin-polar electron acceptor mixture is to serve as a solvent for the oil as an anti-solvent for the wax and also to chill the mixture by autorefrigeration. The removal of these waxes serves to substantially lower the pour point of the oils.

The preferred olefins are those having 2 to 5 carbon atoms, most preferably propylene and butylene. A wide variety of polar electron acceptors may be utilized; it is preferred to use those readily available polar electron acceptors which include nitriles, SO_2 and its derivatives, nitroalkanes and ketones. The mixture comprises about 90 to 40 wt. percent of the olefin and about 10 to 60 wt. percent of the polar electron acceptor. The mixture is added in the liquid phase; the oil is also maintained in the liquid phase. Temperatures at which the liquid mixture may be added vary between 50° and 150° F. and pressures of 50 and 300 p.s.i.a. for the whole mixture including wax and oil, may be utilized. Following the dissolution and autorefrigeration with the mixture of an olefin and a polar electron acceptor, the oil is filtered and a substantially dewaxed oil is recovered which may pour between a temperature of 0° and —20° F. depending on the filtration temperature.

DETAILED DESCRIPTION OF THE INVENTION

In more detail, waxy oil feed, boiling between 700° and 1025+° F. initially and finally between 750° to 1050+° F. which may previously have been subjected to solvent extraction with a suitable solvent such as phenol, furfural, nitrobenzene or other well-known solvent for extraction and/or deasphalting as well as other procedures such as hydrotreating, is mixed continuously with the dewaxing solvent of the instant invention. Suitable olefinic autorefrigerants and solvents include ethylene, propylene, butylene or mixtures thereof with propylene being the most preferred olefin. The other part of the mixture will be a polar electron acceptor such as SO_2, nitroalkanes, ketones, such as acetone and nitriles. It should be emphasized that these are merely preferred polar electron acceptors and the invention is intended to include the various other polar electron acceptors which are satisfactory in varying degrees. A small quantity of dewaxing aid may also be added to the solvent mixture; this would include copolymers of ethylene and vinyl acetate; also condensates of chlorinated paraffin with naphthalene or benzene; also polyacrylates and polymethacrylates of higher aliphatic alcohols. The solvent mixture of the instant invention is added in an amount of 50 to 80, preferably 50 to 60 LV percent. The mixture is about 75 to 63 wt. percent olefin and about 25 to 37 wt. percent of polar molecule. Temperature during addition of the mixture to the oil is about 70 to 120° F. and pressure is about 50 to 200 p.s.i.a. The feed, with the mixture, is then heated to a sufficient temperature to dissolve any wax crystals present; this temperature would approximate 110° to 200° F., preferably 140° to 180° F. The mixture is then sent to a feed retention drum to allow time for complete solution of all wax crystals. Following this, it is cooled to about 50° to 100° F., preferably 70° to 90° F. The feed is next sent to a warm solution drum from which it may be charged to batch chillers. In the chiller, the temperature is gradually dropped to about −25° to −35° F. by vaporizing at least a portion of the solvent mixture. In the preferred case, propylene will be utilized so the invention will be described in terms of this particular olefin; it should be emphasized that there is no intent to exclude the other olefins mentioned in this case. The cooling takes place at a rate of about 1° to 15° F. per minute or an average of about 6° F./minute. The latter part of the autorefrigerative chilling operation is carried out at a pressure of about 100 to 50 p.s.i.g. A plurality of chillers is utilized so that while one chiller is in the chilling operation, another chiller may be emptied and filled for the next operation. The filter feed drum receives the chilled batches from the chiller and in turn feeds one or more rotary filters. The temperature at which the solution is to be filtered is indicative of an important aspect of the instant invention. Traditionally, when utilizing propane alone as a dewaxing solvent, temperatures for filtration varied between −30° and −40° F. and this would result in oils having a pour point of +10° to 0° F. Utilizing the process of the instant invention, filtration may take place at a temperature of −25° to −35° F. with resulting oils having a pour point of 0° to −10° F. The percentage of feed removed as slack wax is about 20 to 60% by weight. The percentage of dewaxed oil obtained will vary between 40 and 80 wt. percent. The dewaxed oil passes through the filters is collected. The filtered wax and the dewaxed oil are separately heated to recover solvent therefrom.

The hydrocarbon fraction which may be treated by this process to produce an improved lube oil will have a boiling range with an initial point between 650° and 1025+° F. and a final point between 750° and 1050+° F. A typical fraction will have an initial boiling range of 700° to 780° F. and a final boiling range of 750° to 850° F. Suitable sources for this hydrocarbon fraction include the following crudes: Aramco, Kuwait, Panhandle, North Louisiana, Tijuana Medium, etc. Pressure within the dewaxing zone will vary between 0 and 20 p.s.i.g., preferably 2 and 10 p.s.i.g. The chilling time in the dewaxing zone will vary between 20 and 60 minutes, preferably 40 and 50 minutes. Using the process of the instant invention, lube and specialty oils may be obtained which have

a pour point of 0° to −15° F. The cloud point of the lube oils obtained is also superior to the cloud points obtained by the existing techniques. They generally will be 5° to 10° F. higher than the pour point of 0° to −15° F. as defined above. Aside from producing lower pour and cloud points, this invention also presents other advantages over existing techniques. Extremely low cost is required to adapt an existing propane dewaxing plant to this process and a grass roots application of the instant process would not require significantly more expenditure than the traditional propane dewaxing plant. Additional advantages of this invention are as follows. Higher filter rates are obtained than with propane alone. The increase depends on the polar solvent used, the stock and the dilution. Lower power requirements, higher temperatures and hence less refrigeration compression for a given pour point represent other advantages.

Although there is no intent to be bound by any particular mechanism, the following explanation is offered for the operation of the instant invention. Theoretically, it appears that the Lewis acid-base interaction of propylenes pi electron system with a polar electron acceptor such as acetone results in a charge-transfer complex whose stability increases as temperature is lowered. Consequently, liquid/liquid miscibility of the ternary oil/propylene/polar acceptor system is greatly enhanced at lower temperatures while wax solid/liquid solubility appears to be largely unaltered. Absence of this interaction in a propane system causes the undesirable precipitation of two liquid phases as well as wax on cooling.

The general effectiveness of the polar additive is probably related to the stability of its charge-transfer complex with the olefin. On this basis, it may be assumed that the more stable the complex formed, the more effective the reduction in pour point. Acetone is particularly good for the purpose intended because it is readily available, cheap and forms a stable complex.

The most obvious use for this invention would be to dewax lubricating and specialty oils. However, it is also intended to be within the scope of the instant invention to make use of it for removing wax from any petroleum derivative. Thus, substantially all hydrocarbons which contain wax may be treated by the instant process to remove the wax. It is also intended to be within the scope of this invention to make use of a mixture of olefin, polar compound and alkane. Particular alkanes which may be used to advantage with the olefins and polar compound are propane and butane as well as ethane. The mixture of olefins and alkanes will increase the volatility of the additive and thus allow one to achieve lower autorefrigeration temperatures.

EXAMPLE 1

In all of the following examples, the identical feedstream was utilized. This feedstream comprised a lube oil fraction having an initial boiling point of 675° to 725° F. and a final boiling point of 850° to 900° F. as well as the following characteristics outlined in Table I below.

TABLE I

Refractive Index, 60° C.	1.4599
Congealing point, °F.	96
Gravity, °API	33.2
Viscosity at 100° F. SUS	112.8
Viscosity at 210° F. SUS	41.03
VI (waxy)	118.4

Crystal modifier of the type and concentration used in propane dewaxing plants was used in the filter-rate studies. This was 0.05% (or in some instances 0.1% of a filter aid consisting of condensates of chlorinated paraffins with naphthalene.

Initially, various polar compounds were used in conjunction with propylene to determine the characteristics of the dewaxed oil which could be obtained. Propylene and the polar liquid in the particular quantity designated with each run comprises the additive. The total amount of lubricating oil was 100 grams, to this was added about 100 grams of additive comprising olefin and a polar component. Waxy oil, acetone and propylene were added, in that order, to the closed pressure vessel which was then heated to ensure miscibility and the contents were then cooled by scraped-surface heat exchange at a rate of about 2° F. per minute. Waxy oil, polar additive and propylene were added at ambient temperature to a chiller/filter pressure vessel and heated to about 100° F. corresponding to a pressure of about 160 p.s.i.g. (acetone as polar additive). After holding for about 15 to 30 minutes at 100° F. to ensure miscibility, the system was cooled at about 2° F. per minute, over a period of about 60 minutes to the filter temperature of —25° F. and pressure of about 30 p.s.i.g.

The following table, Table II, indicates the results which were achieved. It was established that using a filter temperature of —25° F., which would be unsatisfactory for a pure propane system, solid points of below 0° F. were consistently obtained.

TABLE II

Run	Polar molecule: Name	Polar molecule: Wt. percent*	Filter temp., ° F.	Dewaxed oil: Solid Pt., ° F.	Dewaxed oil: Cloud Pt., ° F.	Dewaxed oil: Visc. SUS/210	V.I.	Filter/solid differential T.°F.
1		0	−25	4	16			29
2	Acetone	23.4	−25	−4	12			21
3	do	31.5	−25	−6	8			19
4	do	32	−25		2	43.3	90	
5	do	32	−25	−6	8			19
6	do	32	−25	−8	8			17
7	do	32	−25	−6	12			19
8	do	34	−25	−8	10			17
9	do	37.5	−25	−10	0	43.4	90	15
10	do	42.5	−25	−8	8			17
11	Ethanol	22	−25	−4	14			12
12	do	34	−25	−2	10	43.2	90	23
13	do	41	−25	−10	4	43.2	88	15
14	SO_2	35	−25	−10	6	43.6	90	15
15	do	35	−25	−10	0			15
16	do	35	−25	−5	8			20

*Wt. percent of molecule in solvent.

Increased concentration of the polar additive seems to lower the pour point obtained. The most preferred additive would have about 25 to 37 wt. percent of polar additive and about 75 to 63 wt. percent olefin. Further, the three different polar additives tested, SO_2, ethanol and acetone, produced results which were substantially consistent with one another. Table II indicates that pour points below 0° F. as well as low cloud points may be achieved with the process of the instant invention. It should be noted that in the first run, in which propylene alone was utilized, a solid point of 4° F. was obtained. In all other instances, the solid point was below 0° F.

EXAMPLE 2

In this example comparisons were made between an olefin-polar electron system and a traditional propane system. The results obtained are indicated below in Table III.

TABLE III.—PROPYLENE/ACETONE (75/25) HAS AN ADVANTAGE OVER PROPANE

	Propane	Propylene/ acetone*
Solvent/oil (vol.) ratio	1.5	1.5
Filter temperature, ° F	−40	−39
Solid point, DWO, ° F	−5	−15
Filter temp./solid pt., differential, ° F	35	24
Filter rate, USG/ft.² hr	10	9.5

*75% propane, 25% acetone by volume.

Conditions:

- Cooling rate —2° F. per minute.
- Crystal modifier (chlorinated parafin/naphthalene condensation product) =0.1 wt. percent modifier.
- Quantity of lube oil 100 ml.
- Quantity of propane 150 ml.

- Quantity of propylene, acetone mixture 150 ml.
- Contact time at 100° F. =15 minutes.
- Cooling period at 2° F./min. —60–70 minutes.
- Contact time at filter temperature —5–10 minutes.

From the above table, Table III, it is apparent that the dewaxing solvent of the instant invention is superior to propane alone. Operating under identical conditions, a 0° F. lower pour point is obtained with the propylene-acetone mixture of the instant invention while operating so as to produce the same solid point gives a filter rate 50% higher than propane.

Although this invention has been described with some degree of particularity, it is intended only to be limited by the attached claims.

What is claimed is:

1. A dewaxing process for the recovery of low pour hydrocarbons which comprises contacting a liquid wax-containing hydrocarbon fraction with a liquid autorefrigerating dewaxing agent, said agent comprising an olefin selected from the group consisting of ethylene, propylene and butylene in combination with acetone, vaporizing at least a portion of said agent whereby at least a portion of said wax is precipitated from said hydrocarbon fraction, filtering said hydrocarbon whereby precipitated wax is removed from said hydrocarbon and recovering a hydrocarbon fraction with a lower pour point.

2. The process of claim **1** wherein said olefin is propylene.

3. The process of claim **1** wherein said contracting is carried out in the presence of a dewaxing aid.

4. A process for dewaxing hydrocarbons boiling in the lubricating oil and specialty oil range by contacting with an autorefrigerative dewaxing agent which comprises adding a liquid phase dewaxing agent to said oil, said dewaxing agent comprising a C_2–C_4 olefin in combination with acetone cooling said mixture by vaporizing at least a portion of said dewaxing agent to a temperature level wherein at least a portion of said wax precipitates, filtering said wax and recovering said oil with a substantially lower pour point.

5. The process of claim **4** wherein said mixture of dewaxing agent and oil is heated to a temperature of 100° to 175° F. prior to said chilling whereby substantially all wax present is liquefied.

6. The process for dewaxing a liquid wax-containing oil, said oil having an initial boiling point of 700° to 1025+° F. and a final boiling point of 750° to 1050+° F., in order to reduce the pour point of said oil which comprises admixing with said oil a liquid dewaxing agent, said agent comprising an olefin selected from the group consisting of ethylene, butylene, and propylene in combination with acetone autorefrigerating said mixture by vaporizing at least a portion of said dewaxing agent until a temperature of —25° to —35° F. is reached, filtering said mixture and recovering an oil having a reduced pour point.

7. The process of claim 6 wherein said chilling during said autorefrigerative step takes place at a rate of 1° to 15° F. per minute.

8. A process for dewaxing a lubricating oil in order to lower its pour point which comprises adding a liquid dewaxing agent to said lubricating oil, said dewaxing agent comprising 63 to 75 wt. percent of an olefin selected from the group consisting of ethylene, propylene, and butylene and a polar electron acceptor selected from the group consisting of nitriles, SO_2 nitroalkanes, ketones, and mixtures thereof, in the amount of 25 to 37 wt. percent, heating said mixture to a temperature of 100° to 175° F., chilling said mixture by autorefrigerating said olefin, at a rate of 1° to 15° F. per minute until a temperature of —25 to —35° F. is attained wherein a substantial portion of the wax present is precipitated, filtering said precipitated wax from said mixture and recovering a lube oil having a substantially lower pour point.

9. The process of claim 8 wherein propane is added to the dewaxing agent.

10. The process of claim 9 wherein said polar electron acceptor is acetone.

11. The process of claim 10 wherein said olefin is propylene.

12. A process for dewaxing a lubricating oil in order to lower its pour point which comprises adding a liquid

dewaxing agent to said lubricating oil, said dewaxing agent comprising 90 to 40 wt. percent of an olefin selected from the group consisting of ethylene, propylene, and butylene and a polar electron acceptor comprising acetone in the amount of 10 to 60 wt. percent, heating said mixture to a temperature of 100° to 175° F., chilling said mixture by autorefrigerating said olefin, at a rate of 10 to 15° F. per minute until a temperature of —25° to —35° F. is attained wherein a substantial portion of the wax present is precipitated, filtering said precipitated wax from said mixture and recovering a lube oil having a substantially lower pour point.

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