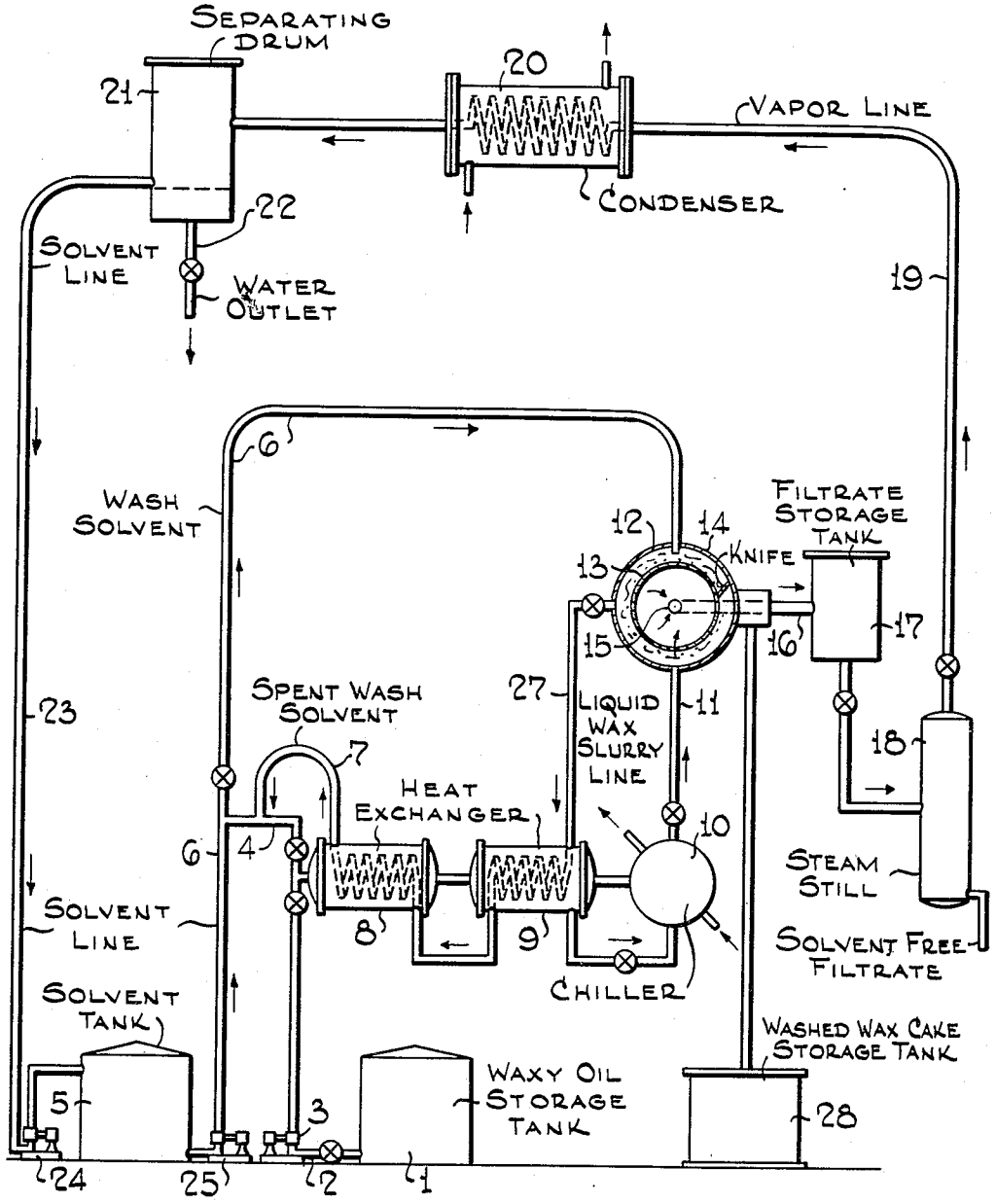
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SOLVENT DEWAXING OPERATION

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SOLVENT DEWAXING OPERATION

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This invention relates to the dewaxing of petroleum oil fractions and in particular to the dewaxing of lubricating oils. The invention particularly concerns the use of a novel combination of solvents, the use of which substantially improves the dewaxing operation.

The subject matter of this invention is related to that disclosed in U. S. Patent 2,160,985, patented June 6, 1939. In this patent it was disclosed that a valuable group of dewaxing solvents are the aliphatic ketones which contain a normal propyl group and have a total of 5 or 6 carbon atoms in the molecule. Preferred ketones of this class are methyl normal propyl ketone and ethyl normal propyl ketone. It is disclosed in U. S. Patent 2,160,985 that this class of solvents is characterized by extremely low wax solubility at dewaxing temperatures, by low miscibility temperatures with oil, and by extremely high filter rates in solution with oil at low temperatures.

It has now been discovered that the value of this class of dewaxing solvents may be substantially improved by incorporation of about 20 to 60% of diethyl ketone. In some manner, the diethyl ketone functions as an anti-solvent for water, minimizing the harmful effects of water contamination during the dewaxing operation.

In the conduct of commercial scale dewaxing of lubricating oils it is impractical to completely exclude all water. Thus, for example, the dewaxing solvents employed generally contain small percentages of water, usually between 0.2 to 0.5 volume per cent, which may be due to steam distillation employed in the finishing of these solvents. Again the lubricating oil fraction to be dewaxed ordinarily is contaminated with a low percentage of water. Finally, water inevitably finds its way into the dewaxing apparatus and feed stream through accidental contamination. The principal sources of this water contamination are:

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1. Water emulsion in the waxy feed stocks caused by sweating in the storage tanks, leakage of steam used in heating coils used to prevent crystallization of waxes, etc.

2. Recovery of last traces of the dewaxing solvent from dewaxed oil or wax by steam stripping and re-using this solvent in the dewaxing step.

The amount of water contamination which is ordinarily encountered is generally sufficient to increase the water content by 0.1 to 0.3 volume per cent per day of dewaxing plant operation.

The presence of contaminating water, even in quantities as low as 1% or less, exerts several undesirable functions. First and most important, the presence of water raises the miscibility temperature of the dewaxing solvent and oil. As will be shown in the data which follows, this effect is so marked that the miscibility temperature of oil and methyl normal propyl ketone, for example, is raised 32° F. by the presence of 1% of water. The result is that higher dewaxing temperatures would have to be employed to avoid contamination of the wax with oil precipitated from the solvent as a result of the presence of water.

In addition to this factor of adversely changing the miscibility temperature, or as a result of this factor, the filter rates which may be maintained are seriously affected by water. This is presumably due to blinding of the filter cloths by the oil which is precipitated out when the immiscibility point is reached. The effect of water contamination on dewaxing plant operation is shown by the following summary of data obtained when using a mixture of methyl normal propyl ketone with methyl normal butyl ketone as a dewaxing solvent:

Charge Stock Extracted Mid-Cont. Distillate SAE, Grade	Percent Water in Solvent	Dewax Temp., ° F.	Dilution V./V. Feed	Wasn Solvent V./V. Feed	Filter Rate, U. S. Gal./sq. ft./hr.		Pour ASTM, ° F.	Percent Dry Wax in Feed Stock	Percent Oil in Wax
					Waxy Feed	Dewaxed Oil			
	0.2	26	2.8	1.8	5.8	5.1	+25	11.6	11.0
	0 15	18	2.8	2.0	4.5	3.9	+20	12.5	8.5
30	0.2	20	2.9	2.2	4.7	4.1	+15	10.8	6.5
	0.8	19	2.3	1.9	4.3	4.0	+15	4.5	23
	1.1	20	2.5	1.9	3.9	3.6	+15	4.5	28
40	1.05	18	3.5	1.9	3.7	3.2	+15	7.0	71
	1.0	24	3.6	2.3	3.4	1.9	+20	6.5	88
60	0.2	24	3.4	2.3	2.8	2.5	+20	9.6	23
	0.15	29	3.3	2.6	3.1	2.7	+25	10.6	13

The above data bring out the disadvantages of water contamination in dewaxing, resulting in large losses of oil into the wax cake and inability to reduce the oil content of wax even

after re-pulping of the wax cake followed by a secondary de-oiling step. The wax finishing operation thus becomes more expensive if not, for practical purposes, impossible.

Again, the effect of dewaxing with methyl normal propyl ketone under conditions of incipient immiscibility resulted in a loss of approximately 10% in dewaxing plant throughput incurred largely due to the more rapid blinding of the filters, necessitating more frequent "hot washing" of the filter cloth. The oil content of stripped wax also increased from 8–11% to between 16 and 28%.

In accordance with this invention, these disadvantages brought about by contamination of the dewaxing operation with water, may be substantially avoided by including about 20 to 60% of diethyl ketone in the dewaxing solvent. The dewaxing solvent thus consists of any one or a mixture of aliphatic normal ketones having a total of 5 or 6 carbon atoms and each containing an aliphatic group of at least 3 carbon atoms together with from 20 to 60% of diethyl ketone. A particularly preferred dewaxing solvent composition for use in this invention is composed of about 65% of methyl normal propyl ketone and about 35% of diethyl ketone.

The manner in which the dewaxing solvent composition of this invention is to be employed may be understood by reference to the accompanying drawing, illustrating a diagrammatic flow plan of a suitable dewaxing operation.

Referring to the drawing, numeral 1 designates a storage tank for waxy oil. The oil is maintained in this storage tank at a temperature above the solidification point of the wax. The oil is removed through line 2 by means of pump 3. Solvent is added to this oil by means of pipe 4 from solvent tank 5 through line 6. In general this is used to put the process in operation, but after the conditions have been settled to a steady state, the bulk of the fresh solvent is not added directly to the oil but is supplied for washing filter cake as will be disclosed below, and the washings from the filter, called "cycle solvent" are added to the oil to be dewaxed through pipe 4, as indicated.

The oil-solvent mixture is then blended in the desired proportion disclosed below, is passed to heat exchangers 8 and 9, then through a chiller 10. In the chiller the temperature is reduced to such a point that the waxy content of the mixture is solidified and the dewaxed oil after removal of wax would be fluid at the desired pour temperature. Pipe 11 conducts this mixture of liquid constituents and solid particles of wax to a filter shown generally at 12. The filter may, of course, be an ordinary plate and frame type, but it is preferred to use a continuous type of filter. This consists of a drum 13, the cylindrical surface of which is covered with the filter cloth. The drum is mounted in a casing 14 on an axle, of which only the end 15 is shown. The operation of a continuous filter is well known, and it need only be said that the drum is continually rotated at a low speed, usually of the order of 2½ minutes per revolution. The liquid wax slurry is introduced at the bottom of the casing and filtration occurs on about 15–40% of the circumference of the filter drum. The filtrate passes through the cloth and finds its way out through one end of the axle 15, which is of course in the form of a pipe. A pipe 16 connected to the end of the axle conducts the filtrate to a storage tank 17. From the storage tank the filtrate is passed to a steam still 18 from which the solvent together with seam passes overhead through vapor line 19 to a condenser 20. The solvent separates from the condensed steam in a separator drum 21. Water is discarded by pipe 22 and solvent passes by pipe 23 and a pump 24 to the tank 5 for re-use.

As indicated above, about 15–40% of the circumference of the drum is continually in use for filtration, being directly submerged in the wax-solution mixture. During this period wax cake is formed which can be described as having a spongy structure, due to the interlocking of wax crystals, in which the volume of "voids" filled with the solution is about 6 to 10 times as great as is the volume of the crystalline paraffin wax which is deposited on the filter blanket. This wax cake continuously moves into the sector (about 40–55% of the circumference) in which it is continuously washed with fresh pre-cooled solvent. The pre-cooled solvent which is used as a washing liquor is drawn directly from tank 5 by a pump 25 and enters the filter casing at the top where it is distributed into 4 to 6 spray or drip pipes which distribute the wash solvent uniformly over the wax cake surface.

In the washing cycle about 25–35% of the solution retained in the voids of the wax cake can be displaced by the wash solvent without changing the concentration of the oil in the filtrate. The filtrate from the washing cycle is therefore split into two fractions. The first fraction, amounting to between 25–35% of the total solution in the wax cake, can easily be displaced, which is identical in composition to the main bulk of the filtrate obtained during the submergence or filtration cycle, and is passed to the filtrate tank. The second fraction which has a substantially lower concentration of oil than the main bulk of the filtrate, is generally called "cycle solvent" and is used for diluting the incoming waxy charge. It will be understood that some admixture of the filtrate and of the washing liquor is unavoidable in the commercial type rotary filters even though the axle of the filtering drum is fitted with a suitable partition, not shown in the drawing. The relatively poor separation of the filtrate and cycle solvent is caused by the slow drainage of liquid held in trays and pipes leading to the slide valve, which is divided into two passageways. This drainage problem becomes particularly critical as the filter speeds faster than 2 minutes per revolution. In the drawing this division is indicated by the filtrate passing out of the axle at one end, while the wash liquor or cycle solvent is removed from the opposite end.

The wash liquor flows through a pipe 21 to the heat exchangers 9 and 8, and then passes through a pipe 7 and is mixed with the original waxy feed through the pipe 4. As stated before, fresh solvent is not commonly used for diluting the waxy stock but is supplied chiefly for washing the wax cake only.

However, when rotary filters operate at filter speeds of the order of 2 minutes per revolution, the hydraulics of the filter design necessitate the adjustment of the slide valve which makes it inevitable that increased volume of wash liquor or cycle solvent is included in the filtrate. The volume of cycle solvent available is then insufficient for maintaining the desired dilution and when this occurs, the difference must be made up by the fresh solvent from a solvent tank 5. The basic principle which governs the filter opera-

tion is to regulate the separation of the filtrate and cycle solvent (wash liquor) so that not more than 15 to 20% of the dewaxed oil is recycled in the dewaxing plant with the solvent used for diluting the waxy feed stock.

The total filtering cycle, i. e. time required for filtration, washing, drying and "blowing" or removing the wax cake, is not materially lengthened by using a relatively large quantity of solvent for washing the wax cake, as the filtering rate of the fresh solvent towards the end of the wash cycle becomes very high. By applying all or most of the fresh solvent as wash solvent it is possible, however, to produce a wax having very low oil content, while the yield of dewaxed oil is close to the theoretical yield. That is, with an overall dilution of 2.0 to 3.0 parts of solvent to 1.0 part of waxy stock, it is possible to obtain a greater yield of dewaxed oil than is possible by the standard procedure described in the literature, in which about twice this volume of solvent is used.

The washed wax cake is carried over into a removal zone, in which the cake is scraped from the filter blanket by means of a suitable doctor knife, and then slides into a trough fitted with a scroll conveyor. It is collected at **28**.

The wax cake removed from the filter contains about 6 parts by volume of solvent per unit volume of paraffin wax. While the solvent to wax ratio can be somewhat reduced by a more prolonged drying on the filter, this would result in a lower throughput. If desirable, a larger reduction can be effected by repulping the wax cake by means of a centrifugal pump or a mixer and conveying the wax slurry to another rotary filter similar to those used for the dewaxing operation. If desirable, the wax slurry is heated to between 60 and 95° F. before filteration to permit de-oiling at elevated temperatures. The removal of low melting point waxes in the de-oiling step materially aids the sweating operation or facilitates the manufacture of micro crystalline waxes from heavy lube distillate and residual oils. The solution thus removed might be recycled back as dilution, while the wax cake is collected and sent to the solvent recovery plant.

It will be understood that the dewaxing operation, i. e. the mechanical separation of the wax from solution, may be accomplished by other means than by filtration. While filtration is perhaps the most advantageous mechanical means to separate the precipitated wax from the solution, centrifuges may also be employed. This method is, however, inefficient and much less desirable than the previously described removal of wax by continuous filtration.

As indicated, the dewaxing solvent to be employed comprises a mixture of diethyl ketone with an aliphatic ketone containing a propyl group and having from 5 to 6 carbon atoms. The preferred solvent is methyl normal propyl ketone together with about 20 to 60% of diethyl ketone. However, in some cases, for example, in the dewaxing of cylinder stocks and residual oils, it is desirable to employ a mixture of methyl normal propyl ketone and methyl normal butyl ketone together with the indicated percentages of diethyl ketone. The desirability of including methyl normal butyl ketone arises from the fact that methyl normal butyl ketone somewhat lowers the miscibility temperature of the solvent composition with oil. A similar effect may also be achieved at least in part by employing other solvents such as benzol, toluene, napthas, O-dichloro benzene, etc., but these solvents have the undesirable effect of reducing the filter rate of methyl normal propyl ketone.

However, mixtures of about equal parts of methyl normal propyl ketone and methyl normal butyl ketone to which are added about 20 to 60% of diethyl ketone are particularly suitable since the filter rate is not adversely affected.

The quantity of solvent used per volume of waxy oil will vary considerably depending upon the viscosity of the oil, the wax content, and the desirability of preparing commercial grades of wax from the wax cake formed on the filter. In general it is possible to use less solvent with the lighter distillates than with the heavier oils. The total amount of solvent used, including that for washing, may be as low as one volume of solvent per volume of waxy oil. With heavier oils, or if it is desirable to produce wax substantially free of oil, it is preferable to use from 2½ to 3 volumes of solvent per volume of oil. It is rare that more than 3½ volumes of solvent are required, although even larger amounts than this may be advantageous when the wax content of the oil substantially exceeds 15 to 20%, chiefly to increase the fluidity of the wax slurry charged to the continuous filters.

The filtration rate in continuous rotary filters with these solvents will also vary with the viscosity of the oil, but even in the case of very viscous residual oils and cylinder stocks it is possible to obtain filter rates in excess of 3.5 gallons of waxy oil per square foot of filter area. The separation between oil and wax is remarkably sharp, and while in most cases the pour point of the filtrate is the same as the dewaxing temperature, it is found that it is even possible to obtain pour points from 10 to 15° F. below the dewaxing temperature.

In considering the desirability of employing diethyl ketone in the solvent compositions described, the following data is significant. First it is important to note that inclusion of diethyl ketone in the dewaxing solvent may be tolerated while substantially maintaining the very filter rates obtainable with the aliphatic propyl ketones. The factor of filter rate is demonstrated in the following table, illustrating the use of methyl normal propyl ketone and diethyl ketone alone and in admixture. The data presented was obtained while dewaxing extracted Mid-Continent SAE–30 distillate diluted with three volumes of solvent chilled at the indicated rate to 26° F., and then filtered to remove wax.

Table I

Solvent Composition		Waxy Dist. Filter Rate,[1] U. S. Gal./sq. ft./hr. for a controlled rate of chilling	
Percent Methyl Norm-propyl ketone	Percent Diethyl Ketone	2° F./Min.	5° F./Min.
100	--------	9.34	6.24
80	20	----------	6.62
70	30	----------	6.43
63	37	8.35	----------
60	40	----------	6.43
50	50	7.61	6.43
40	60	----------	6.43
25	75	7.61	6.62
----------	100	7.61	6.07

[1] Filter speed 2½ min./rev. Filter submergence 30%, wash solvent requirements 150 vol. percent, wax cake contains approximately 12% oil.

These examples indicate the filtering rate which may be obtained. Thus, for example, at a

chilling rate of 2° F. per minute the filter rate when employing 63% of methyl normal propyl ketone and 37% of diethyl ketone is reduced by approximately 10% as compared to the use of methyl normal propyl ketone alone. However, when the chilling rate is increased to 5° F. per minute, which approximates the chilling rate of a commercial dewaxing plant, a substantially equivalent rate of filtration can be obtained.

The temperature differential between the dewaxing temperature and the pour point of the dewaxed oil is not greatly affected by including diethyl ketone in admixture with methyl normal propyl ketone. Thus, in the case of the dewaxing operations summarized in Table I employing a dewaxing temperature of 26° F. the solidification points of the dewaxed oils in all cases were 25° F. plus or minus 2° F., which actually was within the limit of accuracy of the determinations. This figure reasonably checks the temperature difference for an equivalent wax solubility of methyl normal propyl ketone and diethyl ketone as shown in Table II.

Table II

Solubility of 141/143 AMP Wax in dewaxing solvent, grams wax/100 cc. solvent	Temperature, ° F., for equivalent wax solubility	
	Methyl normpropyl Ketone	Diethyl Ketone
0.100	+61	+58½
0.010	+35	+32
0.001 (Extrapolated)	+8½	+6

To further bring out the properties of the solvents to be employed in this invention it is significant that substantially anhydrous methyl normal propyl ketone and diethyl ketone are virtually equivalent in solvent power. That is, each of these compounds has about the same solubility for mineral oil and about the same solubility for water in ketone or ketone in water. This is shown by Table III.

Table III

	Dilution	Methyl Normpropyl Ketone	Diethyl Ketone
Miscibility Temp. with extracted Mid-Continent Lube Oil:			
SAE 30 Grade, 93 V. I.	3:1	−13	−16
SAE 60 Grade, 94 V. I.	2:1	+11	+8
Solubility of Ketone in water at 20° C., wt. percent		5.1	4.6
Solubility of water in Ketone at 20° C., wt. percent		3.3	2.6

Surprisingly, however, it has been discovered that while the presence of water in methyl normal propyl ketone substantially raises the immiscibility temperature with oil, diethyl ketone acts as an anti-solvent causing water to separate out of the mixture without appreciably altering the immiscibility temperature with water. No explanation for this effect has as yet been developed and it is notable that such an effect could not be predicted from the basic data as to the solvent power of these ketones as given in Table III. The effect of water on the solubility of extracted Mid-Continent SAE 30 grade oil in 3 to 1 dilution is shown below:

Table IV

Composition of Dewaxing Solvent		Miscibility Temperature in ° F. after adding—							
Methyl normpropyl Ketone	Diethyl Ketone	--------	0.25% Water	0.5% Water	0.75% Water	1.0% Water	1.25% Water	1.5% Water	2.0% Water
100	------	−13	+1	+5	+12	+19	+24	+24	----
75	25	−14	----	−4	----	±0	----	±0	±0
50	50	−16	----	−10	----	−9	----	−8	−8
----------	100	−16	----	−15	----	−15	----	−15	−15

As indicated by Table IV, for example, when employing substantially anhydrous methyl normal propyl ketone, about a +5° F. pour point oil can be obtained without experiencing difficulties due to immiscibility of the oil with the solvent. However, on water contamination it no longer is practical to obtain oil of this pour point so that with about 1½% water present, the dewaxing temperature would have to be raised so that the pour point of the oil would approximate about 25° F. As compared to this, however, when about 35% of diethyl ketone is added to methyl normal propyl ketone, as much as 1 or 2% of water can be tolerated in the solvent used for dilution while obtaining a pour point of about 5° F. The water contamination is then removed in forms of ice crystals with the wax and the water is thus concentrated in the portion of the solvent recovered by stripping the wax slurries. This in turn facilitates the separation of the water contamination by settling and decanting and greatly reduces the load on the dehydration unit in which the wet ketone is dehydrated by distilling the water-methyl normal propyl ketone azeotrope boiling at substantially lower temperature (182° F.) than either water (212° F.) or the ketone (216° F.).

Consequently as disclosed, in order to obtain the important feature of overcoming the difficulties of water contamination, about 20 to 60% by volume of diethyl ketone is to be included in the dewaxing solvent composition.

What is claimed is:

1. Process of dewaxing mineral oil which comprises diluting the oil with a solvent consisting essentially of about 80 to 40% by volume of at least one aliphatic normal ketone selected from the group of ketones having 5 and 6 carbon atoms in the molecule and containing an aliphatic group of at least 3 carbon atoms together with about 20 to 60% by volume of diethyl ketone, thereafter chilling the mixture to a temperature at which wax is caused to precipitate, removing the wax and recovering dewaxed oil.

2. The process defined by claim 1 in which the said solvent consists essentially of about 80% to 40% by volume of methyl normal propyl ketone together with about 20% to 60% by volume of diethyl ketone.

3. A process defined by claim 1 in which the said solvent consists essentially of about 80% to 40% by volume of a mixture of methyl normal propyl ketone and methyl normal butyl ketone together with about 20% to 60% by volume of diethyl ketone.

4. A lubricating oil dewaxing process which comprises admixing the oil with a solvent consisting essentially of about 80% to 40% by volume of at least one aliphatic normal ketone selected from the group consisting of ketones having 5 and 6 carbon atoms in the molecule and containing an aliphatic group of at least 3 carbon atoms together with about 20% to 60% by volume of diethyl ketone, thereafter chilling the said oil-solvent mixture to a temperature at which wax is caused to precipitate, removing the wax and recovering dewaxed lubricating oil.

5. The process defined by claim 4 in which the said oil-solvent mixture is characterized by inclusion of minor proportions of water.

6. The process defined by claim 4 in which the total amount of solvent employed is about 1 to 3½ volumes of solvent per volume of oil.

7. The process for dewaxing a cylinder stock which comprises admixing the cylinder stock with a solvent consisting essentially of about 80% to 40% by volume of at least one aliphatic normal ketone selected from the group of ketones having 5 and 6 carbon atoms in the molecule and containing an aliphatic group of at least 3 carbon atoms together with about 20% to 60% by volume of diethyl ketone, thereafter chilling the mixture to a temperature at which wax is caused to precipitate, removing the wax and recovering dewaxed cylinder stock.

8. The process defined by claim 7 in which the said solvent constitutes a mixture of methyl normal propyl ketone and methyl normal butyl ketone admixed with about 20% to 60% by volume of diethyl ketone.

9. The process for dewaxing a residual oil which comprises admixing the oil with a solvent consisting essentially of about 80% to 40% by volume of at least one aliphatic normal ketone selected from the group of ketones having 5 and 6 carbon atoms in the molecule and containing an aliphatic group of at least 3 carbon atoms together with about 20% to 60% by volume of diethyl ketone, thereafter chilling the mixture to a temperature at which wax is caused to precipitate, removing the wax and recovering dewaxed oil.

10. The process defined by claim 9 in which the said solvent constitutes a mixture of methyl normal propyl ketone and methyl normal butyl ketone admixed with about 20% to 60% by volume of diethyl ketone.

11. In the dewaxing of a mineral oil with a solvent consisting essentially of at least one aliphatic normal ketone selected from the group of ketones having 5 and 6 carbon atoms in the molecule and containing an aliphatic group of at least 3 carbon atoms, the improvement which comprises combining with said solvent about 20% to 60% by volume of diethyl ketone, based on the total solvent composition, and carrying out the said dewaxing process.

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