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SOLVENT AND PROCESS FOR DEWAXING MINERAL OILS

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This invention relates to a process for separating various waxy substances from mineral oil containing the same. More particularly, it pertains to an improved diluent for decreasing the viscosity of the oil and the solubility of the wax, while improving the solubility of the oil in the liquid phase produced when solid wax is separated from oil, whereby the wax and the oil are separated more readily than has been possible heretofore.

Mineral oils naturally contain varying amounts of waxy hydrocarbons, often designated as paraffin wax or petrolatum and hereinafter generically designated as waxes, which at normal or elevated temperatures are dissolved in the liquid hydrocarbons, hereinafter referred to as oil, but which solidify or become extremely viscous at lower temperatures. If these oils are to be used as lubricants at these reduced temperatures the solidified or highly viscous wax causes the oil to resist flow. When the wax content is too low to impede flow, it may, nevertheless, cause cloudiness in the oil. It becomes necessary, therefore, to effect the removal of all or some of the wax.

The first step in such a process is the creation of conditions under which the wax has a minimum solubility in the phase containing the oil. This wax probably contains aliphatic hydrocarbons and/or naphthenic and other hydrocarbons; it belongs to the group of components of petroleum which are the least soluble in selective solvents. The removal of wax may be accomplished by any of several methods.

In accordance with one of these methods, the oil is chilled to a temperature substantially below that at which the wax solidifies and the wax is separated from the liquid oil by mechanical means. As an improvement in such a process, it is common to add a non-selective diluent, such as liquefied, normally gaseous hydrocarbons, light naphthas, etc., to the oil to reduce its viscosity and facilitate the mechanical separation.

In another method, a selective solvent medium is added to the initial oil, and the wax-free components of the initial oil are dissolved therein. This method necessitates the use of a solvent medium which is sufficiently selective to dissolve the oil at a suitable dewaxing temperature without dissolving the wax. The ordinary selective solvents which are employed for example in liquid-liquid solvent extraction processes to dissolve certain types of oils which are less paraffinic in nature from those which are more paraffinic in nature are not in general suitable for use as solvent media, because in dewaxing processes the solvent is used to dissolve the desired oil which, in the case of extraction processes, it is desired to recover in the liquid phase insoluble in the solvent.

Certain of such selective solvents may, however, be employed for dewaxing purposes by adding thereto a quantity of a secondary solvent, sometimes referred to as a solubility enhancing solvent. The addition of the secondary solvent improves the miscibility of oil and selective solvent, but in most cases destroys the selectivity of the resulting mixture between wax and oil, so that the resulting mixture of primary selective solvent and solubility enhancing solvent is to a great extent equivalent to a non-selective diluent, and functions only to reduce the viscosity of the chilled oil.

We have discovered that the yield of dewaxed oil for a given pour point and/or the pour point of the dewaxed oil can be materially improved by separating solid wax from oil in the presence of a dewaxing solvent containing a mono or di-alkyl ether of ethylene glycol or diethylene glycol as a selective solvent, and a solubility enhancing agent selected from the group: aliphatic alcohols containing one oxygen atom and from four to eight carbon atoms, aliphatic ethers containing one oxygen atom and from four to eight carbon atoms and aliphatic ketones and aldehydes containing from four to ten carbon atoms. Specific examples of the selective solvents which may be employed according to the present invention are: ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono propyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono propyl ether, diethylene glycol isobutyl ether. The alkyl chains may be either straight or branched chain. We prefer, however, to employ the lower mono-alkyl ethers, i. e., monoalkyl ethers of ethyene glycol having from three to six carbon atoms, and monoalkyl ethers of diethylene glycol having from five to nine carbon atoms.

While any solubility enhancing solvent falling within the above group may be employed, it will generally be desirable to select a solubility enhancing solvent which is best suited to the oil being dewaxed, to the operating temperature, to the desired results, and to the particular ether employed as the selective solvent. Thus, when dewaxing highly aromatic oils, such as western oils, and/or when operating at relatively high dewaxing temperatures, and/or when a low pour point is desired, and/or when using a high molecular selective solvent, it is preferable to select those of the above secondary solvents which

have fewer carbon atoms, e. g., butyl alcohol, and diethyl ketone. On the other hand, when working with more paraffinic oils, such as Pennsylvania oils, and/or when operating at lower dewaxing temperatures, and/or when a higher yield is desired, and/or when using a low molecular selective solvent, it is preferable to employ solubility enhancing agents with more carbon atoms.

We have, moreover, found that the secondary and tertiary alcohols are eminently superior to the primary alcohols, the tertiary alcohols being slightly superior to the secondary alcohols. Specific examples of these preferred solubility enhancing solvents are: Secondary and tertiary butyl amyl and hexyl alcohols, diethyel ether, ethyl isobutyl ether, methyl ethyl ketone, methyl butyl ketone, ethyl isopropyl ketone, methyl tertiary butyl ketone, valeraldehyde, and octylaldehyde.

Suitable solvent mixtures may, for example, consist of from 10 to 60% of a selective solvent-like ethylene glycol monomethyl ether, and from 40 to 90% of a solubility enhancing solvent-like secondary butyl alcohol.

The method which is the subject of our invention relies primarily on the peculiar properties of the above mixtures of solvents, which were found to create a condition in which there is a large difference between the solubility of the solid or waxy components of the initial oil and the solubility of the liquid or oil components thereof. In one aspect, our method comprises the steps of mixing a waxy oil, such as lubricating oil, fuel oil, etc., which may be either a residual or distillate oil, with our selective solvent and solubility enhancing solvent, and chilling the resulting mixture to a dewaxing temperature to solidify the wax, which may then be separated from the liquid portion of the system by any mechanical means, such as filtration, cold settling, or centrifuging, depending upon the character of the wax. Our process is, however, particularly suitable for filtration methods. The dewaxing temperature may, for example, be slightly below the melting point of the lowest melting wax which it is desired to remove. The pour point of the dewaxed oil may in certain cases be slightly higher than the dewaxing temperature, but by adjusting the proportions of selective solvent and solubility enhancing solvent, as described below, pour points which are as much as 20° F. below the dewaxing temperature may be obtained.

It is desirable, although not essential, to produce a homogeneous wax-oil-solvent system prior to the precipitation step. To achieve this, the temperature of the system may initially be raised to somewhat above the dewaxing temperature. We have, moreover, found that excellent filtration rates are obtained by heating the oil-solvent mixture to a temperature within the range from 65° C. to 100° C., or higher, and then cooling it slowly to the dewaxing temperature. When the mixture is initially warmed, it is necessary to cool the oil-solvent mixture, and this may be effected by indirect cooling or auto-refrigeration. Where very low pour points are not essential, our solvent mixtures may often be mixed with the oil at ordinary temperatures of the order of 18° C., thereby obviating the necessity of chilling the oil.

The chilling, when used, is not only for the purpose of merely freezing out the wax, as in the processes now practiced, but also for the purpose of increasing the selectivity of the solvent mixture which may have been added to the oil at a temperature at which it is less selective. This feature distinguishes our process from those in which the wax is caused to separate by mere chilling, and a non-selective solvent or diluent is added to reduce the viscosity of the oil and to expedite the separation of the solidified wax. In this connection it should be noted that the above selective solvents become more selective at lower temperatures.

Under certain conditions the wax which is precipitated according to the procedure outlined above, either with or without chilling during precipitation, may be so soft as to make its separation difficult. It is in these cases advantageous to chill the precipitated wax during or just prior to its final removal to harden it. Subsequently the solvent mixture is removed from the separated liquid by any means, such as distillation.

To be filterable or otherwise separable from the oil-solvent phase, the wax particles must be of suitable form, size and strength and/or hardness. We have found that if in precipitating the wax a very small amount of liquid oil is separated out from the oil with the wax crystals, clusters of crystals are formed and the separation of wax from the solution of oil and solvent is facilitated. The amount of oil necessary for this purpose depends upon the size of the initial wax crystals, which, in turn, depends among other things, upon the nature of the wax and the rate of chilling. In processes in which the crystals are extremely small and the wax content of the initial oil is high, as much as 1.0% of the main body of the oil may be desirable. In other cases, as when the crystals are larger, and/or when less wax is present, lesser amounts of oil may be desirable, and it is frequently practical to permit substantially no oil to be separated out with the wax. Since the separation of an excess quantity of oil reduces the yield of dewaxed oil, it is desirable to control the amount of the oil which is separated with the wax, as described below.

A convenient method of controlling this amount of oil is to regulate the concentration of the solubility enhancing solvent in the solvent mixture. The necessary dilution ratio, i.e., the ratio of the combined solvent mixture to the initial oil, is generally determined by the viscosity of the oil and the solvent mixture and by the selectivity of the solvent mixture at the dewaxing temperature, and is made as low as possible with a view of conserving the solvent. When using the new solvent mixtures of our invention, the dilution ratio may be much lower than the ratio employed with the known solvent mixtures. For example, we have obtained excellent results when using a dilution ratio of 2:1, and even lower ratios, such as 1:1 may be employed, although we prefer to employ ratios of about 4:1. At very low temperatures ratios as high as 8:1 may be desirable.

For a given dilution ratio, the greater the concentration of the selective solvent component of the dewaxing mixture, the more complete will be the precipitation of wax, and extremely low pour points may often be obtained. However, since the selective solvent has a relatively low solvent power for the oil, the oil-solvent system will in this case form two liquid phases, in addition to the solid wax phase, and the yield of the dewaxed oil will be extremely low. When an excess of solubility enhancing solvent is employed, the oil-solvent system will exist as a homogeneous liquid phase, and both pour points and yields of dewaxed oil will be increased. Between these concentrations of solubility enhancing solvents, there is a composition of the combined solvent mixture

forming a transition point between the liquid-solid and liquid-liquid-solid phase systems. The transition composition will, of course, depend upon several factors, such as the dilution ratio, the dewaxing temperature, the specific solvents employed, and the character of the oil, but may be easily determined empirically for any given situation.

We have found that when the volume concentration of the solubility enhancing solvent in the mixed dewaxing solvent is lower than about 10% below the concentration corresponding to the transition composition, the yields of dewaxed oil are reduced quite out of proportion to the improvement in the pour point. Moreover, we have found that the most efficient dewaxing operations are those which are carried out by employing dewaxing solvent mixtures having compositions near the transition composition, i. e., in which the concentration of the solubility enhancing solvent fall in the range from 10% below to 20% above the transition concentration. Using greater quantities of solubility enhancing agent results in greater yields, but the pour points of the dewaxed oil will often be undesirably high.

Such solvent mixtures as are used in accordance with the present invention may, for example, at temperatures of about 0° F. to −10° F., have complete or substantially complete solubility for oil having specific gravities

$$d_{15}^{15}$$

between 0.90 and 0.94 and refractive indices n_D^{20} between 1.50 and 1.52, and substantially no solvent power for wax which is solid at the said temperatures, i. e., not more than a few tenths of one per cent of wax will be dissolved at these temperatures; such an oil may, for example, have a viscosity of between 50 and 55 sec. Say. Univ. at 210° F. Mixtures of solvents having this characteristic may, of course, be used also with oils of different refractive indices, specific gravities or viscosities.

The dewaxing process may also be carried out in several steps, the composition of the solvent mixture being regulated, and the process being carried out as described in the U. S. application Serial No. 45,960, filed October 21, 1935.

The yields of dewaxed oil of a given pour point and the filtration rates can often be further increased by adding a small amount, generally between 0.2% and 1% of a pour point reducing substance, such as tetrastearyl glucose, pentaerithrite tetrastearate, distearyl picene, cracked residues, metallic soaps, etc., to the oil, preferably, prior to chilling. Most of the pour point reducer separates from the oil with the wax, so that it is not normally effective to lower the pour point of the filtrate, but is effective in the formation of filterable wax crystals.

The following examples illustrate the superior results obtainable with our improved solvent mixtures. For comparison, the same oil was dewaxed with our mixtures and with acetone-benzol mixtures, the latter mixture being commonly regarded as standard for dewaxing mineral oils.

Example I.—Several samples of a Ventura distillate having a pour point of 95° F. were each diluted with four volumes of various solvent mixtures, heated to about 100° C. for fifteen minutes, gradually cooled, and filtered at between 0° C. and 1° C. The compositions of the solvent mixtures and the yields are given as per cent by volume. The results are shown in Table I.

Table I

Exp. No.	Diluent		Yield of dewaxed oil	Final pour point of oil
	Selective solvent	Solubility enhancing solvent		
	Ethylene glycol monomethyl ether percent	*Sec. butyl alcohol percent*	*Percent*	*°F.*
1	20	80	86	30
2	30	70	88	30
3	35	65	89	30
4	40	60	88	30
5	50	50	70	22.5
6	55	45	61	20
	Acetone percent	*Benzol* percent*		
7	25	75	94	30
8	50	50	92	40
9	65	35	89	35
10	75	25	83	30
11	90	10	53	20

* Contained 10% toluene.

With dilution ratios of 1 to 4 at 0° C., the following compositions of solvent dewaxing mixtures corresponded to the transition point between one and two liquid phase systems: 35% ethylene glycol monomethyl ether, 65% secondary butyl alcohol; 72% acetone, 28% benzol. It will be noted that in each case the yield dropped off sharply when less solubility enhancing agent was employed than corresponds to the transition point for the solvent in question, with a slight lowering of the pour point, but that with our dewaxing mixtures we obtained far higher yields at the transition point than with the acetone-benzol mixture, while in each case the pour point was 30° F. Upon using smaller amounts of solubility enhancing solvent, the pour point was further lowered, our solvent mixtures producing higher yields than acetone-benzol mixtures. We can, therefore, obtain considerably higher yields for a given pour point, and/or lower pour points for a given yield than with the commonly used acetone-benzol mixtures.

Example II.—The distillate described in Example I was similarly dewaxed with four volumes of various of our dewaxing diluent mixtures, the filtration being carried out at between −20° C. and −19° C. The results are shown in Table II:

Table II

Exp. No.	Diluent		Yield of dewaxed oil	Final pour point of oil
	Selective solvent	Solubility enhancing solvent		
	Ethylene glycol monomethyl ether percent	*Sec. butyl alcohol percent*	*Percent*	*°F.*
1	20	80	85	−15
2	25	75	83	−15
3	30	70	80	−17.5
4	40	60	70	−20
	Acetone percent	*Benzol* percent*		
5	35	65	91	+15
6	45	55	90	+10
7	50	50	90	+5
8	60	40	87	0
9	70	30	65	0
10	75	25	58	+5

* Contained 10% toluene.

With dilution ratios of 1 to 4 at −20° C., the following compositions of solvent dewaxing mixtures corresponded to the transition point between one and two liquid phase systems: 25% ethylene glycol monomethyl ether, 75% second-

ary butyl alcohol; 55% acetone, 45% benzol. The superiority of our diluent mixtures is apparent from the above table, which shows that dewaxed oils with considerably lower pour points can be produced with our mixtures. With the acetone-benzol mixtures, 0° F. was the lowest pour point obtainable. It will be noted that our new dewaxing mixtures are particularly advantageous for low temperature dewaxing operations, i. e., those carried out below 0° C., such as —10° C., —20° C., or lower.

These examples are given only for the purpose of illustrating the efficiency of our new solvents, and not by way of limitation. Thus, the oil-solvent ratio may be varied within wide limits, and other specific selective solvents and/or solubility enhancing solvents may be employed. The dewaxing may be carried out either as a continuous or as a batch process. By the term "effective quantity", as used in the claims, we mean a quantity of solvent mixture which will maintain sufficient oil in solution to produce its substantially complete separation from the wax which is precipitated, and which will produce an oil-solvent mixture of the desired viscosity.

We claim as our invention:

1. A selective solvent dewaxing mixture for petroleum oils, consisting of between 10 and 60% ethylene glycol monomethyl ether and between 40 and 90% of a non-primary aliphatic alcohol having one oxygen atom and from four to eight carbon atoms.

2. A selective solvent dewaxing mixture for petroleum oils, consisting of between 10 and 60% ethylene glycol monomethyl ether and between 40 and 90% secondary butyl alcohol.

3. The process for dewaxing mineral oils which comprises mixing the oil with at least an equal volume of a solvent mixture containing between 10 and 60% ethylene glycol monomethyl ether and between 40 and 90% secondary butyl alcohol, chilling the resulting oil solvent mixture to precipitate wax, and removing the precipitated wax from the oil-solvent mixture by mechanical means.

4. The process of dewaxing mineral oils which comprises mixing said oil with a liquid selective solvent comprising ethylene glycol monomethyl ether, chilling the oil to precipitate solid wax, and mechanically removing solid wax from the resulting oil-solvent mixture in the presence of an aliphatic alcohol having one oxygen atom and from four to eight carbon atoms.

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