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SOLVENT DEWAXING

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The present invention relates to solvent dewaxing of oil and more particularly, to the manufacturing of low pour-test lubricating oils from wax-bearing mineral oils.

Broadly, the invention contemplates supplementing the product dewaxed mineral oil with specific soft wax fractions sufficient in amount to increase materially the yield and quality of product without altering the pour point or appreciably changing the cloud point.

Lubricating oils of low pour test, about 0° F., are produced from wax-bearing oils in the usual processes of solvent dewaxing by separating and removing crystallized wax from a chilled solvent-oil-wax mixture. In accordance with the present invention, it has been discovered, however, that specific soft wax fractions contained in the wax cake normally discarded and soluble in the dewaxing solvent at from 10 to 40° F. higher than the dewaxing temperature, but in no event above 25° F., are surprisingly compatible with the separated oil as regards pour test properties, and, in addition to effecting a material increase in oil yield, impart other valuable properties to the final product oil.

More specifically, the invention involves incorporating, in a low pour point oil, dewaxed at a temperature in the range from about -5° F. to -30° F., a soft wax fraction of the primary dewaxing operation which dissolves in the dewaxing solvent at temperatures about 10 to 40° F. higher than the dewaxing temperature, but never greater than a maximum of 25° F. Such soft wax fractions are compatible with the dewaxed product oil from the primary dewaxing step, without appreciable impairment of the low pour properties. Therefore, direct mixture with the dewaxed oil product swells the yield by an amount equal to the added fraction.

On the other hand, according to the preferred embodiment of the present invention, essentially the same result is realized by cycling the soft wax fraction to the charge to the primary dewaxing operation. Under such conditions, the major portion of the recycled fraction tends to pass into the filtrate to augment production, as above. In other words, it has been found that, following this procedure, a substantial portion of the desired soft wax fraction appears in the primary dewaxed oil stream.

Recycle of the soft wax fractions in this manner is advantageous in that it appears to effect an improved fractionation of the waxes so that the resulting oil contains only the desired portions of the soft wax. As a result, the yield of product oil tends to be augmented exclusively with that portion of the soft wax fractions desirable in accordance with the present invention.

It has been proposed to overcome the loss of product oil which tends to remain absorbed, by occlusion or entrainment in the wax cake, by the steps of repulping or reslurrying the oil-contain-

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ing wax cake, separating the slurry, and recycling the resulting filtrate to the dewaxing step. An essential element of this proposal involves carrying out the separation of the slurry at a temperature in the critical range of 30-35° F. It is said that recycle of the resulting filtrate to the dewaxing operation results in an oil-free primary wax cake, all of the oil passing off in the dewaxed oil filtrate. By way of contrast, it is shown that in the absence of such recycle, the wax cake contains 10-30% of oil.

However, this process does not result in incorporation of any appreciable portion of the recycled wax in the product oil filtrate. It accordingly results in a progressive buildup of wax in the system, necessitating periodic by-passing of the repulping operation, to disgorge the excess accumulation of wax.

The present invention, in sharp contrast to this prior proposal, provides a continuously operating process free from wax buildup as the result of selective incorporation of the recycled soft wax fraction in the primary filtrate. Therefore, the product oil, including that otherwise entrained in the primary wax cake, is additionally and substantially supplemented in accordance with the amount of soft wax recycled and caused to pass into the primary filtrate.

In carrying out this invention, a wax-bearing hydrocarbon oil is mixed with a solvent and the resulting mixture chilled to a dewaxing temperature, in the range of from about -5° F. to -30° F. to precipitate the solid hydrocarbons. For an oil of 0° F. pour point, the dewaxing temperature is about -15° F., and for a pour point of 5° F., is usually about -10° F.

The cold mixture is filtered to separate the crystallized waxes and the resulting cake is washed with additional solvent in a primary filter, advantageously of the rotating drum type, which produces a dewaxed filtrate and a filter cake of wax, usually containing a small amount of entrained oil.

The primary filter cake of wax is repulped or mixed with a further quantity of dewaxing solvent and separated at a temperature in the critical range from about 10 to 40° F. above the temperature of the primary dewaxing operation.

As above indicated, if primary dewaxing is carried out above -15° F., then the separation of the repulped wax cake must be lower than the upper limit of the 10 to 40° F. range of increase, because otherwise the retreatment temperature would exceed the critical upper limit of 25° F. At temperatures above 25° F., the wax fraction which passes off with the repulping solvent is no longer compatible with the primary filtrate and therefore, instead of passing into the primary filtrate, builds up in the primary dewaxing operation.

Therefore, at a temperature from 10 to 40° F. above that of primary dewaxing, but not greater

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than 25° F., the repulped wax, together with any small quantity of occluded oil is subjected to a secondary filtration, yielding a final filter cake of hard wax and a filtrate containing relatively soft wax fractions soluble therein at the secondary filtration temperature, together with essentially all the occluded oil.

Instead of simple repulping of the primary wax cake, it may be recrystallized by dissolving in the added solvent at a suitably elevated temperature, followed by a chilling to the range about 10 to 40° F. above the primary dewaxing temperature but not greater than 25° F., as above, and then subjecting the chilled mixture to secondary filtration. In other words, recovery of a secondary filtrate containing the desired soft wax fraction is dependent on the temperature at which the secondary filtration operation is carried out, as a result of the solubility of the wax in the solvent at that temperature. Therefore, similar broad general results are realized whether the recovery of the soft wax fraction is effected by recrystallization or simple repulping of the wax cake. Repulping, however, is advantageous in that a more effective separation is usually obtainable between the hard and the soft wax fractions.

As above intimated, the secondary filtrate containing the desired soft wax fractions is preferably passed continuously as a recycle stream to the primary dewaxing operation. The resulting primary filtrate is continuously subjected to treatment for the recovery of the dewaxed oil, as above. The dewaxed oil product yield is increased by an amount comparable to the amount of soft wax fraction returned from the secondary filtration, in addition to any recovered oil which may have been occluded in the wax cake.

Thus, in a typical operation, the present invention results in a yield increase of, for example, 1½ to 2 or 3 percent over the amount of desired low pour-test product otherwise recoverable without impairment of the desired properties. That is to say, the pour test remains the same as that of oil from the primary dewaxing without recycle of soft wax fractions.

An additional important advantage, however, resides in the fact that the components incorporated in the product oil by practice of the present invention are beneficial from the standpoint of stability and lubricating properties. For example, the oil containing added soft wax fraction in accordance with the present invention is substantially more stable than oil produced by simple dewaxing under the same conditions without return of the repulped filtrate. As a result, the requirement for stabilizing additive necessary to meet exacting lubricating oil stability requirements is substantially decreased.

The solvent used in carrying out the process is preferably of the selective type. By selective solvent is meant a solvent having a substantially complete solvent action upon the liquid hydrocarbon constituents of the oil at such temperatures. A mixture of aliphatic ketone, such as acetone, methyl ethyl ketone or methyl isobutyl ketone, and an aromatic hydrocarbon, such as benzol, or a mixture of benzol and toluol, may serve as solvent. Methylene chloride, per se, is also suitable.

Where a diluent type of solvent is employed, it may be a petroleum naphtha, natural gasoline or a mixture of light hydrocarbons, such as is derived from natural gasoline.

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The invention is particularly adapted to the dewaxing of wax-bearing oil containing wax which is precipitated therefrom in relatively pure form. Examples of such oils are distillates substantially free from naturally occurring wax crystal modifying substances which are derived from crudes such as Pennsylvania, East Texas, Rhodessa, paraffinous Venezuelan, etc. Such distillates contain 5 to 50% of wax by volume of the oil.

The temperature range of secondary dewaxing or filtration is critical from the standpoint that temperatures above the effective range result in a filtrate containing undesirable wax fractions which adversely affect the pour test properties of a dewaxed oil. Therefore, inclusion of these undesirable wax fractions in the final oil even in small amounts adversely affects its pour test. Even when recycled to the primary dewaxing operation, such fractions similarly tend to impair the oil product, and in addition, to build up in the system, overloading and adversely affecting the separation.

Unless the secondary dewaxing operation is carried out at least about 10° F. above the primary dewaxing temperature, there is no appreciable passage of the recycled wax fraction into the primary oil, and there is no determinable improvement in product oil quality.

To further illustrate the operation of the invention, reference will now be made to the accompanying drawing, showing a flow diagram of the present process.

A wax-bearing Pennsylvania oil having a Saybolt universal viscosity of about 45 seconds at 210° F. and containing about 12% wax by volume, is introduced from a source not shown through a pipe 10 leading to a chiller 12. Into the oil charge is introduced from pipe 13, a stream of secondary filtrate which will be hereinafter described.

A solvent liquid consisting of a mixture of about 40% methyl ethyl ketone and 60% benzol is, recycled from a recovery source, also to be further described, and passes through pipe 14 into the oil charge. The oil and solvent are mixed in the proportion of about one part of oil to about three parts of solvent per volume.

The resulting mixture passes to the chiller 12 where it is chilled to a low temperature, as for example, -16° F., in order to precipitate the solid hydrocarbons, and produce a product oil of about 0.0° F. pour test.

From the chiller, the cold mixture passes to a primary feed tank 15, from which it is conducted to a primary filter 17, wherein the solid hydrocarbons are removed as a filter cake of wax, producing a primary dewaxed filtrate drawn off through pipe 18 into primary filtrate receiver 19. The resulting filter cake is washed, in situ, with fresh solvent introduced via pipe 21, using, for example, about 0.5 to 1.0 volume of solvent to one volume of oil charge. The resulting filter cake, containing small quantities of adhering oil and solvent not removed by the washing step, is discharged into receiving and repulping section 22 of the primary filter in which it is repulped with an additional stream of solvent from branch pipe 24.

The repulping solvent in pipe 24 is advantageously at a temperature of around 45° F. as a result of passage through heat exchanger 26 and is added in sufficient proportions such that the final repulped wax-solvent mixture temperature approximates about +15° F. At this tempera-

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ture, the repulped wax cake moves through pipe 27 into secondary feed tank 28. Trim chillers or exchangers, not shown, may be employed where necessary to maintain the desired exemplary temperature of 15° F. in the feed tanks and filters. At this temperature, the mixture is fed to a secondary filter 30 to form a secondary hard wax cake and a secondary filtrate.

The secondary wax cake also is washed in situ with solvent from branch pipe 32, at a temperature controlled by exchanger 33 until it is substantially free from oil. The wash solvent may be employed in the proportion of about $\frac{1}{5}$ part of solvent to one part of original oil charged to the primary operation.

The secondary filtrate, which comprises, in part, wash filtrate, is drawn off through pipe 35 into secondary filtrate receiver 36, and from there, conducted all or in part through the aforementioned pipe 13 into the primary dewaxing stage where it is mixed with the wax-bearing oil and solvent, and introduced into the primary filter 17.

The primary filtrate in the receiver 19 passes through pipe 38 to a dewaxed oil recovery system 39, discharging the final dewaxed product oil as at 40. The solvent recovered in this operation discharges into aforementioned pipe 14 for recycle to the system. To this end, branch pipe 42 connects with the aforementioned washing and repulping solvent lines 21, 24 and 32, respectively.

The secondary wax cake is conducted similarly to a hard wax recovery system 43, discharging the final hard waxes at 44 and returning the separated solvent through pipe 45 into the solvent recycle line 42.

The secondary filtrate in receiver 36 is at a temperature around 15° F. and is mixed with the oil charge in the chiller 12 to maintain in the primary dewaxing step the temperature of about -16° F., which is that desired in order to produce a dewaxed oil having a pour test of about 0° F. and below.

Following is a table comparing the pour point and cloud point of the product dewaxed oil of the foregoing process A to that of an identical oil subjected to the same primary dewaxing treatment but without recycle of soft wax fractions from the primary wax cake B:

	Pour Point, ° F.	Cloud Point, ° F.
A.....	0	+5
B.....	0	+4

In addition, the operation results in a regular overall yield of product oil about 2% greater than that realized by simple primary dewaxing with recovery of any oil occluded in the primary wax cake.

Moreover, the amount of additive required to meet the same dewaxed oil stability specifications is only about half that required to stabilize the dewaxed oil from the primary filtrate when the repulped filtrate is not returned to the primary operation.

By way of explaining theoretically the passage of the recycled soft wax fraction into the primary filtrate, it is believed that this fraction is actually soluble, per se, in the primary dewaxing solvent at the separation temperature, but, nevertheless, is ordinarily caused to precipitate by association

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with the predominant, relatively hard wax crystals. The recycled soft wax, however, appears to raise the concentration of this fraction in the primary separator to a level greater than that which is precipitated by association with the crystallized hard wax. Therefore, the soft wax tends to remain in solution in the oil and pass off with the primary filtrate.

The dotted line portion of the flow diagram represents a modified alternative procedure wherein the soft wax fraction or any portion thereof is mixed directly with the dewaxed oil from the primary dewaxing operation. It contemplates diverting the secondary filtrate from line 13 into dotted line 45, through which the filtrate is introduced into a soft wax recovery section 46. Recovered solvent may be returned through line 47 into solvent return pipe 42. All, or any desired portion of the soft wax, preferably slurried in a small amount of accompanying oil, passes through pipe 50 directly into the dewaxed oil, being recovered through line 40. The soft wax slurry exhibits complete solubility in this oil and yields an oil mixture having essentially the desired low pour-test properties of the oil prior to admixture. Any portion of the soft wax not introduced into the dewaxed oil is discharged from the system through line 49.

Advantageously, recycle of the repulp filtrate to the primary dewaxing operation may be combined with the steps of soft wax recovery and incorporation in the product oil exemplified by the dotted line portion of the flow sheet. For example, a portion of the filtrate in line 13 may be withdrawn through line 45 for treatment, as above, while the remainder is recycled to primary dewaxing.

The operations may be variously modified, if desired. For example, it is possible, and it is frequently desirable, to recycle primary filtrate from the receiver 19 to the inlet of the primary filter in order to procure a liquid-solids ratio favorable for optimum filtration. Moreover, it is contemplated employing heat exchangers, where effective to realize maximum thermal efficiency; for example, it is advantageous indirectly to heat exchange the chilled primary filtrate at, for instance, -15° F., with the incoming oil charge in advance of chiller 12. As a further modification, it is advantageous to inject the solvent into the oil charge in incremental additions, preferably during the course of the chilling operation.

Moreover, as previously indicated, the repulping of the primary wax cake may take place at any desired temperature, followed by later chilling or other temperature adjustment to the range of secondary dewaxing.

Reference has been made to the dewaxing solvent mixture of methyl ethyl ketone, benzol and toluol. Also contemplated are mixtures of ketones and other aliphatic compounds, as well as other solvents composed of a wax antisolvent and an oil solvent.

It is contemplated that the solvent ratios, as set forth in the specific example above, may vary widely, in accordance with known practice, depending upon the nature and source of the wax-bearing oil undergoing treatment and the solvent employed.

Obviously, many modifications and variations of the invention, as above set forth, may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In the production of a low pour-test hydrocarbon oil from wax-bearing stock involving dewaxing said stock from a cold solution thereof in a dewaxing solvent, by steps comprising mixing the oil with a solvent having substantially complete solvent action upon the liquid hydrocarbon constituents of the stock at dewaxing temperature, chilling the mixture to a dewaxing temperature to crystallize waxes, and filtering the cold mixture in a filtration stage to produce a filtrate containing a product oil and a primary filter cake of wax substantially free from oil, the improvement which comprises separating from said primary filter cake a soft wax fraction by repulping said wax cake in said solvent at a temperature within the range from about 10 to 40° F. above said dewaxing temperature, but not in any event at a temperature greater than 25° F., and combining separated soft wax fraction with the dewaxed oil to yield an increased quantity of product oil of unaltered pour properties.

2. The method according to claim 1, wherein the primary dewaxing step is effected at a temperature in the range of about -5° F. to about -30° F.

3. In the production of a low pour-test hydrocarbon oil from wax-bearing stock involving dewaxing said stock from a cold solution thereof in a dewaxing solvent, by steps comprising mixing the oil with a solvent, chilling the mixture to a dewaxing temperature to crystallize waxes, and filtering the cold mixture to produce a primary dewaxed product oil filtrate and a primary wax filter cake, the improvement which comprises treating said primary wax filter cake with additional said solvent at a temperature within the range of from about 10 to 40° F. higher than said dewaxing temperature but not in any event greater than a temperature of 25° F., to separate therefrom an extract soft wax fraction, and continuously introducing separated soft wax fraction as a feed to said primary dewaxing operation thereby causing said soft wax fraction to pass into the primary filtrate to substantially augment the quantity of product oil without detracting from its pour properties.

4. The method according to claim 3, wherein the primary dewaxing step is effected at a temperature in the range of about -5° F. to about -30° F.

5. In the production of a low pour-test hydrocarbon oil from wax-bearing stock involving dewaxing said stock from a cold solution thereof in a dewaxing solvent, by steps comprising mixing the oil with a solvent, chilling the mixture to a dewaxing temperature to crystallize waxes, and filtering the cold mixture to produce a primary dewaxed product oil filtrate and a primary filter cake of wax, the improvement which comprises separating a mixture of primary filter cake with additional said solvent at a temperature in the range from 10 to 40° F. higher than said dewaxing temperature, but not, in any event, greater than a temperature of 25° F., to yield a filtrate containing a soft wax fraction soluble therein at said separation temperature, and continuously supplying separated soft wax fraction as a feed to said dewaxing operation thereby causing said soft wax fraction to pass into the primary filtrate to substantially augment the quantity of primary product oil without detracting from its pour properties.

6. The method according to claim 5, wherein the primary dewaxing step is effected at a tem-

perature in the range of about -5° F. to about -30° F.

7. In the production of a low pour-test hydrocarbon oil from wax-bearing stock involving dewaxing said stock from a cold solution thereof in a dewaxing solvent of the selective type, by steps comprising mixing the oil with the solvent, chilling the mixture to a dewaxing temperature to crystallize waxes and filtering the cold mixture to produce a dewaxed product oil filtrate and a primary filter cake of wax, the improvement which comprises repulping said filter cake with additional said solvent at a temperature in the range from 10 to 40° F. higher than said dewaxing temperature, but not in any event greater than a temperature of 25° F., separating from the repulped mixture solvent containing soft wax fractions of the filter cake filterable therewith at said repulping temperature, and supplying thus separated soft wax fractions as a feed to said dewaxing operation thereby causing said soft wax fraction to pass into the primary filtrate to substantially augment the quantity of dewaxed product oil without detracting from its pour properties.

8. The method according to claim 7, wherein the primary dewaxing step is effected at a temperature in the range of about -5° F. to about -30° F.

9. In the production of a low pour-test hydrocarbon oil from wax-bearing stock involving dewaxing said stock from a cold solution thereof in a dewaxing solvent of the selective type having substantially complete solvent action upon the liquid hydrocarbon constituents of the stock at dewaxing temperature, by steps comprising mixing the oil with the solvent, chilling the mixture to a dewaxing temperature to crystallize waxes, and filtering the cold mixture to produce a dewaxed product oil filtrate from which dewaxed product oil is recovered, and a filter cake of wax substantially free from oil, the improvement which comprises repulping said filter cake with additional said solvent at a temperature in the range from 10 to 40° F. higher than said dewaxing temperature, but not in any event greater than a temperature of 25° F., separating from the repulped mixture a filtrate containing soft wax fractions of the filter cake filterable therewith at said repulping temperature, and combining thus separated soft wax fractions with the dewaxed product oil to substantially augment the quantity of product oil without detracting from its pour properties.

10. The method according to claim 9, wherein the primary dewaxing step is effected at a temperature in the range of about -5° F. to about -30° F.

11. The method according to claim 1 wherein said wax bearing stock is substantially free from naturally occurring wax crystal modifying substances.

12. The method according to claim 3 wherein said wax bearing stock is substantially free from naturally occurring wax crystal modifying substances.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,229,659	Carr	Jan. 28, 1941
2,348,459	Engel	May 9, 1944
2,463,845	Backlund et al.	Mar. 8, 1949