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SOLVENT DEWAXING

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This invention relates to an improved method for effecting the removal of wax from waxy materials. More particularly, this invention relates to the solvent dewaxing of waxy materials, such as a waxy petroleum fraction. In accordance with one embodiment this invention is related to the solvent dewaxing or fractional crystallization of mixtures such as mixtures of fatty acids, vegetable oils, animal oils and fats, fish oils and the like.

In the solvent dewaxing of waxy materials such as mineral oils it is the practice to admix the waxy material to be dewaxed with a liquid dewaxing solvent and to cool the resulting admixture to a suitable low dewaxing temperature to precipitate substantially all of the waxy material. The resulting precipitated wax is then removed by filtration from the resulting dewaxed oil.

In many dewaxing plants the filtration step wherein the precipitated wax is separated from the dewaxed oil, is the critical operational step in the sense that the filtration operation is the limiting factor with respect to the capacity of the dewaxing plant. In many instances if the rate of filtration of the precipitated wax from the dewaxed oil is increased the plant capacity for the production of dewaxed oil can be proportionally increased.

Accordingly it is an object of this invention to provide an improved dewaxing process.

Another object of this invention is to provide an improved process for the solvent dewaxing of waxy mineral oils.

Still another object of this invention is to provide a method for increasing the dewaxing capacity of a dewaxing plant such as a plant for the dewaxing of waxy mineral oils, or a plant for the solvent fractional crystallization of fatty acids and/or their glycerides, such as vegetable oils, e.g. tung oil, soy bean oil, perilla oil, cotton seed oil, linseed oil, animal oils and fats such as lard, sperm oil, etc. and fish oils such as cod fish oil, herring oil, sardine oil, etc.

Yet another object of this invention is to provide a method for controlling the number and size of crystals such as wax crystals in a solvent dewaxing operation.

How these and other objects of this invention are accomplished will become apparent in the light of the accompanying disclosure. In at least one embodiment of the practice of this invention at least one of the foregoing objects will be achieved.

In accordance with this invention it has now been discovered that an improved solvent dewaxing or solvent fractional crystallization operation is obtained by shock chilling the waxy oil or mixture to be dewaxed or fractionated from a temperature just above the cloud point or initial haze temperature, to a temperature in the range 10–50 degrees Fahrenheit below said cloud point. Following the shock chilling operation the resulting chilled admixture is then cooled in the usual manner to the final dewaxing or crystallization temperature at which temperature the resulting precipitated solids, waxy material and the like, are removed by filtration.

More particularly, in accordance with this invention it has been discovered that an improved dewaxing operation is provided when a liquid waxy mixture, such as a waxy mineral oil, is cooled in the substantial absence of dewaxing solvent to a temperature at or just above the cloud point of said waxy mineral oil. The resulting cooled waxy oil is then shock chilled by directly admixing therewith cold dewaxing solvent. The amount and/or temperature of the cold dewaxing solvent which is directly admixed with the waxy oil during the shock chilling operation is such that the waxy oil in the resulting admixture of oil and dewaxing solvent is substantially instantaneously chilled from a temperature at or slightly above the cloud point of the oil to a temperature in the range 10 to 50 degrees Fahrenheit below said cloud point. The resulting chilled admixture is then gradually cooled, preferably in the presence of additional dewaxing solvent, to the usual dewaxing temperature, such as a temperature in the range 20° F. to −40° F., more or less, and the resulting precipitated wax separated by filtration.

Explanatory of the practice of this invention it is speculated that by shock chilling the waxy material undergoing dewaxing or fractionation, thereby subjecting the waxy material to a rapid initial chilling through a definite temperature range, control of the type of wax crystal formed as a result of this shock chilling is effected. It is also speculated that the number of wax crystals formed during this shock chilling operation is also controlled depending upon the extent of shock chilling, i.e. how far below the cloud point the temperature of the resulting admixture is after shock chilling. Accordingly, it is speculated, after the initial shock chilling has established the number and characteristic or type of wax crystals, the cooling of the resulting admixture comprising precipitated wax, waxy oil and dewaxing solvent can be continued in a normal and conventional manner to permit increasing the size of the individual wax crystals, already started or produced during the wax chilling operation without substantially increasing the number of wax crystals. More particularly, it is speculated that this subsequent cooling operation can be carried out at a rate low enough and adjusted to permit wax to accumulate on or to crystallize on the initially-formed wax crystals rather than to form new, smaller crystals as this subsequent cooling operation with consequent wax crystal formation or wax removal is continued.

As indicated, the practice of this invention is generally applicable to the dewaxing of mineral oils, such as waxy residual petroleum fractions or waxy distillate petroleum fractions. The practice of this invention is also applicable to the fractionation, by solvent fractional crystallization, of animal or vegetable fats or oils, wherein a fraction thereof is precipitated by cooling in the presence of a solvent and the resulting precipitated fraction separated by filtration.

The practice of this invention is generally applicable to any solvent dewaxing operation such as a propane dewaxing operation or the well known solvent dewaxing operation employing as the dewaxing solvent a mixture of a mineral oil solvent such as an aromatic hydrocarbon, e.g. benzene, toluene and the like, and a wax anti-solvent such as a normally liquid aliphatic ketone containing from 3 to 9 carbon atoms per molecule, e.g. acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl n-propyl ketone and the like. In this type of solvent dewaxing the dewaxing solvent would comprise a suitable aliphatic ketone and a normally liquid aromatic hydrocarbon in an amount in the range 20–80% and 80–20% by vol., respectively.

In the practice of this invention the material undergoing dewaxing or solvent fractional crystallization, just prior to shock chilling, is at a temperature at or just above the cloud point or initial haze temperature of said mixture, such as a temperature in the range 0–10 degrees Fahrenheit above said cloud point. By cloud point or initial haze temperature is meant that temperature at which crystals or precipitated solid material first begin to appear and to be observed, as by the observation of

a haze therein, in the mixture to be fractionated in the substantial absence of a solvent.

In the shock chilling step in the practice of this invention the temperature of the resulting admixture, waxy mixture and dewaxing solvent, after shock chilling is in the range 10–50 degrees Fahrenheit below the cloud point of the waxy material undergoing dewaxing. The shock chilling of the waxy mixture is carried out under conditions such that the temperature of the waxy material is substantially instantaneously reduced from a value at or just above the cloud point to a value in the range 10–50 degrees Fahrenheit below the cloud point. This is achieved in the practice of this invention by directly introducing into contact with the waxy mixture an amount of cold dewaxing solvent. The temperature of the dewaxing solvent and the amount of dewaxing solvent with respect to the waxy material to be shock chilled is adjusted so that substantially instantaneous cooling or chilling of the waxy material through or from the cloud point thereof to a temperature 10–50 degrees Fahrenheit and below is effected. It is pointed out that the lower the temperature of the dewaxing solvent employed in the shock chilling operation the less the amount of dewaxing solvent required to effect the desired shock chilling. This initial shock chilling of a given portion of the waxy mixture undergoing dewaxing is effected substantially simultaneously upon admixture of the cold solvent, or within a relatively very short time, dependent upon the time required to effect substantially complete admixture of the cold dewaxing solvent with the waxy mixture undergoing dewaxing, certainly not longer than about 30 to 60 seconds and usually in the range 5–20 seconds, more or less.

Following the shock chilling operation the resulting chilled admixture of waxy material, now containing some solids or solid waxy material precipitated therein, is gradually cooled in the conventional manner and in the presence of additional solvent, if sufficient solvent has not already been added during the shock chilling operation, to the final dewaxing temperature. This cooling of the waxy mixture together with dewaxing solvent, subsequent to the shock chilling operation, is carried out at a normal rate, such as a cooling rate in the range 0.3–3.0 degrees Fahrenheit, more or less, per minute. Upon reaching the final dewaxing temperature, such as a temperature in the range 20° F. to −40° F., the resulting admixture of precipitated wax, dewaxing solvent and dewaxed oil is subjected to filtration, preferably by means of a vacuum rotary filter wherein the admixture of oil, dewaxing solvent and solid wax is drawn through a filter medium, the solid wax being retained on the filter medium, washed, dried and removed in a continuous manner.

The following tests are illustrative of the practice of this invention.

In test No. 1 portions of a waxy petroleum distillate fraction having a cloud point or initial wax haze temperature of about 50° F. were cooled from about 60° F. to about 52° F., about the cloud point of 50° F. in the substantial absence of dewaxing solvent. The cooled oil was then subjected to shock chilling by directly admixing therewith 0.5 part by volume, based on the oil, of dewaxing solvent having the composition 55% vol. methyl ethyl ketone and 45% vol. toluene. The dewaxing solvent prior to admixture with the waxy oil was at a temperature of 18° F. As a result of shock chilling the waxy oil by directly admixing therewith the cold dewaxing solvent the temperature of the admixture was 36° F., a temperature decrease of about 14 degrees Fahrenheit with respect to the initial temperature of the waxy oil. Following the shock chilling operation the resulting admixture was then cooled from 30° F. to −6° F. at a rate of about 1.2 degrees Fahrenheit per minute. During this subsequent cooling operation there was added to the cooled admixture 0.1 part by volume, based on the oil, of additional cold dewaxing solvent at a temperature of 0° F. This additional dewaxing solvent was added to the cooled admixture at an admixture temperature of about 0° F. Following this operation the resulting precipitated wax was removed from the dewaxed oil-solvent admixture at a temperature of −6° F. by means of a rotary filter. During the wax filtration operation the rate of filtration of the admixture was observed.

In another test, test No. 2, portions of the same waxy distillate oil having a cloud point of about 50° F. were cooled to this temperature. At this temperature there was directly admixed with the cooled oil 0.2 part by volume, based on the oil, dewaxing solvent at a temperature of 50° F., substantially the same temperature as the oil. It was observed that the temperature of the resulting admixture of oil and dewaxing solvent was 46° F. substantially immediately after the addition of the dewaxing solvent to the oil. This reduction in temperature was attributed to the negative heat of solution of the dewaxing solvent in the oil. Following the admixing of the dewaxing solvent with the oil the resulting admixture was cooled from 46° F. at a rate 1.1° F. per minute over the temperature range 46° F. to −5° F. During this cooling period 0.3 part by vol. additional solvent was added to the oil-solvent admixture at an admixture temperature of 35° F. and 0.5 part by vol. solvent added to the admixture at the admixture temperature of 0° F. When the resulting admixture of precipitated wax, dewaxed oil and dewaxing solvent reached the temperature of −5° F. the precipitated wax was separated therefrom by means of a rotary filter. The rate of filtration during this operation was observed.

In another test, test No. 3, portions of a waxy distillate oil having a cloud point of about 63.5° F. at a temperature 120° F. were admixed with 0.9 part per volume, based on the oil, of dewaxing solvent. The resulting admixture was then cooled at a rate of about 1.0 degree Fahrenheit per minute from a temperature of about 120° F. to 46° F., the cooling rate was then reduced to 0.7 degree Fahrenheit per minute. When the resulting cooled admixture reached a temperature of −6° F. there was added thereto 0.4 part per volume, based on the oil, of additional dewaxing solvent at a temperature of −6° F. The resulting admixture was then cooled to −10° F. Following this cooling operation the admixture containing the precipitated wax, dewaxed oil and dewaxing solvent was then subjected to filtration by means of a rotary filter. During this filtration operation the rate of filtration of the admixture was observed.

The results of these tests with respect to filtration rates are set forth in accompanying Table I.

TABLE I

Filter Production Rates in gals per hr. of Dewaxed Oil per sq. ft. of filter surface

	For Dewaxed Oil Yield and vol. percent of charge	
	91	88
Test No. 1: Shock chilling from about 2° F. above initial haze temperature	5.8	8.2
Test No. 2: Shock chilling from 2° F. below initial haze temperature	4.7	5.8
Test No. 3: Normal solvent dewaxing and cooling	3.8	5.3

As clearly indicated in the data set forth in accompanying Table I, by employing the practice of this invention, shock chilling waxy oil in the substantial absence of dewaxing solvent from a temperature at or just above the cloud point to a temperature 10–50 degrees Fahrenheit below said cloud point by admixing cold dewaxing solvent therewith, and then cooling the resulting admixture in the presence of additional dewaxing solvent to the final dewaxing temperature, and separating the resulting precipitated wax by filtration, the rate of filtration is

substantially improved, thereby potentially increasing the capacity of a dewaxing plant, particularly those plants where the wax removal or wax filtration step is the limiting operation with respect to dewaxing plant capacity. It is to be noted that the benefits of the practice of this invention are obtainable independent of the yield of dewaxed oil, i.e. the wax filtration rate increased whether or not the yield of dewaxed oil was increased, the yield of dewaxed oil being dependent upon the dewaxing temperature employed and the severity of wax cake washing.

In the practice of this invention various ratios of solvent, such as dewaxing solvent, to the mixture, such as waxy oil mixture, to be fractionated or dewaxed may be employed depending upon the character of the mixture to be fractionated and/or the amount of wax or component therein to be separated and/or the character of said component and/or the extent of removal of said component desired. Usually a solvent to charge mixture ratio in the range 0.3–10.0, more frequently in the range 1.0–5.0, gives satisfactory results.

As will be apparent to those skilled in the art many modifications, changes and substitutions may be made in the practice of this invention without departing from the spirit or scope thereof.

I claim:

1. A method of solvent dewaxing a waxy petroleum fraction which comprises cooling a waxy petroleum fraction in the substantial absence of dewaxing solvent to a temperature in the range 0 to 10 degrees Fahrenheit above the cloud point of said petroleum fraction, shock chilling the resulting cooled petroleum fraction by admixing therewith cold dewaxing solvent effecting substantially instantaneous cooling of the resulting mixture to a temperature in the range 10–50 degrees Fahrenheit below the cloud point of said petroleum fraction, and subsequently cooling the resulting admixture to dewaxing temperature and separating by filtration the resulting precipitated wax from said admixture.

2. A method in accordance with claim 1 wherein said dewaxing solvent comprises a liquid admixture of methyl ethyl ketone and toluene.

3. A method in accordance with claim 1 wherein the cloud point of the waxy petroleum fraction is in the range 40–140° F.

4. A method in accordance with claim 1 wherein said waxy petroleum fraction is cooled to a temperature about 2 degrees Fahrenheit above the cloud point prior to shock chilling by contact with cold dewaxing solvent.

5. A method of dewaxing a waxy petroleum fraction which comprises cooling said waxy petroleum fraction in the substantial absence of dewaxing solvent to a temperature just above the cloud point or initial wax haze temperature of said waxy petroleum fraction, shock chilling the cooled waxy petroleum fraction substantially instantaneously to a temperature in the range 10–50 degrees Fahrenheit below said cloud point by directly admixing with said cooled waxy petroleum fraction cold dewaxing solvent, cooling the resulting admixture of waxy petroleum fraction and dewaxing solvent in the presence of additional dewaxing solvent to a temperature in the range 15° F. to −20° F. and separating by filtration the resulting precipitated wax.

6. A method in accordance with claim 5 wherein said dewaxing solvent comprises an aliphatic ketone having from 3 to 9 carbon atoms per molecule and a normally liquid aromatic hydrocarbon.

7. A method in accordance with claim 6 wherein said dewaxing solvent comprises an aliphatic ketone having from 3 to 9 carbon atoms per molecule and said aromatic hydrocarbon in an amount in the range 20–80% and 80–20% by vol., respectively.

8. A method in accordance with claim 5 wherein said dewaxing solvent comprises methyl ethyl ketone and toluene in an amount in the range 20–80% and 80–20% by volume, respectively.

9. A method in accordance with claim 5 wherein said waxy petroleum fraction is shock chilled by contact with cold dewaxing solvent to a temperature in the range 10–20 degrees Fahrenheit below said cloud point.

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