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K. G. ARABIAN ET AL
DEWAXING HYDROCARBON OIL

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2 Sheets-Sheet 1

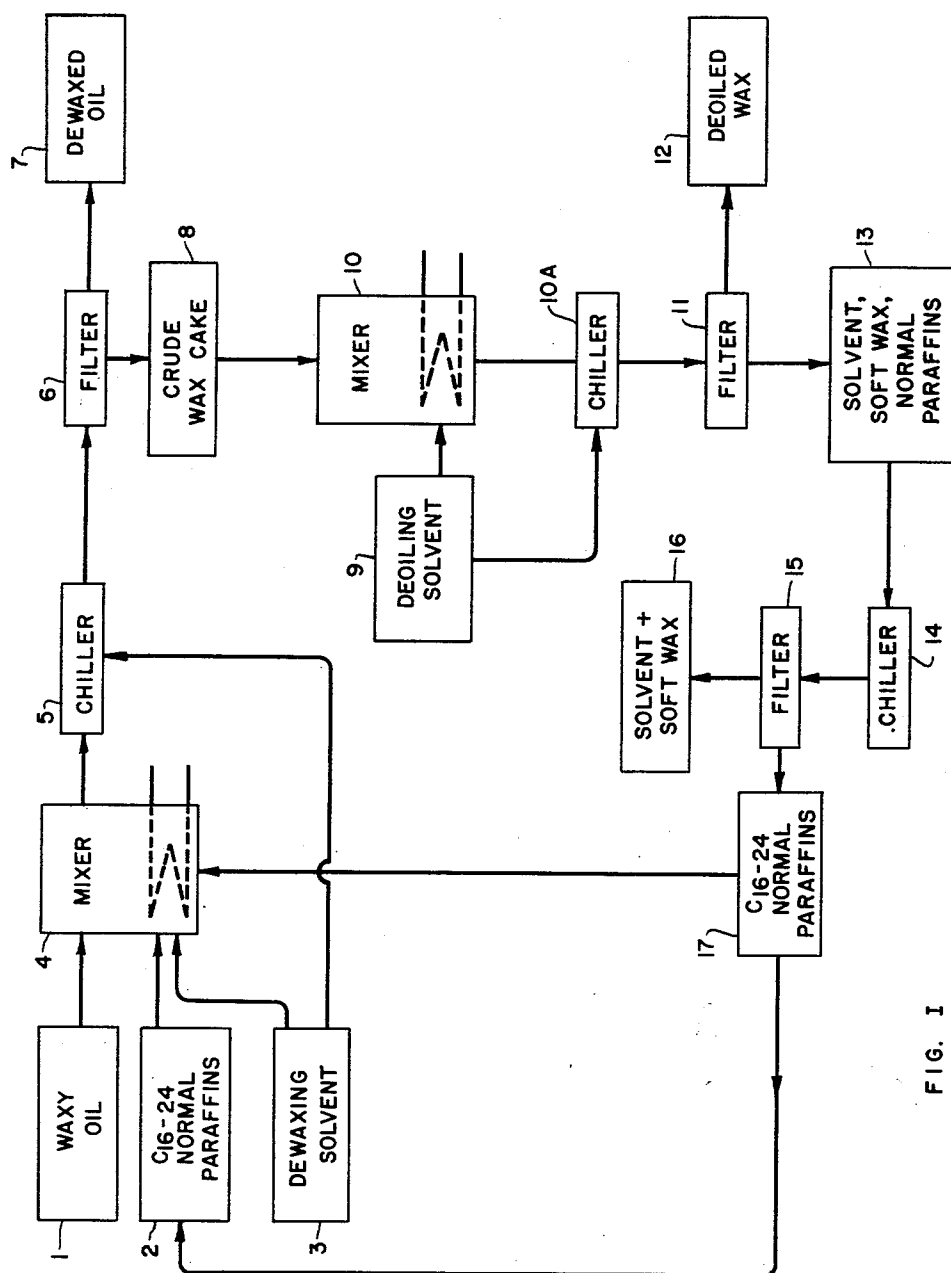


FIG. 1

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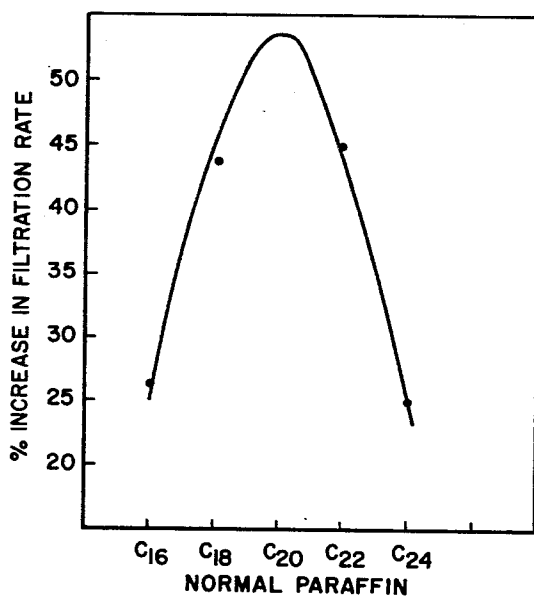


FIG. II

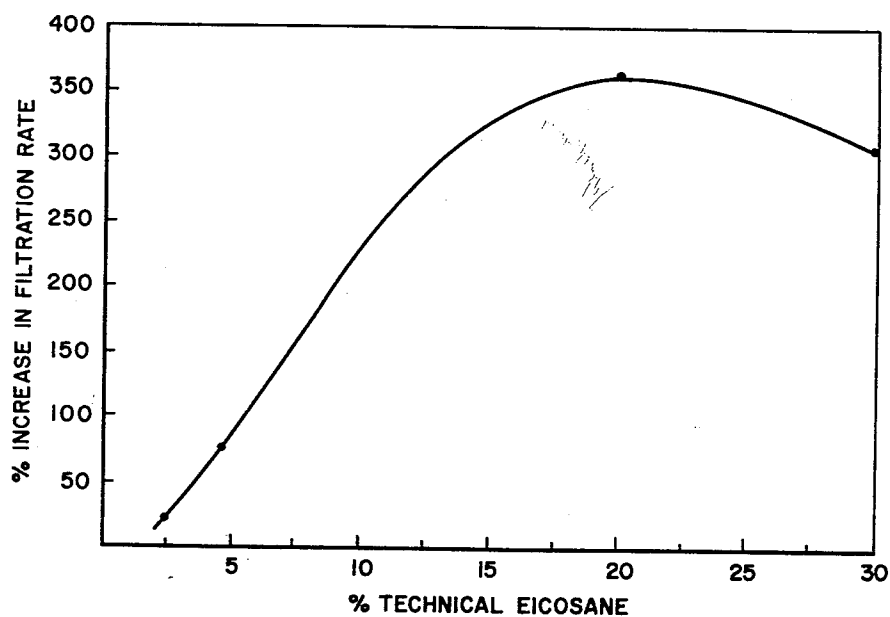


FIG. III

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1

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DEWAXING HYDROCARBON OIL

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8 Claims. (Cl. 208—33)

This invention relates to dewaxing of hydrocarbon oils. More particularly, it relates to an improved process for the dewaxing of heavy distillate and residual lubricating waxy oils.

A widely used method of removing waxes from petroleum lubricating oils comprises the dilution of the oil with suitable solvents or solvent combinations, such as gasoline, esters, ketones, hydrocarbons, such as propane, benzene and toluene, brominated hydrocarbons, chlorinated hydrocarbons, fluorinated hydrocarbons and many others. The principle of the methods utilizing these agents is to compose a diluting liquid which has the property of being homogeneously miscible with the oil at low temperatures while its solvent power for waxes present at this low temperature is relatively insignificant. The solidified wax is then removed from the chilled and diluted oil with the aid of centrifuge, filter or electrostatic means.

While this process is relatively successful when applied to low or medium viscosity lubricating oil distillates, difficulties are encountered, particularly with respect to filtration or other separation rates when residual oils or heavy distillates are so treated. These difficulties appear to be caused by the presence of components in the waxy oil which form relatively weak crystals, such as would be expected from naphtheneic or isoparaffinic hydrocarbons, which predominate in the waxes derived from these two types of oils. Opposed to this, the lighter distillates have increasing amounts of normal paraffin waxes present and coincidentally show increasingly rapid filtration rates during the filtration step (or its equivalent) of the dewaxing process.

Numerous types of substances have been combined with waxy oils for the purpose of increasing filtration rates during dewaxing or deoiling processes. For the most part these have been non-waxy materials. In instances where waxes have been used, they have been simply recycled for the purpose of building up thicker wax cakes which were believed to be more readily scraped off the filter cloth without plugging the interstices thereof. Another difficulty which has been inherent with the types of substances employed for altering the filtration characteristics has been the contamination either of the oil or of the wax product by the added material. This is undesirable since both oils and waxes are usually sold to meet relatively rigid specifications for many objectives. For example, in the wax carton and wax paper industry, the components present in the wax must conform to Federal Food and Drug regulations. Many of the components useful for increase in filtration rates are inoperative for the simple reason that the products containing them turn out to be off-specification in one respect or another.

It is an object of the present invention to improve the process of dewaxing. It is a particular object of the present invention to improve the dewaxing and/or deoiling of heavy distillate and residual lubricating oil fractions. It is a further special object of the invention to

2

increase the filtration rates during dewaxing and deoiling of said fractions. Other objects will become apparent during the following detailed description of the invention, which will be made with reference in part to the accompanying drawings wherein:

FIG. I is a generalized flow diagram of a process embodying the present invention;

FIG. II shows the effect of chain length of the additive upon filtration rate; and

FIG. III shows the effect of concentration of technical eicosane on change in filtration rate.

Now, in accordance with the present invention, it has been found that the separation of wax from heavy distillate or residual petroleum lubricating oils may be expedited by modification of the waxy oil (or the oily wax) with 2–30% by volume based on the wax-bearing oil of straight chain paraffin hydrocarbon having 16–24 carbon atoms per molecule. The straight chain paraffin additives (as they will be referred to hereinafter) are added to the waxy oil and dewaxing solvent prior to or during precipitation of wax during the chilling step wherein the waxy oil and solvent are chilled prior to filtration or other equivalent separation step. The addition of the straight chain paraffin additive has been found to unexpectedly and materially increase the filtration rate when the waxes are separated from the oil and solvent.

It will be noted that the dual objective of the present invention is, first, to improve the filtration rate during separation of waxes from heavy distillates or residual oil (bright stock) streams; and, secondly, to do so without contaminating either the wax product or the oil derived from the dewaxing process. In accordance with the present invention it has been found that this dual objective is achieved with remarkable success, the increase in filtration rate being from 25 to 400% dependent upon the specific low molecular weight normal paraffin additive employed and the concentration of the additive present.

The utilization of the present invention comprises not only the increase in the filtration rate during the primary dewaxing of the lubricating oil but also during the so-called deoiling step, wherein the crude wax separated in the primary dewaxing step is dispersed in a deoiling solvent and chilled to a temperature (usually higher than a dewaxing temperature) so as to reprecipitate the wax while leaving any contaminating oils and/or soft waxes still in the deoiling solvent. In this step also the presence of the straight chain paraffin additive performs the function of increasing the filtration rate of the waxes which are otherwise objectionably slow in filtration. A part of the present invention comprises the selection of a deoiling temperature such that the low molecular weight straight chain paraffins remain in solution together with the oil while the high molecular weight isoparaffinic and naphtheneic waxes precipitate and thus are separated from the straight chain paraffin additive and contaminating oil together with the solvent and any "soft waxes" which are to be removed from the wax product.

The combination of a selected volume and identity of deoiling solvent as well as deoiling temperature can be established by routine examination well known to experts in this art. Variations in this procedure may be in accordance with established practices in the art wherein the dewaxing solvent is added in increments either prior to or during the chilling procedure and even may be added subsequent to achievement of the dewaxing filtration temper-

ature. Efforts are made to cause cocrystallization of the molecular weight straight chain paraffin additive and the microcrystalline or highly naphthenic-isoparaffinic waxes contained in the two lubricating oil cuts with which the present invention is especially successful. It has been found, in fact, that addition of the straight chain paraffin additives to the lighter distillates results in no beneficial increase in filtration rates.

Following chilling of the originally homogeneous mixture and allowing the predetermined time for achieving the correct precipitation of waxes and formation into filtrable crystals, the mixture is conducted to a filter which may be conveniently a rotary drum continuously operating filter of known type, although other equivalent types of apparatus (such as centrifuges and the like) may be employed.

Referring now to FIG. I, a waxy oil from storage 1 is combined with the straight chain paraffin additive from source 2 and the dewaxing solvent from tank 3. These are combined, for example, in mixer 4, where if necessary, the charge is warmed sufficiently to form a homogeneous solution. This solution is passed to the chiller 5 wherein the solution is cooled to a dewaxing temperature. Optionally, additional solvent is injected step-wise during the cooling. The chilled mixture, containing precipitated waxes, is then sent to filter 6 for separation of wax 8 from dewaxed oil 7.

The present invention is especially applicable to separation of the wax and oil by means of a filter since the primary objective is to obtain crystals which do not cause plugging of the filter cloth interstices. The presence of the straight chain paraffin additives increases the rate at which the solvent and oil percolate through the wax cake deposited on the filter surface and can be removed to a receiver 7 shown in FIG. I. Hence, while the additive has performed its essential function of increasing filtration rates, it now is present as a modifier of the wax. However, this can be separated as and if desired by taking the cake 8 to a mixer 10 wherein it is mixed with a deoiling solvent from source 9 which may be the same or different from the dewaxing solvent previously employed. Again, as in the mixing step described above, the wax cake and deoiling solvent may be heated if necessary to cause the formation of a homogeneous solution wherein the wax is effectively dissolved in the solvent together with the additive and any contaminating oil. The same general steps are then performed, namely, passing the homogeneous solution to a chiller 10A wherein it may be chilled without further modification to a filtration temperature or may be modified by incremental addition of further quantities of deoiling solvent from source 9. The chilled mixture in which the suspended wax separates from the solution of contaminating oil and the combination of soft wax and low molecular weight straight chain paraffin additive is then passed to a filter 11, wherein the waxes 12 are separated from the solution of solvent, soft wax, oil and additives which is taken to a storage tank 13.

Optional further steps include the separation of the straight chain paraffin additive from the soft wax, solvent and contaminating oil by first distilling off the solvent under the usual conditions for recovery of the solvent from the products of dewaxing operations, then distilling the mixture of oil, soft wax and straight chain paraffin additive under sub-atmospheric conditions so that the straight chain paraffin additives are recovered as an overhead product and the soft wax and oil remain in the unvaporized residue.

The waxy oil streams to be treated in accordance with the present invention include the so-called heavy distillate stream and the residual oil stream. The former can be roughly defined as that lubricating oil fraction which is the last to distill from a fractionating column and normally will have a boiling range between about 750° F. and about 1000° F. The residual lubricating oil stream may also be referred to as waxy bright stock and is the next higher

boiling cut than the heavy distillate cut. The distillate or residual oils may be solvent extracted and/or clay treated prior to dewaxing in order to remove or decrease aromatics.

The waxes present in the two cuts may be divided into two general classes. The waxes in the heavy distillate fraction include a relatively high proportion of isoparaffinic and naphthenic hydrocarbons, particularly in comparison to the waxes in lower boiling waxy lubricating oil distillates which are predominantly normal paraffinic hydrocarbons with lesser amounts of isoparaffinic and naphthenic hydrocarbons present. The waxes present in the bright stock waxy charge are microcrystalline in character sometimes mixed with smaller amounts of extremely high molecular weight and high boiling point paraffins. In either case the waxes precipitated by prior processes from the higher boiling fractions have been found to have poor filtration characteristics due apparently to the weak crystal structure occasioned by the presence of major proportions of isoparaffinic or naphthenic wax molecules. The high molecular weight normal paraffins naturally occurring or isolated from the subject petroleum fractions do not alleviate this situation. Furthermore, in the case of the bright stock waxy charge the crude waxes obtained may be split into a very high melting point predominately normal paraffin wax fraction and a higher molecular weight but lower melting point microcrystalline wax fraction. This can be conducted either prior to or subsequent to a deoiling operation.

The optimum low molecular weight straight chain paraffin additive for increasing the filtration rate of these classes of waxy oils and waxes will have to be chosen by trial and error to suit the particular waxy oil being processed. The key to the proper choice of the additive is to select a straight chain paraffin additive of such molecular weight and melting point that it will precipitate from the solution at about the same temperature as the isoparaffinic and naphthenic components in the wax, and preferably will cocrystallize with the isoparaffinic and naphthenic components in the range 20 to 30° F. above the filtration temperature for maximum effectiveness. The choice of the proper straight chain paraffin additive will then vary somewhat with the feed stock characteristics, the degree of solvent dilution, and the filtration temperature. In the present instance, it has been found for the waxy oils being treated that an optimum range for the low molecular weight normal paraffins is from 18 to 22 carbon atoms per molecule and that maximum rates of filtration rate increase were obtained by the use of normal eicosane.

The straight chain paraffin additives to be employed may have from 16 to 24 carbon atoms per molecule and may be individual paraffins or mixtures within this range. Technical products such as "technical eicosane" are preferred because of their low cost and ready availability. Technical eicosane is a mixture of normal paraffin hydrocarbons, over 96% of which have from 18 to 22 carbon atoms per molecule and about 75% of which are from 19-21 carbon atoms per molecule.

The proportion of straight chain paraffin additives to be employed will depend again upon the specific waxy oils to be modified and the percentage increase in filtration rate and production rate which is desired for the available apparatus. Hence, amounts between about 2% and about 30% of the straight chain paraffin additive based on the oily wax (or waxy oil) from the two categories given hereinbefore may be utilized. Optimum results are obtained, however, when this proportion of additive is between 4% and about 25% and still more preferably from about 8% to 25% on the same basis.

The dewaxing solvents employed are those well known in the art and do not constitute a novel feature of the present invention. The proportions of dewaxing solvent utilized are also well known in the art and need no further description here. Preferably, however, mixtures of ketones, such as methyl ethyl ketone with aromatic hydro-

carbons, such as toluene, are employed, the proportion of dewaxing solvent being between about 2 parts and 4 parts of dewaxing solvent for each part by volume of the waxy oil charge.

As stated hereinbefore, the dewaxing solvent may be added in a single portion or may be added incrementally before, during or after the chilling of the charge to the filtration temperature. It is preferred that the mixture of solvent and waxy oil be heated to a temperature in the order of 140–180° F. so as to dissolve the waxy oil completely in the dewaxing solvent. The homogeneous solution is then cooled, preferably by chilling rapidly to about the cloud point and thence to about 60–80° F. at a rate of 7–12° F. per minute with stirring. Cooling is then continued at about 5–7° F. per minute to a temperature in the order of 0–20° F. at which point additional dewaxing solvent precooled to approximately the same temperature is added. Cooling is then continued to approximately –15 to +15 after which the slurry of wax is filtered. Filtration is preferably effected on a continuous basis through a textile surfaced rotary drum filter. The present invention is most advantageous at this point, since the unmodified wax has been found to exhibit a slow filtration rate. In the presence of the low molecular weight normal paraffin additives, however, this filtration rate is substantially increased.

The crude wax cake normally contains from 3 to about 35% by weight of oil as a contaminant. Therefore, it is a preferred procedure for most uses to subject the crude wax to a deoiling procedure which is substantially the same as the dewaxing procedure except that different ratios of deoiling solvents and higher filtration temperatures are employed than were utilized during dewaxing. Using the same approximate proportions of deoiling solvent and using substantially the same solvent for deoiling as was used in dewaxing, the wax filtration temperature in deoiling is normally 30–60° F. higher than the filtration temperature in the dewaxing step. Because of the higher temperature of deoiling, it can be expected that the straight chain paraffin additive which will be most effective for increasing the deoiling filtration rate will be different from that which was optimum for dewaxing the waxy oil.

The recycling of preferred proportions of wax from the heavy distillate or residual oil wax streams does not result in the same increase in filtration rates as is effected by the use of the present invention. This is due to the fact that the same straight chain paraffin additives are not present in these two streams as are added according to the present invention. For example, in the splitting of a residual wax stream, the two types of wax produced are as referred to above, namely, microcrystalline wax, which is highly isoparaffinic and naphthenic in character and is of high molecular weight, and on the other hand a very high melting point, high molecular weight normal paraffinic petroleum wax which is unsuitable for use in the present process. Most resins found in crude oils have been found to adversely affect filtration rates and are preferably absorbed or extracted from the feed streams, such as by clay absorption or propane extraction or extraction with solvent for aromatics.

The following examples illustrate the use of the present invention:

EXAMPLE I

The filtration rates experienced in the filtration of wax from a waxy bright stock raffinate previously extracted with phenol were investigated, the stock being dewaxed in the absence of any modifier in one sample, and in a second series of samples in the presence of 4% of individual straight chain paraffins varying from 16 to 24 carbon atoms per molecule. The results obtained are given in Table 1 and shown in FIG. II of the specification.

Dewaxing was effected in this case by heating 100 parts by weight of the waxy oil (with or without the paraffin

additive) together with 150 parts by weight of a 50–50 methyl ethyl ketone-toluene mixture to an initial temperature of 160–170° F. The solution so formed was then cooled rapidly to the cloud point and thereafter to 70° F. at a rate of 7–12° F. per minute and finally to 10° F. at a rate of 5–7° F. per minute. At this point 150 parts by weight of 50–50 methyl ethyl ketone-toluene was added which had been precooled to 10° F. Cooling was continued to 0° F. and the mixture was filtered on a filter cooled to the same temperature, the vacuum on the filter being 15 inches of mercury. The filtration rates were determined by pouring the slurry on the filter, noting the time, collecting the filtrate and noting the time at each 50 cc. increment of filtrate. This was continued until the filtration rate was less than 1 drop per second. The filtrate and oil were then examined.

Deoiling of the wax cake was then effected as follows: The wax cake was redissolved in 150 grams of methyl ethyl ketone-toluene solvent (50:50) and cooled to 120° F. at 7 to 12° F. per minute after which it was then cooled to 65° F. at 5–7° F. per minute at which point 150 parts by weight of methyl ethyl ketone-toluene were added. Cooling was continued to 55° F. at which point the mixture was filtered in order to separate the microcrystalline wax from the solution of solvent, oil, soft wax and straight chain paraffin additives.

Table 1

YIELD OF OILS OBTAINED FROM DEWAXING OF BRIGHT STOCK RAFFINATE TO WHICH INDIVIDUAL STRAIGHT CHAIN PARAFFIN ADDITIVE HAD BEEN ADDED

Charge	Bright stock raffinate, alone	4% C ₁₆ in raffinate	4% C ₁₈ in raffinate	4% C ₂₀ in raffinate	4% C ₂₂ in raffinate	4% C ₂₄ in raffinate
Run number.....	FR-60	FR-68	FR-69	FR-70	FR-71	FR-72
Weight raffinate in charge (g.).....	100	96	96	96	96	96
Weight solvent in system (g.).....	300	300	300	300	300	300
Weight filtrate when run was stopped (g.).....	266.0	285.0	285.0	282.0	267.0	253.0
Weight oil in filtrate (g.).....	52.0	54.3	54.3	51.2	50.0	47.7
Weight solvent in filtrate (g.).....	214.0	230.7	230.7	230.8	217.0	205.3
Weight oil basis total solvent in system (total in solution) (g.).....	73.0	70.6	70.6	66.6	69.1	69.9
Yield of oil in total solvent (basis raffinate) (percent weight).....	73.0	73.3	73.3	69.4	72.0	72.9

It will be noted that according to Table 1 above and FIG. II of the specification maximum filtration rates are obtained by the use of straight chain paraffin additive having 20 carbon atoms per molecule although additives having 18 and 22 carbon atoms respectively were almost as beneficial. The rate of filtration drops off rapidly on either side of this optimum area.

EXAMPLE II

The effect of technical eicosane concentration was investigated and data obtained are shown in Table 2 and FIG. III which follow. The process was essentially as described in Example I above except that where 4% of the individual paraffin additive was added in each of the examples previously, the proportion of technical eicosane employed in the present series of tests was varied from 2 to 30%. Technical eicosane utilized in these experiments has been described hereinbefore. It will be noted according to the data and FIG. III that an optimum rate of filtration is obtained especially between about 8 and 25% by weight, the maximum being at about 20% by weight based on the oil charge.

Table 2

YIELD OF OILS OBTAINED FROM DEWAXING OF BRIGHT STOCK RAFFINATE TO WHICH "TECHNICAL EICOSANE" HAD BEEN ADDED

Charge	Bright stock raffinate, alone	2% technical eicosane in raffinate	4% technical eicosane in raffinate	20% technical eicosane in raffinate
Run number	FR-60	FR-57	FR-63	FR-64
Weight raffinate in charge (g.)	100	98	96	80
Weight solvent in system (g.)	300	300	300	300
Weight filtrate when run was stopped (g.)	266	269	270	234
Weight oil in filtrate (g.)	52	51.4	50	33
Weight solvent in filtrate (g.)	214	217.6	220	201
Weight oil basis total solvent in system (total in solution) (g.)	73	71.2	68.2	49.2
Yield of oil, in total solvent (basis raffinate, percent weight)	73	73	71	61.5

We claim as our invention:

1. In the art of solvent separation of waxes and oils in mixtures of the group consisting of mixtures of heavy distillate petroleum lubricating oil with heavy distillate wax and mixtures of residual petroleum lubricating oil with residual petroleum wax feed mixtures containing at least about 25% by weight of wax by filtration involving the forming, washing, drying and discharging of a wax cake, the steps comprising mixing a dewaxing solvent with the wax-bearing oil, which mixture if unmodified tends to deposit a wax filter cake permitting only a relatively slow filtration rate, modifying the mixture by adding thereto 2-30% by volume based on the wax-bearing oil waxes consisting essentially only straight chain hydrocarbons having 16-24 carbon atoms per molecule, chilling the mixture to a temperature between -15° F. and +15° F. to precipitate wax whereby co-crystallization of the added straight chain wax with waxes in the waxy oils occurs, and passing the chilled mixture to the filter to remove the wax and to separate dewaxed oil, the filtration rate of the modified mixture being substantially higher than that of the unmodified mixture.

2. In the art of dewaxing wax-bearing oils of the group consisting of heavy distillate petroleum lubricating oils and residual petroleum lubricating oils feed mixtures containing at least about 25% by weight of wax by filtration involving the forming, washing, drying and discharging of a wax cake, the steps comprising mixing a dewaxing solvent with the wax-bearing oil, which mixture if unmodified tends to deposit a wax filter cake permitting only a relatively slow filtration rate, modifying the mixture by adding thereto 2-30% by volume based on the wax-bearing oil waxes consisting essentially only straight chain hydrocarbons having 16-24 carbon atoms per molecule, chilling the mixture to a temperature between -15° F. and +15° F. to precipitate wax whereby co-crystallization of the added straight chain wax with waxes in the waxy oils occurs, and passing the chilled mixture to the filter to remove the wax and to separate dewaxed oil, the filtration rate of the modified mixture being substantially higher than that of the unmodified mixture.

3. In the art of dewaxing wax-bearing residual petroleum lubricating oils containing at least about 25% by weight of wax by filtration involving the forming, washing, drying and discharging of a wax cake, the steps comprising mixing a dewaxing solvent with the wax-bearing oil, which mixture if unmodified tends to deposit a wax filter cake permitting only a relatively slow filtration rate, modifying the mixture by adding thereto 2-30% by volume based on the wax-bearing oil waxes consisting essentially only straight chain hydrocarbons having 16-24 carbon atoms per molecule, chilling the mixture to a temperature between -15° F. and +15° F. to precipitate wax whereby co-crystallization of the added straight chain wax with waxes in the waxy oils occurs, and passing the chilled mixture to the filter to remove the wax and to separate dewaxed oil, the filtration rate of the modified mixture being substantially higher than that of the unmodified mixture.

4. A process according to claim 1 wherein the modifying straight chain hydrocarbons have 18-22 carbon atoms per molecule.

5. A process according to claim 1 wherein the modifying straight chain paraffin is present in an amount between about 4 and 25% by weight of the wax-bearing oil.

6. In the art of dewaxing and deoiling wax-bearing petroleum lubricating oils of the group consisting of heavy distillate oils and residual oils feed mixtures containing at least about 25% by weight of wax, the steps comprising mixing a dewaxing solvent and 2-30% by weight straight chain paraffin hydrocarbons having 16-24 carbon atoms per molecule with the waxy oil, chilling the mixture to precipitate wax and said hydrocarbons, passing the chilled mixture to the filter to remove the wax and hydrocarbons, dissolving the removed wax and hydrocarbons in a deoiling solvent and chilling to a deoiling temperature, said deoiling temperature being sufficiently high to dissolve oil and said hydrocarbons and sufficiently low to precipitate a substantial proportion of the wax and passing the chilled mixture to a filter to remove the precipitated wax, the filtration rates in both filtration steps being substantially increased by the presence of the hydrocarbons.

7. A process according to claim 6 wherein the straight chain hydrocarbons have from about 18 to about 22 carbon atoms per molecule.

8. A process according to claim 6 wherein the straight chain paraffin hydrocarbons are present in the dewaxing step in an amount between about 4% and about 25% by weight of the wax-bearing oil.

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