ABSTRACT

Lubricating oil fractions are dewaxed by contacting them with successive increments of cold solvent at a plurality of points along a vertical tower while maintaining a zone of intense agitation at each point of solvent injection so that substantially instantaneous mixing occurs at each point, continuing the chilling by means of cold solvent injection until a temperature greater than the filtering temperature but less than about 35°F. above the filtering temperature is reached and completing the cooling of the oil to the separation temperature in a scraped-surface cooler.
COMBINATION OF DILUTION CHILLING WITH SCRAPED SURFACE CHILLING IN DEWAXING LUBRICATING OILS

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to a dewaxing process for the preparation of high quality lubricating oils.

BACKGROUND OF THE INVENTION

This invention relates to the dewaxing of lubricating oils. It is known in the prior art to dewax petroleum oil stocks by cooling an oil/solvent solution in scraped surface exchangers before separating the crystallized wax from the oil by physical means. In this type process, the oil and selective solvent are admixed at a temperature sufficient to effect complete solution of the oil and its contained wax in the solvent. The extent of dilution is dependent upon the particular oil and the particular solvent employed and is adjusted to facilitate easy handling and optimum filtration rates. The solution is cooled at a uniformly slow cooling rate; e.g. 1–5° F./min. under conditions which are controlled so as to avoid any substantial agitation of the solution during precipitation of the wax. Notwithstanding the carefully controlled conditions used in this type process, there are several deficiencies which hamper successful commercial operation. Most significant among these deficiencies is the loss of good heat transfer due to wax deposition on the exchange surfaces. Such fouling has been repeatedly noted after short periods of operation; e.g. 24–48 hours. Associated directly with the loss of good heat transfer is the loss of careful control over the cooling rate and a corresponding loss of uniform crystal growth. This nonuniform crystal growth then results in lower filtration rates. The high pressure drop through the chilling section also reduces the maximum feed rate attainable. Physical mashing of the wax crystals by the action of the scrapers may also contribute to poor filtration.

The chilling must be continued until the desired separation temperature is reached. This temperature is governed by the “pour point” or solidification temperature of the dewaxed oil which it is desired to produce. For example, to make an oil of +10°F. “pour point” it is necessary to separate the crystallized wax from the chilled slurry of oil, solvent and wax crystals at 0° to 5°F., when using an MEK-MIBK mixture as the dewaxing solvent. This separation is normally accomplished using continuous rotary drum filters but other separation means such as centrifuges may be employed.

It is also known in the prior art to dewax petroleum oil stocks by cooling in scraped surface exchangers using an incremental solvent addition technique, prior to filtration.

In this technique the solvent is added at several points along the chilling apparatus. The wax oil is chilled without solvent until some wax crystallization has occurred and the mixture has thickened considerably. The first increment of solvent is introduced at this point and cooling continues. Each increment of solvent is added as necessary to maintain fluidity until the desired separation temperature is reached, at which point the remainder of the solvent desired for filtration is added. In this technique, which is in common industrial use, it is well known and has been repeatedly demonstrated that the temperature of each increment of solvent should be the same as those of the main stream at its point of addition. Having the solvent at a lower temperature causes shock chilling of the slurry at that point, with resulting formation of crystal fines and impairment of filter rate; having the solvent warmer throws an unnecessary additional load on the scraped surface chillers. It should be clearly understood that all the chilling of the slurry in this well-known process is accomplished through the walls of the scraped surface chillers, rather than by means of cold solvents. This process requires somewhat less of the costly scraped surface heat exchange than the first one cited, because less of the solvent chilling is done in scraped surface. Dewaxed oil yield is also higher on some stocks, but otherwise, it suffers from the same disadvantages previously cited.

In copending application Ser. No. 666,268 filed Sept. 8, 1967, now abandoned, there is proposed, in one embodiment of the invention, a method of dewaxing oils in which the oil is shock chilled by contacting it with a cold solvent at a plurality of points along a vertical tower while maintaining a zone of intense agitation at least a portion of the points of solvent injection such that substantially instantaneous mixing occurs at each point, i.e. within a second or less.

In this process which is known as “dilution chilling” substantially all of the chilling of the slurry is accomplished in the tower by the cold solvent. The intense agitation more than overcomes the well-known harmful effects of shock chilling and results in the formation of a wax slurry having a unique crystal structure with markedly superior filtering characteristics — a relatively high filter rate and good dewaxed oil yield. It is disclosed in Ser. No. 666,268 that the intense agitation is provided by mechanical mixers, driven by a variable speed mechanism.

In Ser. No. 666,268 it is believed to be inadvisable to use any scraped surface, indirect chilling along with the dilution chilling there described.

SUMMARY OF THE INVENTION

In accordance with the present invention it has now been found that superior results can be obtained by dilution chilling, according to the process of Ser. No. 666,268, from the cloud point to a temperature greater than the separation temperature of the wax and oil but less than about 40°F. above the separation temperature, followed by additional cooling, such as in scraped surface chillers, to the separation temperature.

This has a large practical advantage over dilution chilling all the way to the filtering temperature in that:

1. Since the temperature range over which the feed is chilled in the dilution chilling zone has been reduced by up to 40°F., preferably up to about 35°F., (a) either higher temperature solvent can be used in the chilling zone to maintain the same solvent/oil ratio or (b) the solvent/oil ratio can be reduced by maintaining the solvent temperature at the same level. In either case less refrigeration is required. 2. Since the chilling temperature range in the chilling zone has been reduced by...
40°, preferably 35°F., the capacity of the chilling zone can be increased by maintaining the same average chilling rate as that when chilling all the way to the filtering temperature in the chilling zone.

Consequently, the process provides not only more flexibility in the operation but also offers substantial savings in refrigeration requirements and reduces the load on solvent recovery equipment.

Thus according to this invention a waxy petroleum oil stock is introduced into a first chilling zone divided into a plurality of stages and is passed from stage to stage of the chilling zone. A dewaxing solvent is introduced into at least a portion of the stages and a high degree of agitation is maintained in at least a portion of the solvent-containing stages, thereby effecting substantially instantaneous mixing of the solvent and oil. The solvent-oil mixture is cooled as it progresses through the chilling zone to a temperature greater than the separation temperature ("separation temperature," as defined as the temperature at which the wax is separated from the oil such as by centrifugation or filtration and the like; but less than about 40°F. above said separation temperature, preferably less than about 35°F. above said separation temperature, thereby precipitating at least a portion of the wax from the waxy oil. The mixture is then withdrawn from the first chilling zone and introduced into a second chilling zone wherein it is cooled to the separation temperature, thereby precipitating a further portion of the wax from the waxy oil.

In one embodiment of the invention, the mixture from the second chilling zone is removed and is passed to a first separation zone wherein at least a portion of the wax is separated from the mixture at the separation temperature. The separated wax is then mixed with cold solvent and the resulting mixture passed to a second separation zone wherein at least a portion of the wax is separated therefrom. At least a portion of the latter solvent can then be recovered from the mixture and used in the first chilling zone.

In the first cooling operation, high levels of agitation are only required during the initial stages of crystal nucleation and growth. Once crystals of the appropriate size and shape have formed, the need for high agitation levels diminishes. It is noted, however, that high agitation levels may be used in each of the stages of the zone if so desired. The cooling zone may be of any shape with a vertical tower being preferred.

The second chilling operation may incorporate any conventional cooling process such as scraped surface chilling, autorefrigeration and the like; however, scraped surface chilling is preferred.

The separation zones referred to hereinabove may comprise any conventional separation apparatus such as filtration equipment, centrifuges and the like.

The extent of further chilling, after the dilution chilling operation is completed, is important. Thus, for example at a constant solvent/seed ratio the filter rate is not substantially impaired by scraped surface chilling over the final 40°F. to the filtering temperature. However, if the scraped surface chilling substantially exceeds the 40° range, there is a sharp drop off in filter rate, and the dewaxed oil yield is also impaired.

The combination of dilution chilling and conventional chilling preferably utilizing scraped surface chilling, reduces overall solvent circulation and refrigeration requirements without any penalty in performance as compared with dilution chilling all the way to filtering temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram of one method for carrying out the invention using two-stage filtration with recycle of secondary filtrate.

FIG. 2 is a flow diagram of another method for carrying out the invention using a single-stage filtration.

DETAILED DESCRIPTION OF THE DRAWINGS

Referring to FIG. 1, the oil stock to be dewaxed is conducted from the storage tank 1, through line 2, to the top of the vertical cooling tower, where it enters the first stage of the cooler 4(a). The selected solvent is passed from sorage tank 5 through line 6, through heat exchanger 7 and 8 where the solvent temperature is reduced to that sufficient to cool the oil to the desired temperature. Coolant enters the heat exchangers 7 and 8 through lines 24 and 25, respectively and leaves through lines 26 and 27. The solvent leaves the heat exchanger 8, through line 9, and enters manifold 10. The manifold comprises a series of parallel lines providing solvent inlets 11 to the several stages of the cooling tower 3. The rate of flow through each inlet is regulated by flow control means (not shown). The rate of solvent flow is regulated so as to maintain a desired temperature gradient along the height of the cooling tower 3.

The first portion or increment of the solvent enters the first stage, 4(a), of the cooling tower 3 where it is substantially instantaneously admixed with oil due to the action of the agitator 12(a). The agitator is driven by a variable speed motor 13 and the degree of agitation is controlled by variation of the motor speed, with due allowance for the flow rate through the cooling tower. The oil-solvent mixture may pass upwardly or downwardly through the cooling tower 3 (downward flow only has been shown). At various heights along the cooling tower, additional prechilled solvent is introduced to each of the several stages 4, through lines 11 so as to maintain substantially the same temperature drop from each mixing stage to the next and at the same time to provide the desired degree of dilution. It should be noted that any number of stages up to 50 may be employed; however, at least six stages is preferred.

The oil-solvent solution with precipitated wax passes from the final stage of the cooling tower through line 14 at a temperature no higher than 35°F. above the filtering temperature. At this temperature it passes to scraped surface chiller 15 where it is cooled to the filtering temperature. After reaching the filtered chilling temperature in the scraped surface chiller 15, the wax-oil mixture is passed by line 16 to primary filter 17 where the wax is separated from the oil. This filter is preferably of the conventional rotary type. Chilled solvent is applied as wash through line 18. Dewaxed oil is removed through line 19 and wax by line 20. This wax is mixed with additional solvent (15°-30°F. below temperature in filter 17) introduced through line 21 and passed by line 22 through filter 23. The filter cake is washed with cold wash solvent (15°-30°F. below temperature of filter 17) introduced through line 29 and is removed by line 30 to slack wax recovery. Impure solvent is removed through line 31 and recycled to line 9.

Referring now to FIG. 2 a simpler embodiment of the invention is presented in which the wax-oil mixture from the scraped surface chiller, flowing in line 16, is
subjected to only a single filtering step. Thus the oil-wax mixture is passed to filter 40 and the filter cake washed with solvent from line 41. The wax is removed through line 42 and dewaxed oil through line 43.

Any petroleum oil stock or distillate fraction thereof may be dewaxed by the process of this invention. In general, these oil stocks or distillate fractions will have a boiling range within the broad range of about 500°F. to about 1,300°F. The preferred oil stocks are the lubricating oil and specialty oil fractions boiling within the range of 550°F. and 1,200°F. These fractions may come from any source, such as the paraffinic crudes obtained from Aramco, Kuwait, the Panhandle, North Louisiana, Western Canadian, etc.

Any low viscosity solvent for oil may be used in the process of this invention. Representative of such solvents are the ketones having three to six carbon atoms, such as acetone, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) and the low molecular weight hydrocarbons such as ethane, propane, butane, propylene, and the like, as well as mixtures of the foregoing ketones and mixtures of the aforesaid ketones with aromatic compounds such as benzene and toluene. In addition, the halogenated low molecular weight hydrocarbons such as dichloromethane and dichloroethane and mixtures thereof may be used as solvents. Specific examples of suitable solvent mixtures are methylethyl ketone and methyl isobutyl ketone; methylethyl ketone and toluene; acetone and toluene; acetone and propylene, benzene and toluene, and dichloromethane and dichloroethane. The preferred solvents are the ketones. A particularly preferred solvent mixture is a mixture of methyl ethyl ketone and methyl isobutyl ketone or a mixture of acetone and propylene.

During the operation of the process of the present invention, the petroleum oil stock is fed to the cooling tower 3 at a temperature above its pour and cloud point. In the case of an oil fraction containing a relatively low amount of wax, the oil may be fed at ambient temperature. In the case of an oil containing a relatively large amount of wax an elevated temperature will be used. In general, the wax content of the oil feed will vary between 10% and 25% weight percent and the pour and cloud points will range between 70°F. and 150°F. and 75°F. and 155°F., respectively.

The solvent, or solvent mixture, will be prechilled to a temperature sufficient to permit cooling of the oil to the desired temperature. It will be apparent to those skilled in the art that the exact solvent temperature employed will depend upon the amount of oil to be cooled and the amount of solvent to be added to the oil; i.e., the degree of dilution which is sought during the filtration step. The prechilled solvent is added incrementally along the height of the cooling tower so as to maintain an overall average chilling rate below about 10°F./minute and preferably between 1°F. to about 5°F./minute. Since the tower consists of several equal sized stages the chilling rate increases from stage to stage. This is the ideal situation as the wax nucleation rate is minimized and the growth rate maximized in the critical early stages. In general, the amount of solvent added will be sufficient to provide a liquid/solid weight ratio between the range of 5/1 and 20/1 at the dewaxing temperature and a solvent/oil volume ratio between 1.5/1 and 5/1.

In general the degree of agitation must be sufficient to provide substantially instantaneous mixing, i.e., substance complete mixing of the oil-solvent mixture in one second or less. In this way, the deleterious effects of shock chilling are offset; the chilling rate is more readily controlled and increased filtration rates are obtained.

In one embodiment, the cooling tower of the present invention will be operated at a pressure sufficient to prevent flashing of the solvent. Atmospheric pressure is sufficient when the ketones are employed as solvents, although higher pressures may be used if desired; however, superatmospheric pressure is required when the low molecular weight hydrocarbons, such as propane, are employed.

EXAMPLE 1

Two feedstocks, Barosa 56 and MCT-10 (150 neutral) were each dewaxed in a series of runs with a mixture of methyl-ethyl ketone (MEK) and methyl isobutyl ketone (MIBK), cooling first in a dilution chilling tower to a series of temperatures varying from the filtering temperature to 40°F.–45°F. above the filtering temperature and then cooled to filtering temperature in a conventional scraped surface chiller. The variation in the dilution chilling tower outlet temperature was obtained by either (1) varying the solvent temperature in order to maintain constant solvent/feed ratio or (2) holding the solvent temperature constant and adding an additional amount of solvent at the filtering temperature to maintain constant solvent/feed ratio into the filters. The relative dewaxed oil filter rate was determined on each batch. The following data were obtained.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Barosa 56</th>
<th>MCT-10/100N</th>
<th>Waxy Distillate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent composition</td>
<td>63/37 MEK/MIBK</td>
<td>50/50 MEK/MIBK</td>
<td></td>
</tr>
<tr>
<td>Solvent/feed ratio</td>
<td>15</td>
<td>0 to 20</td>
<td></td>
</tr>
<tr>
<td>Tower outlet temperature, °F.</td>
<td>3.7</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Washing temperature, °F.</td>
<td>1.4</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Filtering temperature, °F.</td>
<td>15</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Relative DWO yield</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Relative DWO per</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

The above data clearly show that the amount of chilling accomplished in the dilution chilling tower must be sufficient to bring the temperature of the wax-oil mixture to within about 40°F. preferably 35°F. of the filtering temperature. Thus if the filtering temperature is 15°F., then the temperature of the wax-oil mixture withdrawn from the bottom of the dilution chilling tower must not be greater than about 55°F. If the filtering temperature is 6°F. then the outlet temperature must not be greater than about 40°F.
What is claimed is:

1. A method for dewaxing a waxy petroleum oil stock comprising introducing said waxy oil at a temperature above its cloud point into a first chilling zone divided into a plurality of stages, passing said waxy oil from stage-to-stage of said chilling zone, introducing a dewaxing solvent into at least a portion of said stages, whereby a solvent-waxy oil mixture is formed, maintaining a high degree of agitation in at least a portion of the stages containing solvent and waxy oil, thereby effecting substantially instantaneous mixing of said solvent and said waxy oil while cooling said solvent-waxy oil mixture as it progresses through said first chilling zone to a temperature greater than the temperature at which the wax is separated from the oil, i.e., the separation temperature, but less than about 40°F above said separation temperature, whereby a substantial portion of the wax is precipitated from said waxy oil under conditions of said high degree of agitation and forming a solvent-oil mixture containing precipitated wax, withdrawing said mixture containing precipitated wax from said first chilling zone, and cooling the same to the separation temperature in a second chilling zone while maintaining a low degree of agitation, relative to the agitation in said first chilling zone, thereby precipitating a further portion of said wax from said waxy oil and recovering a dewaxed petroleum oil stock.

2. The process of claim 1 wherein said oil stock is a petroleum oil fraction.

3. The process of claim 1 wherein said solvent/oil mixture is cooled to a temperature less than about 35°F above said separation temperature in said first chilling zone.

4. The process of claim 1 wherein the dewaxing solvent is a mixture of propylene and acetone.

5. The process of claim 1 wherein the dewaxing solvent is a mixture comprising methyl ethyl ketone and methyl isobutyl ketone.

6. The process of claim 1 wherein the dewaxing solvent is chosen from the group consisting of a mixture of (1) methyl ethyl ketone and toluene, (2) acetone and toluene, (3) acetone, benzene and toluene, and (4) dichloroethane and dichloromethane.

7. A method for dewaxing a waxy petroleum oil fraction comprising introducing said waxy oil at a temperature above its cloud point into a chilling zone divided into at least six stages, passing said waxy oil from stage-to-stage of said chilling zone, injecting a cold dewaxing solvent into said chilling zone at a plurality of spaced points along said chilling zone, whereby a solvent-waxy oil mixture is formed, maintaining a high degree of agitation in each of said stages thereby effecting substantially instantaneous mixing of said solvent and said waxy oil while cooling said solvent-waxy oil mixture as it progresses through said chilling zone to a temperature greater than the temperature at which the wax is separated from the oil, i.e., the separation temperature, but less than about 35°F above said separation temperature, whereby a substantial portion of the wax is precipitated from said waxy oil under conditions of said high degree of agitation and forming a solvent-oil mixture containing precipitated wax, withdrawing said mixture containing precipitated wax from said chilling zone and cooling the same to the separation temperature in a scraped surface chiller, thereby precipitating a further portion of said wax from said waxy oil, and recovering a dewaxed petroleum oil fraction.

8. The process of claim 7 wherein the dewaxing solvent is a mixture of methyl ethyl ketone and methyl isobutyl ketone.

9. A method for dewaxing a waxy petroleum oil stock comprising introducing said waxy oil at a temperature above its cloud point into a first chilling zone divided into a plurality of stages, passing said waxy oil from stage-to-stage of said chilling zone, introducing a cold dewaxing solvent into a plurality of said stages at a plurality of spaced points along said chilling zone, whereby a solvent-waxy oil mixture is formed, maintaining a high degree of agitation in at least a portion of the stages containing solvent and waxy oil thereby effecting substantially instantaneous mixing of said solvent and said waxy oil while cooling said mixture as it progresses through said chilling zone to a temperature greater than the temperature at which the wax is separated from the oil, i.e., the separation temperature, but less than about 40°F above said separation temperature, thereby precipitating a substantial portion of the wax from said waxy oil under conditions of high degree of agitation and forming a solvent-oil mixture containing precipitated wax, withdrawing said mixture containing precipitated wax from said first chilling zone and cooling the same to the separation temperature in a second cooling zone while maintaining a low degree of agitation, relative to the agitation in said first chilling zone, whereby precipitating a further portion of said wax from said waxy oil, withdrawing an oil-solvent mixture containing precipitated wax from said second cooling zone and passing said mixture to a first separation zone wherein at least a portion of the wax is separated from said mixture at the separation temperature, mixing said separated wax with additional cold solvent and passing the resulting solvent-wax mixture to a second separation zone wherein at least a portion of said wax and solvent are separated, and, thereafter, introducing at least a portion of said separated solvent into said first chilling zone.

10. The process of claim 1 wherein the solvent-waxy oil mixture in said first chilling zone is cooled at a rate of less than about 10°F per minute.

11. The process of claim 7 wherein the solvent-waxy oil mixture in said first chilling zone is cooled at a rate of less than about 10°F per minute.

12. The process of claim 9 wherein the solvent-waxy oil mixture in said first chilling zone is cooled at a rate of less than about 10°F per minute.

13. The process of claim 7 wherein the dewaxing solvent is a mixture of propylene and acetone.

14. The process of claim 7 wherein the dewaxing solvent is chosen from a mixture consisting of (1) methyl ethyl ketone and toluene, (2) acetone and toluene, (3) acetone, benzene and/or toluene, or (4) dichloroethane and dichloromethane.

15. The process of claim 9 wherein the dewaxing solvent is a mixture of propylene and acetone.

16. The process of claim 9 wherein the dewaxing solvent is chosen from a mixture consisting of (1) methyl ethyl ketone and toluene, (2) acetone and toluene, (3) acetone, benzene and/or toluene, or (4) dichloroethane and dichloromethane.