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PROCESS FOR FRACTIONATING HYDRO-CARBON OILS

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This invention relates to a process for the separation of hydrocarbon mixtures, such as mineral oils, particularly gasoline, kerosene, gas oil, and lubricating oil, which may or may not contain paraffin wax, into fractions of different properties by cooling the mixture below the temperature at which the solid wax crystallizes to separate one or more fractions in the solid state. The invention may, for example, be applied for the manufacture of a lubricating oil fraction of high viscosity index from a lubricating oil fraction which may or may not contain wax; or to the concentration of constituents of fuels for internal combustion engines which have superior anti-detonating properties, such as high octane gasoline or high cetene Diesel fuel; or to the concentration of burning oils of good burning quality.

It is known that wax contained in mineral oil can be separated in a solid form by diluting the oil with a thinning agent, cooling the diluted mixture to a temperature at which the wax solidifies, and mechanically separating the precipitated wax from the liquid by filtration, settling or centrifuging. The extent of the cooling can be varied according as it is desired to produce a dewaxed oil having a lower or a higher pour point or cloud point, or other equivalent cold test. In view of the current demand for low pour test oils, the oil is generally cooled to as low as -20°C . and at times even lower.

In the manufacture of lubricating oils the separation of paraffin wax is generally for the purpose of producing an oil which is sufficiently liquid at low temperatures to serve as a lubricant. The viscosity index of the lubricating oil is, however, lowered as a result of the removal of the wax, since the high melting components in paraffin wax have a high viscosity index. Further, it has been established that the components which crystallize out by cooling the oil somewhat below the lowest dewaxing temperature—which components are also hydrocarbons with strongly saturated aliphatic characteristics—also possess high viscosity indices and possess excellent lubricating properties, and are, moreover, free from wax which might have a deleterious influence on the pour point.

In order to isolate these valuable wax-free components of the oil it has heretofore been proposed to cool the initial oil in the presence of a liquid of high fluidity, such as a liquefied normally gaseous substance, as, for example, methane, ethane, propane, butane, ethylene, acetylene, dimethyl ether, ethyl chloride, dichlor-difluor

methane, methylene fluoride, etc., or mixtures of the above normally gaseous liquids with normal liquids, such as hexane or diethyl ether. If the oil contains wax, it is first dewaxed by separating the wax which is solid at ordinary dewaxing temperatures. The wax-free oil is then further chilled to between -45° and -130°C . to crystallize the desired fraction, which is afterwards separated from the liquid solution by filtration.

In accordance with the present invention it has been found that the crystallization of such normally liquid hydrocarbon fractions can be carried out far more efficaciously by diluting the initial mixture with a mixture of a selective solvent and a solubility-promoting solvent, the latter being preferably liquid at ordinary temperature and pressure. It has, moreover, been found that the separation of the crystallized hydrocarbon fraction from the liquid solution, e. g. by centrifugation, can be carried out far more readily by employing as a solvent a liquid having a specific gravity greater than 1.0.

The process according to the present invention has the advantage over the aforementioned known processes that, in order to obtain a particular yield of the desired fraction, the cooling need not be carried so far, while, moreover, the fractionation is much sharper, resulting in the crystallization of a fraction of higher quality. Further, by the use of such selective solvent mixtures, it becomes possible to treat not only the more viscous hydrocarbons, such as lubricating oils, but also the less viscous fractions, such as transformer oil, fuel oil, gas oil, kerosene and gasoline.

The solvent mixtures employed according to the present invention must not be solid in the presence of the oil at the low temperatures employed, although the solvents may individually possess higher melting points. The expression "selective solvent", as used in the present specification and claims, designates any substance having a preferential solubility for the less paraffinic and less saturated hydrocarbons. Such solvents will, at normal temperatures, or at the low temperatures of the process, be at least partly immiscible with the most paraffinic components of the oil. Specific examples of suitable selective solvents are: heterocyclic ring compounds, such as pyridine, and furfural, lower aliphatic ketones, aldehydes, esters, alcohols, such as acetone, diethyl ketone, formaldehyde, methyl formate, ethyl acetate, methyl alcohol, ethyl alcohol, normal- and iso-propyl alcohols, normal butyl alcohol, and certain inorganic substances, such as

sulfur dioxide, or mixtures of these liquids. As solubility-promoting solvents any solvent may be employed which is capable of bringing the selective solvent and the liquid hydrocarbons into solution, such as, for example, low melting aromatic hydrocarbons, such as toluol, technical benzol, halogenated lower aliphatic hydrocarbons, such as trichlorethylene, ethylene dichloride, unsymmetrical dichlorethane, ethyl bromide, dimethyl malonate, carbon disulfide, and low-boiling distillates, such as naphtha, and SO₂-soluble extracts from gasoline and kerosene, or mixtures of same.

The ratio selective solvent: solubility-promoting solvent is preferably chosen so that the low temperature at which part of the hydrocarbons is crystallized and separated is close to the critical solution temperature of the mixture of solvents and hydrocarbons. Preferably, the mixture of selective solvent, solubility-promoting solvent and hydrocarbons should at the working temperature be so near to its critical solution composition that its temperature of demixing differs not more than 15° C. from the working temperature. By critical solution composition is meant that composition which at a given temperature marks the transition point between one- and two-liquid phase systems. Therefore, by operating near the critical solution composition, the formation of two liquid phases will be just avoided, or two liquid phases will just have formed. In the latter case the crystallized hydrocarbons will contain a certain amount of oil which, however, is not a great disadvantage. The ratio selective solvent: solubility-promoting solvent which corresponds to the critical composition may be very easily determined in any particular system by those skilled in the art; it will depend upon the nature of the hydrocarbon mixture, upon the solvent characteristics of the solvents, upon the operating temperature, and upon the dilution ratio, i. e. the ratio of hydrocarbons to solvent mixtures, which, in turn, may be varied within wide limits, depending upon the viscosities of the solvents and of the hydrocarbons. In general, it is preferred to employ between one and ten volumes of combined solvent mixture to one part of hydrocarbon oil.

In practising the process of the present invention the hydrocarbons, or the solvent or both can be separately cooled to the final temperature of separation, although it is preferred to mix the hydrocarbons and solvents at temperatures at which the resulting mixture is liquid, and chill the resulting mixture. The required low temperature can be obtained in many different ways, as by indirect cooling or by auto-refrigeration by evaporating a portion of the solvent, or a different volatile material added for the purpose.

In general, the process may be carried out at temperatures between -25° C. and -125° C., depending upon the nature of the hydrocarbon fraction being treated, and the yield and properties of the desired products.

The crystallized oil may be separated from the oil solution by any suitable means, such as filtration, cold settling, or centrifugation. Since the crystallized fractions are in most cases readily filterable, filtration is quite suitable for this purpose. Cold settling is, however, generally most economical. For this method, as well as for that of centrifuging, it is desirable that there be a sufficiently large difference in the specific gravities of the solid and liquid components, and it will in this case be desirable to employ solvent

mixtures having densities greater than 1.0. Thus, such solvents as ethylene bromide, dichlorethane, ethyl bromide, and dimethyl malonate are particularly suited for use in operations involving settling or centrifugation. It should be noted that in this case the solids will collect at the top of the settling tank, or in the centre of the centrifuge.

By judiciously choosing the temperature and the solvent it is possible to obtain several crystallized fractions at successively lower temperatures. If desired, additional solvent may be added before or during each successive chilling operation, to compensate for the increased viscosity at the reduced temperatures, and/or to bring the mixture to its critical solution composition for the new temperature. Thus it will often be desirable to add more of the solubility-promoting solvent as the temperature is lowered.

For the separation of the fractions in question the initial materials may be hydrocarbon mixtures which do or do not contain solid wax. Should the hydrocarbon mixture contain solid wax, dewaxing may be carried out beforehand, or the dewaxing and the separation of the fraction in question may be carried out simultaneously, so that as a result of cooling to the low temperature a mixture of wax and the fraction in question is separated from the hydrocarbon mixture in solid form. The solid mixture obtained is then treated to separate the desired fraction from the wax in any desired manner as, for example, by a sweating operation, if desired in the presence of solvents or diluents, or treated with solvents in which the desired fraction is soluble but in which the wax is insoluble.

It should be noted that this process differs from the known dewaxing methods involving the step of de-oiling wax cake which has been separated from oil at ordinary dewaxing temperatures in that in these prior processes the oil which is washed from the wax cake was separated therewith by adhesion to the wax crystals, or by occlusion between the same. In the present process the desired hydrocarbon fraction is separated from the liquid in a solid state. If desired, such liquid hydrocarbons as are entrained may be washed from the crystallized fraction prior to the melting thereof, or, if wax is separated simultaneously, prior to the sweating thereof, with a solvent having a composition similar to that employed in the crystallization step.

The crystallized fraction which solidifies next below the wax can be used as such for lubricating oil, or it may be blended with other lubricating oils, in order to improve the properties of the latter. When the fraction contains asphaltic and/or resinous bodies, these can be removed together with the wax, or by any other preliminary treatment, as is well known in the art.

In the case in which an oil is first dewaxed and afterwards separated by crystallization, it is of special advantage to use in both steps largely the same components for the solvent, as in those cases the solvent need not be separated from the filtrate obtained in the dewaxing process. This means a considerable saving in costs.

As further illustrations it is possible, for example, to obtain a gasoline fraction having a higher anti-knock value from distillates of lower anti-knock value, or a Diesel fuel having a higher cetene value.

The invention may be further understood from the following examples which are, however, presented only for the purposes of making a more

complete disclosure of the application of the invention, and not for the purpose of restricting the scope thereof.

Example I

A residue from a Mid-Continent crude oil with a viscosity index of +57 and a refractive index n_D^{24} of 1.5218 was dewaxed by a known process by means of a mixture of benzol and acetone, to produce a filtrate having a pour point of -15°C . and a refractive index n_D^{24} of 1.522. 100 parts by volume of this dewaxed oil were mixed with 62.5 parts by volume of acetone and 187.5 parts by volume of toluol, and cooled to -65°C ., resulting in the precipitation of a solid, readily filterable substance which was found to be a very suitable lubricating oil with a pour point of $+5^\circ\text{C}$., a refractive index n_D^{24} of 1.5023 and a viscosity index of +98 (viscosity: 136 c. s. at 110°F .; 13.1 c. s. at 210°F .). The yield of the oil thus separated in solid form was 20 parts by volume. The oil in the filtrate had a refractive index n_D^{24} of 1.5242 and a viscosity index of +35 (viscosity: 548 c. s. at 100°F .; 22.7 c. s. at 210°F .).

Example II

100 parts by volume of a commercial lubricating oil with a refractive index n_D^{21} of 1.4890 and a viscosity index of +106 (viscosity: 156 c. s. at 100°F .; 15.4 c. s. at 210°F .) were mixed with 80 parts by volume of acetone and 220 parts by volume of toluol and cooled to -45°C .; 9 parts by volume of oil with a pour point of 0°C . and a refractive index n_D^{21} of 1.4818 separated in solid form. The filtrate was cooled further to -70°C . and filtered; the filter cake contained 69 parts by volume of an oil having a refractive index n_D^{21} of 1.4832 and a viscosity index of +125 (viscosity: 91 c. s. at 100°F .; 12.1 c. s. at 210°F .). The final filtrate contained oil having a refractive index n_D^{21} of 1.5040 and a higher viscosity.

Example III

200 parts by volume of a dewaxed oil (V.I.=+61) are mixed with 400 parts by volume of a mixture consisting of 215 parts by volume of methyl ethyl ketone and 185 parts by volume of gasoline. This gasoline contains 35% aromatics. The mixture of oil and solvent is cooled to -62°C . The proportion oil: solvent mentioned above is such that the demixing point (temperature at which two liquid phases begin to form) is just below -62°C . After cooling the mixture is partly solid. After filtration a cake was obtained with a viscosity index of 74 (79% by weight of the original oil) and a filtrate with a viscosity index of 12 (21% by weight). The cake (which is, of course, an oil at normal temperature) was again fractionated. For this purpose 125 parts by volume of the cake were mixed with 250 parts by volume of a mixture consisting of 100 parts by volume of methyl ethyl ketone and 150 parts by volume of the gasoline mentioned above. In this mixture the components were thus present in another proportion, more suitable for the second fractionation. The mixture of "cake" and solvent was cooled to -55°C . and filtered. Calculated on original oil 32% by weight of a filtrate with a viscosity index of 58 and 47% by weight of a second cake with a viscosity index of 90 were obtained. If desired, the second and possible further fractionations may be carried out with mixtures of solvents other than the mixture used for the first fractionation.

Example IV

100 parts by volume of a dewaxed lubricating oil (V.I.=+61) were mixed with 200 parts by volume of a mixture containing 80 parts by volume of ethyl acetate and 20 parts by volume of toluene. The mixture of oil and solvent was chilled to -45°C . After filtration a cake (C_1) was obtained, which at room temperature was an oil, with a V.I. of +87 (65% by volume of the original oil) and a filtrate (F_1), 35% by volume with a V.I. of -7.

The cake C_1 and the filtrate F_1 were now treated again in the above way, the working temperatures being respectively -35°C . and -60°C .

From the cake (C_1) was obtained a cake (C_1C_2), which at room temperature was an oil with a V.I. of +102 (38% by volume of the original oil), and a filtrate (C_1F_2), 27% by volume of the original oil with a V.I. of +60.

From the filtrate (F_1) a cake (F_1C_2) was obtained, which at room temperature was an oil with a V.I. of +53 (19% by volume of the original oil) and a filtrate (F_1F_2) with a V.I. of -148 (16% by volume of the original oil).

The filtrate C_1F_2 and the cake F_1C_2 were mixed and treated again in the same way at -50°C . From this mixture a cake was obtained, which at room temperature was an oil with a V.I. of +77 (32% by volume of the original oil).

We claim as our invention:

1. A process for separating hydrocarbon fractions having melting points below that of paraffin wax and contained in a hydrocarbon mixture which is free from paraffin wax, comprising the steps of mixing said mixture with a solvent mixture containing a selective solvent which has a preferential solubility for the less saturated hydrocarbons and at the separating temperature is at least partly immiscible with the most paraffinic constituents of the oil, and a solubility-promoting solvent which promotes the miscibility of said selective solvent and the hydrocarbon mixture, and cooling the hydrocarbon mixture to a temperature between -25°C . and -125°C . sufficiently low to solidify a fraction of said mixture without solidifying the solvent mixture, and separating the solidified fraction from the resulting solution of the unsolidified fraction and the solvent mixture.

2. The process according to claim 1 in which the hydrocarbon mixture is mixed with and dissolved in the solvent mixture prior to cooling.

3. A process for separating hydrocarbon fractions having melting points below that of paraffin wax and contained in a hydrocarbon mixture which is free from paraffin wax, comprising the steps of mixing said mixture with a solvent mixture containing a selective solvent which has a preferential solubility for the less saturated hydrocarbons and at the separating temperature is at least partly immiscible with the most paraffinic constituents of the oil, and a solubility-promoting solvent which promotes the miscibility of said selective solvent and the hydrocarbon mixture, and cooling the hydrocarbon mixture to a temperature between -25°C . and -125°C . sufficiently low to solidify a fraction of said mixture without solidifying the solvent mixture, the ratio of the selective solvent to the solubility-promoting solvent being such that the temperature of separation differs not more than 15°C . from the critical solution temperature of the solvent mixture and the unsolidified fraction dissolved therein, and separating the solidified frac-

tion from the resulting solution of the unsolidified fraction and the solvent mixture.

4. A process for separating hydrocarbon fractions having melting points below that of paraffin wax and contained in a hydrocarbon mixture which is free from paraffin wax, comprising the steps of mixing said mixture with a solvent mixture containing a selective solvent which has a preferential solubility for the less saturated hydrocarbons and at the separating temperature is at least partly immiscible with the most paraffinic constituents of the oil, and a solubility-promoting solvent which promotes the miscibility of said selective solvent and the hydrocarbon mixture, and cooling the hydrocarbon mixture to a temperature between -25°C. and -125°C. sufficiently low to solidify a fraction of said mixture without solidifying the solvent mixture, the ratio of the selective solvent to the solubility-
- 5
- 10
- 15

promoting solvent being such that the temperature of separation is below the critical solution temperature of the solvent mixture and the un-solidified fraction dissolved therein, and separating the solidified fraction from the resulting solutions of the unsolidified fraction and the solvent mixture.

5. The process according to claim 1 in which the solvent mixture has a specific gravity greater than 1.0.

6. The process according to claim 1 in which the selective solvent is ethyl acetate and the solubility-promoting solvent is a low boiling aromatic liquid.

WILLEM RHLJNVIS VAN WIJK.

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