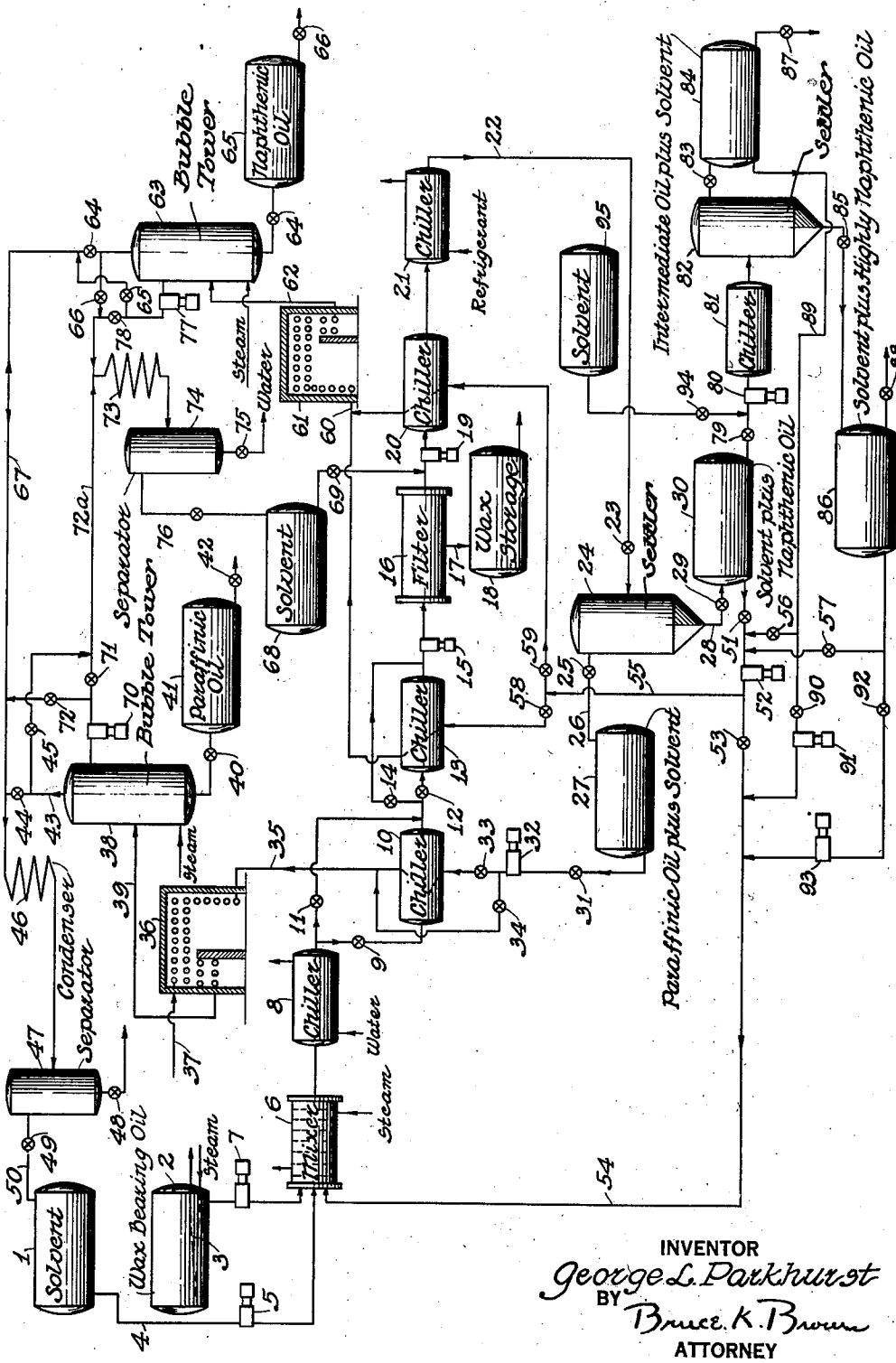
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FRACTIONATION OF OILS

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FRACTIONATION OF OILS

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This invention relates to the fractionation of wax-bearing oils, and particularly wax-bearing mineral oils, into one or more wax fractions and one or more oil fractions by the use of special solvents.

One object of this invention is to provide a more efficient method for dewaxing mineral oils by the use of special solvents. Another object is to provide a dewaxing process in which the solvent loss can be minimized. A further object is to provide such a dewaxing process in which a portion of the filtrate is separated from the remainder thereof and recycled to the beginning of the dewaxing process. A still further object is to provide a dewaxing process using special solvents, in which the dewaxed solution is separated into two or more liquid fractions containing lubricating oils differing in quality. Another object is to provide a process of the type last mentioned in which one of the liquid fractions is recycled to the beginning of the dewaxing process. Another object is to provide a process to accomplish the aforementioned ends with high thermal efficiency.

Further objects will become apparent as the description proceeds. My invention may be more readily comprehended by reference to the accompanying drawing which represents a conventionalized flow diagram of the process.

Referring now more particularly to the drawing, 1 represents a suitable storage receptacle for the solvent or solvent mixture used in the process. As to the selection of a suitable solvent or solvent mixture, more will be said hereafter. Another storage receptacle 2 provided for the wax bearing mineral oil which is the stock on which the process of my invention operates. Since in many cases this wax bearing mineral oil will be very viscous, or even solid, it is generally advisable to provide heating means for storage receptacle 2. In the diagram this is accomplished by means of steam coils 3. In operating the process solvent is removed, preferably continuously, from receptacle 1 through line 4 by means of pump 5 into mixer 6. Simultaneously the wax-bearing oil is removed from receptacle 2 by means of pump 7 and introduced into mixer 6. Mixer 6 may be of any type adapted to effect complete solution of the wax-bearing oil in the solvent. For instance, it may be of the well-known orifice type. In some cases it may be desirable to add heat prior to or during the mixing operation in order to effect complete solution. In the diagram shown, this is done by means of a steam jacket surrounding mixer 6, but it will readily be comprehended that other means can be used when it is necessary to supply heat. It is desirable that solution be effected at the lowest possible temperature so as to minimize the chilling which is necessary in the next step of the process. The dissolved oil passes out of mixer 6 and through a preliminary chiller 8, which is preferably cooled by means of cold water. This chiller may be of any type, for instance, the conventional tubular heat exchanger. The chilled solution from chiller 8 will commonly pass through valve 9 and into chiller 10 where it will be chilled by contact with one of the intermediate products of the process. In some cases, to be described hereafter, it may be desirable to by-pass chiller 10 by closing valve 9 and opening valve 11. The solution will commonly pass out of chiller 10 through valve 12 into a still further chiller 13 where the temperature of the solution is lowered by heat exchange with still another intermediate product of the process. Facilities are also provided for by-passing chiller 13 by closing valve 12 and opening valve 14. By means of this or a similar series of chillers the temperature of the solution of wax-bearing oil is lowered to the temperature desired for the removal of wax. In other words, the plant is so constructed that the major portions of the wax will be precipitated at the temperature produced by the final chiller. More will be said hereafter as to the degree of chilling required. The solution from the last chiller will generally need to have its pressure raised in order to force it through the wax removing equipment. This is done by means of pump 15 in the case of the process illustrated by the drawing. The solution is then passed through filter 16 where the precipitated wax is removed. This filter may be of any desired type. For instance, it may be a continuous rotary filter or it may be a battery of plate and frame presses arranged so that continuous operation can be maintained by using a portion of the presses while the remainder are being cleaned. Although my process is devised more particularly for conditions where wax will be precipitated in substantially crystalline form, it may nevertheless be desirable in some cases to replace filter 16 by some other type of wax removing equipment, such as a centrifuge or settling tank and it is to be understood that the use of such equivalents in place of filter 16 is within the scope of my invention. Suitable provision, not shown, may be made for washing the filter cake, etc. The separated wax is removed through line 17, which may suitably be a heated pipe or a screw conveyor, into a storage receptacle 18,

from which the wax can be removed for further treatment or use as desired. The filtrate from filter 16 is then further chilled, first passing through pump 19 and then in series through chillers 20 and 21. Part of this additional chilling may be done by means of heat exchange with one of the intermediate products of the process, but for the final chilling it will generally be necessary to use external refrigeration, such as can be provided by cold brine or direct ammonia expansion. The final chiller is adapted to lower the temperature of the solution to a point at which it will become separated into two liquid phases. The cold solutions from the final chilling operation pass through line 22 and valve 23 into settler 24 wherein the two liquid phases are allowed to settle and are separately removed. Settler 24 may be of any conventional type. The one diagrammatically shown is a simple continuous gravity settler, the mixed liquids formed by the chilling being introduced into the settler at an intermediate point; the two phases separating under the force of gravity, the lighter one being continuously removed from a point near the top through valve 25 and line 26 into a storage receptacle 27, while the heavier phase is removed from a point near the bottom through line 28 and valve 29 into storage receptacle 30. The rate of removal of these materials from settler 24 is such as to balance the rate at which they are introduced into the settler through valve 23. It is to be understood that other types of continuous settling equipment may suitably be used or that settler 24 may be replaced by a battery of batch settlers.

An inspection of the process as thus far described reveals that it consists in dissolving a wax-bearing oil, preferably a wax bearing mineral oil, in a selected solvent or solvent mixture, the chilling of the solution thus formed to a dewaxing temperature, the removal of the wax, the further chilling of the dewaxed solution to a point at which two liquid phases separate in predetermined proportions and the separate removal of these two liquid phases. The purpose of the dewaxing step is well known. The advantage of combining it with the solvent fractionation of the lubricating oil constitutes one of the major discoveries included within the scope of the present invention. It has been found that when an oil is dissolved in a suitable selective solvent or solvent mixture and chilled to a point at which two liquid phases are formed that one of these phases will contain a relatively large proportion of the solvent and a relatively small proportion of the oil, whereas the other phase will contain a relatively small proportion of solvent and a relatively large proportion of oil. It will be found, moreover, that there is a great difference in the chemical nature, as well as in the physical properties of the oils contained in the respective liquid phases. Thus, for example, when the process is operated on a wax bearing mineral oil of the mixed-base type, it will be found that the phase containing the greater proportion of solvent will in general contain a mineral oil of relatively naphthenic characteristics, whereas the phase containing the smaller proportion of solvent will contain an oil of a considerably more paraffinic nature. This latter oil will, of course, be much more valuable for ordinary lubricating purposes than the former. For instance, it will have a much lower temperature co-efficient of viscosity and a much greater resistance to oxidation and sludging. In other words, by means of my process the oil is first dewaxed and then separated into a fraction containing an oil relatively desirable for ordinary lubricating purposes and a fraction containing an oil relatively undesirable for this type of use.

In the drawing, the paraffinic oil containing the smaller proportion of solvent is shown as being removed from the upper portion of settler 24 into receptacle 27, while the phase containing the larger proportion of solvent, together with the dissolved naphthenic oil, is removed from the bottom of settler 24 into receptacle 30. It will be understood that the specific gravity of the solvent or solvent mixture selected will generally have a controlling influence upon which of these two liquid phases is the lighter and it will further be understood that in some cases the phase containing the naphthenic oil will be the lighter and will therefore be removed from the top of the settler while that containing the paraffinic oil will be removed from the bottom thereof. In any event, it is possible by means of my process, to separate the dewaxed oil solution by chilling it to a selected temperature into one liquid phase containing the more desirable portions of the oil, together with a relatively small proportion of the solvent and another liquid phase containing the bulk of the solvent and, in general, a relatively small proportion of an oil which is inferior for ordinary lubricating purposes.

In the flow diagram of the process, the separated paraffinic oil, having characteristics superior to those of the original dewaxed oil, passes out of receptacle 27, through valve 31, pump 32 and valve 33 to chiller 18 where its capacity to absorb heat is utilized to lower the temperature of the incoming solution. In some cases it will be understood that the paraffinic oil containing some solvent may be sufficiently viscous at the low temperatures involved to make it impractical to utilize its capacity to absorb heat and in this event chiller 18 may be by-passed by closing valve 33 and opening valve 34. When this is done it will generally be desirable to remove chiller 18 and shunt the incoming solution around it by closing valve 9 and opening valve 11, as hereinbefore described. In either mode of operation the paraffinic oil, containing some dissolved solvent, will pass through line 35 into still 36, which is shown as a pipe heater. The solution is heated in this still to a temperature adapted to the efficient operation of bubble tower 38. This temperature will depend on the nature of the solvent and oil, the concentration of the oil and other factors. Steam should, in most cases, be injected into still 36, through line 37 and/or into the base of bubble tower 38 in order to effect distillation without injury to the paraffinic oil. The vapors from still 36 pass through line 39 and enter bubble tower 38 at an intermediate level therein. Bubble tower 38 is adapted to the removal of the solvent or solvent mixture, which in general has a relatively low boiling point, from the oil. The oil will pass out of the base of bubble tower 38, through valve 40, into a suitable storage receptacle 41 from which it may be removed through valve 42, as desired, for further treatment or use. In some cases it may be possible to use the paraffinic oil from storage receptacle 41 directly as an improved lubricant, but in other cases it will be desirable to give it further treatments, as for instance, with sulphuric acid and/or fuller's earth. The solvent vapors from bubble tower 38 ordinarily pass out through line 43 and valve 44 (valve 45 being closed) into condenser 46 where

they are condensed and pass into separator 47 where the water formed from the injected steam is continuously removed through valve 48. The solvent condensate is simultaneously removed from separator 47 through valve 49 and is returned to receptacle 1 through line 50. If the solvent being recovered is heavier than water, it will, of course, be drawn off at the lower level and the water at the upper level. Furthermore, it is to be understood that this whole arrangement of still, bubble tower, condenser and separator is merely for the purpose of separating the paraffinic oil separated in settler 24 from the relatively small amount of solvent which is necessarily carried with it. This equipment can conveniently be replaced by any other suitable type of separating equipment. For instance, the solvent may be stripped from the oil by means of a vacuum still. In many cases it will be desirable to so arrange the distillation equipment that it will be unnecessary to vaporize the oil.

Returning now to the other intermediate product removed from settler 24, it will be recalled that this constitutes the bulk of the solvent carrying in solution therein certain naphthenic portions of the original lubricating oil. This second liquid phase is shown as being removed from settler 24 through line 28 and valve 29 into storage receptacle 30. From storage receptacle 30 this material may optionally be passed through one or more of three alternative series of operations. These three series of operations may be succinctly described as (1) recycling to the dewaxing operation, (2) separate recovery of the solvent and naphthenic oil, and (3) further chilling to form two further liquid phases.

These various alternative procedures will be discussed in the order named, together with their concomitant advantages. In the first procedure, the solution from receptacle 30 is removed therefrom through valve 51 by means of pump 52 and thence through valve 53, ultimately passing into mixer 6, through line 54. It will be readily comprehended that this constitutes recycling the solution contained in receptacle 30 back to the beginning of the process and it will furthermore be readily seen that this could alternatively be done by leading line 54 into receptacle 1 or receptacle 2 or by introducing it into chiller 10 or by introducing it at some other point in the process prior to the removal of wax by means of filter 16. In any of these procedures it will be seen that complete utilization of the capacity of the solution from receptacle 30 to absorb low temperature heat will be had. This makes for a very high degree of thermal efficiency, since the solution in receptacle 30 will generally constitute by far the larger proportion of the total filtrate from filter 16 and since it will pass, at a very low temperature, directly into the material to be dewaxed, thereby cooling it very materially and efficiently. In many cases this will allow chillers 8, 10 and 13, or part of them, to be dispensed with and thereby greatly increase the thermal efficiency of the process. It will be understood, of course, that if line 54 is led into mixer 6 it would be thermally inefficient to heat the said mixer 6 and that in case it is necessary to introduce heat in order to effect complete solution, it would be preferable to introduce the material from line 54 into some subsequent step of the process, for instance, just prior to introduction of the solution into filter 16.

In addition to the high thermal efficiency obtained by operating this process in this manner there is another very prominent advantage in that solvent losses are kept at an unusually low figure. In operating dewaxing processes using special solvents, the largest item of expense has, in the past, resulted from the loss of considerable volumes of solvent during the operation of the process. The special solvents used are, without exception, relatively expensive and these losses represent a very important economic consideration. In the operation of a conventional dewaxing process using special solvents, the solvent is recovered from both the wax and the oil by means of distillation and since it is difficult, if not completely impossible, to arrange distillation equipment in such manner as to obviate all solvent losses, a large proportion of the total solvent loss occurs in the distillation step. It will be observed that operating my process in the manner described the great majority of the total solvent passes into storage receptacle 30 and is removed therefrom and recycled back to the dewaxing operation in the liquid phase. Thus the great bulk of the solvent circulated in the process is never vaporized and solvent losses are thereby maintained at an exceedingly low figure. Furthermore, it has been found that in some cases the recycling of the more naphthenic portions of the oil has a desirable effect on the dewaxing operation which may possibly be explainable as a favorable influence exercised upon the crystallization of the wax tending to promote a type of wax crystallization more consonant with efficient wax removal than that otherwise prevailing.

Coming now to the second alternative procedure which can be applied to the solution in receptacle 30, it will be recalled that this, in brief, consists of separating the naphthenic oil from the solvent and separately recovering it. In order to accomplish this the solution is removed from receptacle 30, through valve 51, pump 52 and line 55 (valves 53, 56, and 57 being, in general, closed). By closing valve 58 and opening valve 59 this solution may then be passed through chiller 20 where its capacity to absorb low temperature heat is utilized in lowering the temperature of the solution passing from the dewaxing operation. Under different conditions of operation it may be desirable to utilize this capacity to absorb low temperature heat, in whole or in part, prior to, rather than subsequent to the passage of the incoming solution through filter 16. This can be done by means of valve 58 which allows the solution from receptacle 30 to be passed through chiller 13. The solution passes out of chiller 20 and/or chiller 13 through line 60 and into still 61 which may be similar to still 36. The heated stream from still 61 passes out therefrom through line 62 and into an intermediate section of bubble tower 63, the naphthenic oil being removed from the base of bubble tower 63 through valve 64, into storage receptacle 65 from which it can then be withdrawn through valve 66 for any purpose to which it is desired to put it. The solvent vapors from bubble tower 63 will commonly pass out therefrom through valve 64 (valves 65 and 66 being closed) and thence through line 67 into condenser 46 where it joins the solvent vapors from bubble tower 38, being condensed together with them and returned to storage receptacle 1 or to some other point in the process, preferably prior to mixer 6. It will be seen that by operating this process in the manner last aforementioned the original wax-

bearing oil is first dewaxed at a selected temperature and then rechilled to a temperature at which the solution separates into two liquid phases, one of them containing a relatively paraffinic oil and one of them a relatively naphthenic oil, each oil being separately recovered as a product of the process and the separated solvent being recycled to the beginning of the process.

This procedure constitutes, under many circumstances, one of the most desirable modes of operating the process of my invention since it allows efficient removal of wax, which is commonly necessary in order to produce high quality oils from wax-bearing stocks, and then, without removal of the solvent from the dewaxed oil and without loss of the low temperature of the solution containing the dewaxed oil, proceeds by further steps to separate the oil into two fractions, one of them of highly improved characteristics for ordinary lubricating purposes and the other of them, although not highly suitable for use as an ordinary lubricant, possessing interesting potentialities as a by-product.

Another advantage of this type of operation lies in the fact that the oil which is subjected to the solvent fractionation is a wholly, or at least partially, dewaxed oil and this fact lends itself to efficient separation of the oil into two liquid phases, since the presence of excess wax during the solvent fractionation step tends to interfere therewith by rendering one of the separated phases semi-solid or slushy.

Two procedures to which the solution in storage receptacle 30 may be subjected have been described; namely, recycling the solution to the dewaxing operation and recovery of its components (solvent and naphthenic oil) separately. It will be understood, however, that my invention contemplates, and in many cases it will be desirable, to use both of these procedures simultaneously. That is, by opening valve 53 as well as valve 58 and/or valve 59, a portion of the solution from receptacle 30 may be recycled and another portion passed through chiller 13 and/or chiller 28 and then separated into its components. This type of operation will allow to a considerable extent a combination of the advantages of each of the two types of operation when separately used. Thus a considerable portion of the total solvent will be recycled without being distilled, thereby reducing solvent losses and accomplishing a large amount of chilling by direct heat exchange, while another portion of the solution is separated into its components, a portion of the more naphthenic oil being continuously removed from the system, which tends to increase the quality of the paraffinic oil produced by the process and at the same time yields a useful by-product in the form of the naphthenic fraction itself.

Before discussing the third alternative procedure which may be applied to the solution in receptacle 30 it will be desirable to discuss some of the features of the process as thus far described.

As to the selection of a suitable solvent or solvent mixture for use in my process, it will be readily comprehended that in general the most satisfactory solvent will be composed of a single component, since by using a single component solvent fewer difficulties are encountered in the removal of the solvent from the oil and in recycling it. Furthermore, another important advantage of using a single component solvent is that the solvent carried by the paraffinic oil and by the naphthenic oil will be the same and it will therefore be unnecessary to provide for returning the solvent from these two sources to the beginning of the process at the same rate. Another advantage is that difficulties due to the separation of a portion of the solvent as a separate liquid or solid phase during the chilling operation are more rarely met with. Nevertheless it will be comprehended that in some cases suitable solvents comprising two or more components may be used as hereinafter described.

Since one of the unique features of my process is that the oil is wholly, or to a major degree, dewaxed prior to its fractionation into two liquid phases, it will be understood that it will be desirable in many cases to select the solvent used in the process according to its properties as a dewaxing agent. It is known that in order to remove wax by the use of special solvents at any given temperature as completely as possible it is necessary to use a solvent of such nature and in such amount that a portion of the oil will be on the verge of precipitation therefrom at the dewaxing temperature since when the oil is barely soluble the wax will have the maximum insolubility. Furthermore, it is known that in order to remove wax completely from typical wax-bearing lubricating oil fractions it is necessary that this dewaxing operation take place at a fairly low temperature, say minus 10° F. or below. Consideration of these principles leads to the conclusion that for many types of operation the most satisfactory solvent or solvent mixture for use in my process is one which is adapted to remove the wax as completely as possible at a selected dewaxing temperature. Such a solvent not only produces final oils which are wholly or substantially wax free, but it removes the wax as efficiently as possible at the selected temperature. Furthermore, since this efficient removal of the wax carries with it as an inevitable concomitant, the condition that the oil be on the verge of precipitation, it will be apparent that the dewaxed oil solution may be separated into two liquid phases with the minimum amount of additional chilling, since any chilling substantially below the dewaxing temperature will tend to throw a portion of the oil out of solution or, in other words, it will cause the oil to separate into two liquid phases, one of them containing an oil of a relatively paraffinic nature and the other an oil of a relatively naphthenic nature.

A considerable number of solvents and a much larger number of solvent mixtures are capable of accomplishing this purpose and their selection is, for the most part, a simple matter of experiment in accordance with the principles laid down in this disclosure. Among the solvents which may suitably be used under many circumstances may be mentioned butyl formate, butyl acetate, amyl acetate and isopropyl ether. Any of these solvents may be used in the ratio of about two or three volumes for each volume of wax-bearing lubricating oil fraction and the wax can be removed, in most cases substantially completely, by chilling the solution thus formed to a temperature in the neighborhood of minus 10° F. or minus 15° F. A further chilling to a temperature of from 15° F. to 60° F. lower than the dewaxing temperature will serve to separate the dewaxed oil solution into suitable proportions of two liquid phases. The exact temperature chosen for this latter operation will depend upon the respective quantities of the two liquid phases desired and more particularly upon a balance between

the desirable effects which may result from additional chilling and the cost of the additional refrigeration. Other factors may also affect the decision as to the desired temperature of the final chilling, such as, for instance, the viscosity and resultant ease of separation of the two liquid phases formed. These considerations, however, are mere matters of conventional engineering practice and will not be considered in detail here.

As a specific example of a process of this general type a wax bearing lubricating oil fraction produced by the fractional distillation of a typical Mid-Continent crude, said lubricating oil fraction having a viscosity at 210° F. of approximately 75 seconds Saybolt, may be dissolved continuously at slightly elevated temperatures in two and one-half times its own volume of isopropyl ether and the solution thus formed may be chilled to a temperature of minus 10° F. The wax contained in the wax-bearing mineral oil will be substantially completely precipitated at this temperature and may be removed by suitable means, as for instance, by filter pressing. The dewaxed oil solution from this operation may then be additionally chilled to a temperature of minus 45° F., at which temperature the solution will separate into two liquid phases, one of which will contain the bulk of the oil and a relatively small proportion of the isopropyl ether and the other of which will contain, in most cases, a smaller proportion of the oil and a larger proportion of the isopropyl ether. Furthermore, it will be found that the oil which was thrown out of solution (i. e. the oil containing the smaller proportion of isopropyl ether) have different properties and will be more paraffinic than that retained in solution in the bulk of the isopropyl ether.

These two liquid phases may be continuously separated from each other in a continuous settler or in a battery of batch settlers and it is generally desirable to utilize their capacity to absorb low temperature heat by passing them through chillers or heat exchangers whereby their temperature is raised and the temperature of the incoming solution lowered. Thereafter the two oil fractions may be separated from the isopropyl ether carried therewith by means of suitable distillation equipment and the two oil fractions may be removed to storage prior to further treatment or use. The separated isopropyl ether is conveniently recycled to the beginning of the process. As an alternative, the whole or a portion of the isopropyl ether containing dissolved naphthenic oil may be directly recycled to the beginning of the process, thereby securing the advantages in heat exchange and low solvent loss which have previously been described.

Although the advantages of operating in such manner and at such temperature as to remove substantially all the wax prior to the separation of the oil in two liquid fractions have been mentioned and are important when it is desired to produce low cold test oils, it is nevertheless to be understood that it is possible, and under some circumstances desirable, to so operate as to remove only the major portion of the wax prior to further chilling and this is contemplated as an important part of my invention. The principal advantage of this method of operation is the lower refrigeration requirement. In some instances, no refrigeration at all beyond ordinary cooling water temperature is necessary. Furthermore, by operating at higher temperatures the viscosities of the solutions are higher and therefore pumping costs are lower and less difficulty is encountered in the separation of the various phases produced. The principal disadvantage of working with these higher temperatures is that the incomplete removal of wax sometimes introduces complications in the later cooling stages.

As an example of such a process operating at a higher temperature, nitrobenzene may be used as a solvent in dewaxing a lubricating oil of the general type discussed above, the solution being effected at an elevated temperature, say 130° F., the dewaxing taking place after chilling to about 50–70° F. and the separation of the two liquid phases taking place at a temperature of approximately 20–40° F. Another suitable solvent is pyridine. In its use dewaxing can conveniently be accomplished at 40–50° F. and the separation into two liquid phases can be accomplished at 0–20° F.

Although certain specific solvents have been described for use in my process it will be understood that a great many organic liquids which are solvents for the oils and waxes in question may be used with greater or less efficiency if the conditions of operation are properly selected. Petroleum fractions or wholly hydrocarbon solvents are generally unsuitable. Amongst solvents which are suitable for use alone or in mixture in my process when operating on various types of oils may be mentioned methylethyl ketone, dichlorethyl ether, isopropyl alcohol, butyl alcohol, acetone aniline, phenyl acetate, benzaldehyde, propionic acid, etc. It is to be understood, however, that with any specified oil some of these solvents will not work efficiently due to the solubility of the oil and/or wax being higher or lower than is desired under suitable operating conditions. Furthermore, these various solvents will be found to vary greatly in selectivity, that is, in the degree of difference between the relatively paraffinic and relatively naphthenic fractions produced.

It will be readily comprehended that, as a variant of the process illustrated in the drawing, a portion of the wax may be removed at a relatively high temperature and that another portion may be separately removed after chilling to a somewhat lower temperature. Such processes may be advantageous under some circumstances. Furthermore, it is to be understood that if the wax is only incompletely removed prior to separation of the oil into two fractions, it will generally occur that the remainder of the wax, or most of it, will be thrown out of solution together with the more paraffinic oil during the liquid fractionation step of the process and this wax can be removed by suitable subsequent operations if desired.

Although in the process as thus far described it has been assumed that the composition of the solvent did not vary throughout the different stages of the process, it will be readily seen that it is possible, and may, under certain conditions, be desirable, to modify the composition and/or change the amount of the solvent or solvent mixture between the dewaxing step and the subsequent fractionation of the oil. In the diagram this possibility is shown by means of a supplemental solvent receptacle 68 from which, by means of valve 69 and pump 19, an additional amount of the solution contained in receptacle 1 or of a different solvent may be introduced into the solution flowing from the dewaxing filter 16 to chiller 20 or at some other point between filter 16 and settler 24. If the solvent added at this

point is of the same composition as that contained in receptacle 1, receptacle 68 can be dispensed with and solvent may be supplied at this point directly from receptacle 1 or alternatively a portion of the solvent flowing from separator 47 to receptacle 1 may be diverted to receptacle 68 by means of a suitable line not shown.

This introduction of an additional amount of solvent may be desirable in some cases to reduce the viscosity of the solution being separated in settler 24 in order to enhance the settling operation. In other cases, however, it will be found more desirable to add an additional solvent subsequent to the dewaxing step in order to bring about a more effective separation of the dewaxed oil solution into two liquid phases. In this case, since solvents of two different compositions are being introduced at two different points of the process, it will be necessary to provide in the solvent recovery system suitable means for separating these two components, wholly or partially, in order to separately return them to receptacles 1 and 68 respectively. It will be apparent that when operating in this fashion the solvent mixture carried by the two separated liquid phases will, in general, be of different composition but that, in general, both of these solutions will contain some of the solvent introduced from receptacle 1 and some of the solvent introduced from receptacle 68. Means are therefore provided for returning to each of these two receptacles a solvent or solvent mixture of substantially the same composition as that withdrawn therefrom in order to maintain the process on a constant basis. In order to accomplish this the solution withdrawn from receptacle 27 and ultimately passing in vapor form into bubble tower 38 may be separated into three fractions rather than two. Specifically, the paraffinic oil may be removed from the base of bubble tower 38, through valve 49, into storage receptacle 41 as heretofore shown and the solvent vapors may be fractionated into two components, the lighter of them being withdrawn from the top of the bubble tower through line 43 and the heavier of them being withdrawn from an intermediate point in the bubble tower 38 through pump 76. Suitable auxiliary fractionation means, such as reflux equipment, or dephlegmators, may of course be provided. If the vapors removed through line 43 correspond to the liquid material in receptacle 1 they will be passed as heretofore described through valve 44, condenser 46, separator 47, valve 49 and line 50 back to receptacle 1 and the liquid withdrawn from bubble tower 38 from an intermediate point therein by means of pump 76 will pass through valve 71, (valves 72 and 45 being closed), line 72a, condenser 73 (if necessary), separator 74 (water being withdrawn from the bottom thereof through valve 75) and valve 76 back to solvent receptacle 68 from which it may be returned to the process. However, it will be understood that in some cases the lighter fraction from bubble tower 38 may correspond to the material which it is desired to return to receptacle 68 rather than to receptacle 1 and that, correspondingly, the material withdrawn from bubble tower 38 through pump 76 may be that which it is desired to return to receptacle 1 rather than to receptacle 68. In order to accomplish this end, material from line 43 is passed through valve 45 (valves 44 and 71 being closed) and line 72a into condenser 73 and separator 74 and thence through valve 76 back to receptacle 68. Simultaneously the heavier solvent fraction is withdrawn from bubble tower 38 by means of pump 76 and passed through valve 72, condenser 46, separator 47, valve 49, and line 50 back to receptacle 1. It will thus be seen that by appropriate manipulations of valves 44, 45, 71 and 72 either the lighter or heavier solvent fraction can be returned to receptacle 1 and the other fraction to receptacle 68.

Similarly, in the case where the solvent or solvent mixture in receptacle 68 is different from the solvent or solvent mixture in receptacle 1, it will generally be necessary, in recovering the solvent from the solution in receptacle 30, to separate it into two fractions, returning one of them to receptacle 68 and the other to receptacle 1. This can be done by means of distillation equipment similar to that described in the last paragraph as being applied to the solution contained in receptacle 27. In detail, this can be accomplished by passing the solution from receptacle 30 out thereof through valve 51, pump 52, and line 55, thence through valve 58 and/or valve 58 through chiller 13 and/or chiller 20 into line 60, still 61, line 62 and bubble tower 63. Bubble tower 63 is arranged on the same general principle as bubble tower 38. In other words, the lighter solvent vapors pass out from the top of the tower and the heavier solvent fractions are drawn out from a lower portion or tray of the tower. If the lighter solvent fraction is the one which it is desired to return to receptacle 1 it will be passed out of bubble tower 63, through valve 64 (valves 65 and 66 being closed) into line 67 and thence through condenser 46, separator 47, valve 49 and line 50 back to receptacle 1. Simultaneously, the heavier solvent fraction would be drawn off through pump 77 and valve 78 passing through condenser 73 and separator 74 (condensed steam being drawn off through valve 75) and out therefrom through valve 76 back to receptacle 68. However, as previously described, in the case of the solvent contained in receptacle 27, it will sometimes be desired to return the heavier solvent fraction to receptacle 1 and the lighter fraction to receptacle 68 instead of vice versa. In this case valves 65 and 66 will be opened and valves 64 and 78 will be closed. It will be noted that this will accomplish the passage of the heavier fraction into the line formerly carrying the lighter one and the lighter fraction into the line formerly carrying the heavier one.

Bubble towers 38 and 63, or other suitable fractionating equipment, may be designed in accordance with well known principles in such manner as to effect the return into receptacles 1 and 68 respectively of solvents or solvent mixtures having the proper composition necessary for the operation of the process. Other suitable types of fractionating equipment may be employed.

It will furthermore be readily comprehended, although means therefore are not specifically shown in the drawing, that the composition of the solvent or solvent mixture passing from the dewaxing step of the process to the oil fractionation step may be modified, not only by the addition of more of the same or a different solvent, but also by the removal of a portion of the solvent. Thus, for instance, it is possible, by releasing the pressure subsequent to the passage of the solution through filter 16, to remove a portion of the lighter solvent in vapor form, thereby modifying the composition of the solution and rendering it, under some circumstances, more effective for the oil fractionation step.

It will generally be found more desirable, however, to modify the composition of the solution, if at all, by the addition of extra material from receptacle 68, as previously described, rather than by removal of a portion of the solvent. As has previously been suggested, the composition of the solvent or solvent mixture in receptacle 68 may be identical with that in receptacle 1. In this case considerable simplification in the solvent recovery system may be effected. However, about the only purpose which is served by adding an additional quantity of the same material subsequent to the dewaxing operation would be to dilute the solution and thereby to lower its viscosity in order to enhance separation of the two liquid phases subsequently formed. In many cases it is more desirable to add a different solvent or solvent mixture subsequent to the dewaxing operation rather than the one initially used. Furthermore, it will be found most generally desirable that the solvent or solvent mixture added be one having a lower solvent power for oil than does the one initially used. This will enhance separation of the solution into two liquid phases or, in other words, will decrease the solubility of the more paraffinic oil in the solution. The net effect of this is that a more complete separation into two liquid phases may be had at any given temperature or the same separation can be effected with less refrigeration. In some instances if a large amount of a material having poor solvent power for the oil is added, it is possible to effect efficient fractionation into two liquid phases without any additional chilling whatever.

As an example of an operation of my process using two separate solvents, a wax-bearing lubricating oil fraction of the type previously described may be continuously dissolved at ordinary or slightly elevated temperatures in two and a half times its own volume of isopropyl ether. The temperature may be lowered by suitable heat exchange means similar to those which have been described, to a temperature somewhat below zero degrees Fahrenheit, whereupon the great preponderance of the total wax content will be precipitated and may be removed by means of a filter press. Subsequent to this dewaxing, acetone may be added in proportion equivalent to one-half the volume of the original oil. This acetone should preferably be added cold, thus assisting in reducing the temperature of the modified solution to a point in the neighborhood of minus 25 to minus 40° F., whereupon the more paraffinic oil is precipitated, together with some portion of the solvents. A more complete precipitation is obtained in this way than when isopropyl ether is used alone without the addition of acetone. A portion of each of the two solvents used will be found in each of the two liquid phases formed at the low temperature mentioned and they can be separately recovered in distillation equipment similar to that which has previously been described. It will be found in this case that the vapors passing off from the top of the bubble tower will be rich in acetone and should be returned to receptacle 68 while those passing off from the intermediate point in the bubble tower will have relatively little acetone in them and should be returned to receptacle 1 for reuse. However, it is usually difficult, or impossible, to completely separate the two solvents and when the process reaches equilibrium the solvent contained in receptacle 1 will contain some acetone and that contained in receptacle 68 will contain some isopropyl ether. This, however, does not introduce any material difficulties or vitiate the operation but should be taken into account in selecting the desired dewaxing and oil fractionation temperatures, etc.

Considerable has been said relative to the recovery of solvent from receptacle 30. It will be understood, however, that in one of the alternative methods of operating my process the material contained in receptacle 30 is recycled back to the beginning of the process without recovery of the solvent and in this case it will, of course, be unnecessary to use the second solvent recovery system at all.

Returning now to the discussion of the aforementioned third alternative method of operating my process, it will be recalled that this consists in rechilling the solution contained in receptacle 30 to a still lower temperature to effect its separation into two additional liquid phases. Referring again to the drawing, the solution in receptacle 30 may be withdrawn therefrom through valve 79 by means of pump 80 into chiller 81 where its temperature is lowered by contact with a suitable refrigerating medium and thence into settler 82, which may be of any of the types described in the case of settler 24. Two liquid phases will be separated in settler 82, the relative volumes of each of them will be dependent upon the temperature to which the solution is chilled and said temperature should be selected to achieve the results which are desired in any given case. The lighter fraction formed will be continuously drawn off from settler 82, through valve 83, into receptacle 84 while the heavier fraction will be drawn off continuously through valve 85 into receptacle 86.

It will be found that the fraction in receptacle 86 is, in general, composed of the more paraffinic fractions of the generally naphthenic oil contained in receptacle 30, together with a portion of the solvent. The oil contained in the solution in receptacle 86 will, of course, be more naphthenic than that contained in receptacle 27, but it will be more paraffinic than the fraction drawn off into receptacle 86. In other words, the oil contained in the solution in receptacle 84 will be an intermediate oil whereas that contained in receptacle 86 will be highly naphthenic. It must be understood, however, that with some solvent mixtures the fraction containing the intermediate oil may be heavier than that containing the highly naphthenic oil and in this case the two fractions will be drawn off into the opposite receptacles.

Either or both of the two additional liquid phases thus formed may be withdrawn from the system for further treatment or use through valve 87 and/or valve 88 respectively. Furthermore, either of them may be recycled back to the beginning of the process, thus the intermediate oil carrying some solvent may be withdrawn from receptable 84, through line 89 and valve 90 (valve 56 being closed) by means of pump 91 and thence back to a point at or near the beginning of the process. Similarly, the material contained in receptacle 86 can be withdrawn therefrom through valve 92 (valve 57 being closed) by means of pump 93 into line 54 and thus recycled. When it is chosen to recycle one of these two fractions it will, in general, be desirable to recover the solvent and oil separately from the other. Since, in operating my process in accordance with this third alternative procedure, it will not generally be desired to recover separately any of the naphthenic oil contained

in receptacle 38, it will be possible to utilize the recovery system formerly applied to the material in receptacle 38 for the recovery of oil and solvent from the material contained in receptacle 84 or that contained in receptacle 86. If it is desired to recover the solvent and intermediate oil from the material in receptacle 84, it will be passed out therefrom through line 89, valve 56 (valves 51 and 98 being closed), pump 52, line 55 (valve 53 being closed) valve 58 and/or valve 59, chiller 13 and/or chiller 20, line 60, still 61, etc., the solvent ultimately returning to receptacle 1 and/or receptacle 68 and the intermediate oil passing into receptacle 65.

Similarly, if it is desired to recover the highly naphthenic oil and solvent from receptacle 86, this may be done by closing valves 51 and 92 and withdrawing the material from receptacle 86 through valve 57, pump 52, line 55, etc., the solvent being ultimately returned to receptacle 1 and/or receptacle 68 and the very naphthenic oil being collected in receptacle 65. It will be understood that in some cases it will be desired separately to recover oil and solvent in the case of both the material in receptacle 84 and the material in receptacle 86. In this case a separate solvent recovery system similar to the two previously described must be installed.

It will also be understood that it is possible to modify the composition of the solution passing out of receptacle 38 prior to its further chilling or separation into two liquid phases and this can be done by introducing more of the same or a different solvent through valve 94 from receptacle 95. This will generally necessitate further complications in the solvent recovery system which are not shown but which may readily be worked out in accordance with the general principles previously discussed.

When operating my process in accordance with this third alternative procedure the choice of the exact method used will depend upon the individual circumstances and the results which it is desire to obtain. Very often it will be desirable to recover the intermediate oil in receptacle 84 and to recycle the material in receptacle 86. This, as will be apparent, will result, looking at the process as a whole, in the recovery of two oil fractions, one a highly paraffinic fraction and the other an intermediate fraction. The most naphthenic portions of the oil would be recycled together with the bulk of the solvent, thereby accomplishing efficient heat exchange and low solvent losses. However, this mode of procedure would not result in the removal of any of the most naphthenic portions of the oil and this would in turn work to the detriment of the quality of the fractions which are recovered since, the highly naphthenic fraction not being removed, would have to pass ultimately into the material recovered in receptacle 84. Therefore it may sometimes be desirable to separately recover the very naphthenic oil from receptacle 86 and to recycle the intermediate fraction from receptacle 84, thus removing from the process a highly paraffinic oil and a highly naphthenic oil, continuously recycling the intermediate portion, and thereby accomplishing a greater ultimate separation into paraffinic and naphthenic portions.

It is to be understood that the words "paraffinic" and "naphthenic" as used in the specification and claims are relative terms and are not intended to imply that other types of constituents are absent. The term "paraffinic" is applied herein to the fraction having the lower temperature coefficient of viscosity, lower carbon-hydrogen ratio, etc., and the term "naphthenic" to the relatively "non-paraffinic" fraction, i. e. the fraction having the higher temperature coefficient of viscosity, higher carbon-hydrogen ratio, etc.

It is to be understood that although my process is particularly designed for the dewaxing and fractionation of wax-bearing mineral lubricating oils, it may also be applied with suitable modifications to vegetable and animal oils containing waxes or other high melting point substances.

Although my invention has been described in connection with a variety of specific embodiments thereof, it is to be understood that I am not limited thereby to any greater extent than the scope of the appended claims, I claim:

1. A process of dewaxing and fractionating a wax-bearing oil into fractions relatively paraffinic and naphthenic with respect to the original oil which comprises mixing the oil with a selective solvent adapted to assist the precipitation of wax at low temperatures, chilling the mixture to a low temperature to cause precipitation of substantial wax, removing said wax, and chilling the remainder of the mixture containing said solvent to a lower temperature to cause the mixture to separate into two liquid phases, separating said phases and recovering the solvent therefrom.

2. A process of dewaxing and fractionating a wax-bearing lubricating oil comprising dissolving it in a selective solvent adapted to precipitate therefrom a major portion of the wax contained therein, chilling to precipitate said wax, removing said precipitated wax, chilling the oil solution thus produced to a lower temperature than that used to precipitate the wax, said lower temperature being adapted to induce the formation of two liquid phases in said oil solution, separating the said two liquid phases from each other, each of said liquid phases containing a portion of the oil and a portion of the solvent, separately recovering oil and solvent from one of said two liquid phases, and recycling at least a substantial portion of the other of said two liquid phases back to a point in the process prior to the wax removal step.

3. A process according to claim 2 in which the oil solution passing from the wax removal step is modified prior to further chilling to decrease its solvent power for relatively naphthenic oil fractions.

4. A process according to claim 2 in which the liquid phase recycled is that one of the two liquid phases which contains the greater proportion of solvent.

5. A process according to claim 2 in which the liquid phase recycled is that one of the two liquid phases which contains the more naphthenic oil.

6. A process of dewaxing and fractionating a wax-bearing lubricating oil comprising dissolving it in a selective solvent adapted to precipitate therefrom a major portion of the wax contained therein, chilling to precipitate said major portion of the wax contained therein, removing said precipitated wax, chilling the solution resulting from the removal of said precipitated wax to a lower temperature to produce two substantially liquid phases therefrom, each of said two substantially liquid phases containing a portion of the oil and a portion of the solvent, separating said two substantially liquid phases from each other, separately recovering oil and solvent from that sub-

stantially liquid phase containing the more paraffinic oil, separately recovering oil and solvent from a portion of that substantially liquid phase containing the more naphthenic oil and recycling the remainder of the liquid phase last aforementioned back to a stage of the process prior to the wax removal step.

7. A process according to claim 6 in which the composition of the solution passing from the wax removal step is modified by the addition thereto of a fresh portion of the solvent originally used to dissolve the wax-bearing lubricating oil.

8. A process according to claim 6 in which the composition of the solution passing from the wax removal step is modified by the introduction thereinto of an additional solvent, said additional solvent being ultimately separately recovered from the products of the process.

9. A process for the dewaxing and fractionating of a wax-bearing mineral oil containing relatively paraffinic and relatively naphthenic constituents comprising dissolving said oil in a selective solvent, chilling the solution thus formed to precipitate wax therefrom, removing the precipitated wax, chilling the solution to a temperature lower than that at which the said wax was precipitated to induce the formation of two substantially liquid phases from the said solution, each of said substantially liquid phases being formed in substantial quantity, one of said substantially liquid phases containing a portion of the solvent and a relatively paraffinic portion of the oil, the other of said substantially liquid phases containing a portion of the solvent and a relatively naphthenic portion of the oil, separating said two substantially liquid phases from each other, distilling the phase containing the more paraffinic oil to recover solvent therefrom, returning the solvent thus recovered to the process, chilling at least a portion of the phase containing the more naphthenic oil to a temperature lower than the temperature of any of the oil solutions at any previous stage of the process, to induce the formation of two additional substantially liquid phases from the aforementioned phase containing the more naphthenic oil, one of said two substantially liquid phases containing a portion of the solvent and a highly naphthenic portion of the oil and the other of said two substantially liquid phases containing a portion of the solvent and a portion of the oil intermediate in properties between the relatively paraffinic and highly naphthenic portions previously mentioned, separating said two additional phases from each other, returning at least a part of one of the two phases last aforementioned to a previous stage of the process, separately recovering oil and solvent from the other of said phases, and returning the solvent thus recovered to a previous stage of the process.

10. A process according to claim 9 in which the solution is modified at at least one point between the various phase removal steps to promote phase separation in the next successive step.

11. A process of dewaxing and fractionating a wax-bearing oil comprising dissolving said oil in a selective solvent adapted to precipitate therefrom at least a substantial portion of the wax contained therein, precipitating said wax, removing said wax, chilling the dewaxed solution to cause the formation of two phases therefrom, each of said phases containing a portion of the oil and a portion of the solvent, separating said two phases, recovering solvent from one of said two phases and from a portion of the other of said two phases, and recycling the remainder of said last-mentioned phase to a point in the process prior to the dewaxing step.

12. A process according to claim 11 in which the selective solvent comprises a substance selected from the group consisting of butyl formate, butyl acetate, amyl acetate and phenyl acetate.

13. A process of dewaxing and fractionating a wax-bearing oil comprising dissolving said oil in a selective solvent adapted to precipitate therefrom at least a substantial portion of the wax contained therein, precipitating said wax, removing said wax, decreasing the oil solvent power of and chilling the dewaxed solution to cause the formation of two phases therefrom, each of said phases containing a portion of the oil and a portion of the solvent, separating said two phases, recovering solvent from one of said two phases and from a portion of the other of said two phases, and recycling the remainder of said last-mentioned phase to a point in the process prior to the dewaxing step.

14. Process for the solvent fractionation of oils comprising the solvent fractionation of an oil into two phases, one of said phases containing a relatively paraffinic portion of the oil and a portion of the solvent, the other of said phases containing a relatively naphthenic portion of the oil and a portion of the solvent, chilling the last mentioned of said phases to cause the formation of two further phases therefrom, one of said two further phases containing a highly naphthenic portion of the oil and a portion of the solvent, the other of said two further phases containing a portion of the solvent and a portion of the oil intermediate in properties between said naphthenic portion and said highly naphthenic portion, separating said two further phases, and recycling at least a part of the last mentioned of said two further phases back to a point in the process prior to the first solvent fractionation step.

15. A process of dewaxing and fractionating a wax-bearing oil comprising dissolving said oil in a selective solvent adapted to precipitate therefrom at least a substantial portion of the wax contained therein, precipitating said wax, removing said wax, chilling the dewaxed solution to cause the formation of two phases therefrom, separating said phases, further chilling at least a substantial portion of one of said phases to cause the formation of two further phases therefrom and recycling at least a substantial portion of one of said last-mentioned phases to a point in the process prior to the dewaxing step.

16. A process according to claim 15 in which the selective solvent comprises nitrobenzene.

17. A process for dewaxing and fractionating of wax-bearing mineral oil containing relatively paraffinic and relatively naphthenic constituents, comprising dissolving said oil in a selective solvent, chilling the solution thus formed to a temperature adapted to precipitate wax therefrom, removing the precipitated wax, adding to the dewaxed solution a substantial amount of a second selective solvent having a lower solvent power for relatively naphthenic oil fractions than said first-mentioned selective solvent, chilling the solution to a temperature lower than that at which the said wax was precipitated, the addition of said second selective solvent together with said chilling being adapted to induce the formation of two phases from the solution, separating the two phases thus formed and separately recovering a portion of said oil, a portion of said first-mentioned selective solvent and a portion of said

second selective solvent from each of said phases.

18. A process for dewaxing a wax-bearing mineral oil at a low temperature and then fractionating said mineral oil at a lower temperature which comprises dissolving said wax-bearing mineral oil in a solvent adapted to precipitate wax from said wax-bearing mineral oil at said low temperature, chilling to said low temperature to precipitate said wax, removing the precipitated wax, adding a relatively poor oil solvent to the solution to decrease the solvent power of said solution for a portion of the oil to the extent that a second liquid phase would precipitate from said solution at said low temperature, chilling to said lower temperature to precipitate an amount of a second liquid phase in excess of the amount which would precipitate at said low temperature and separating the two liquid phases formed at said lower temperature from each other.

19. In a combined process for separating a wax bearing oil into wax and fractions respectively paraffinic and naphthenic with respect to the original oil, the steps which include dissolving the oil in a solvent which at a given temperature is selective between normally solid hydrocarbon constituents and normally liquid hydrocarbon constituents of the wax bearing oil and which at somewhat lower temperatures is selective between paraffinic and naphthenic constituents of the oil, which solvent also at the dewaxing temperature has a substantially minimum solvent power for wax, consistent with the retention of substantially all of the oil in solution, chilling the solution thus formed to a dewaxing temperature at which substantially all of the wax is insoluble, removing the wax while maintaining approximately said temperature, reducing the temperature of the remaining solution below the dewaxing temperature, and sufficiently low to cause a separation of said remaining solution into two liquid phases, one of said phases containing a relatively large proportion of the solvent and a relatively naphthenic fraction of the oil, and the other of said phases containing a relatively small proportion of the solvent and a relatively paraffinic fraction of the oil, separating said two phases and separating the solvent from each of said phases.

20. In a combined process for separating a wax bearing oil into wax and fractions respectively paraffinic and naphthenic with respect to the original oil, the steps which include dissolving the oil in a solvent which at a given temperature is selective between normally solid hydrocarbon constituents and normally liquid hydrocarbon constituents of the wax bearing oil and which at temperatures approximately 15° F. to 60° F. lower than said given temperature is selective between paraffinic and naphthenic constituents of the oil, which solvent at said given temperatures has a substantially minimum solvent power for wax, consistent with the retention of substantially all of the oil in solution, chilling the solution thus formed to said given temperature to precipitate wax, removing the precipitated wax substantially at said given temperature, reducing the temperature of the remaining solution to a point from about 15° F. to about 60° F. lower than said given temperature to cause a separation of said oil into two liquid phases, one of said phases containing a relatively large proportion of the solvent and a relatively naphthenic fraction of the oil, and the other of said phases containing a relatively small proportion of the solvent and a relatively paraffinic fraction of the oil, separating said two phases and separating the solvent from each of said phases.

21. The process of fractionating a lubricating oil into fractions which are respectively relatively paraffinic and relatively naphthenic with respect to the original oil, which comprises mixing the oil with a selective solvent, chilling the mixture to a sufficiently low temperature to cause the separation thereof into two phases, removing one phase from the other phase, further chilling one of said phases to effect a further phase separation into a fraction consisting chiefly of oil and a fraction consisting chiefly of solvent, and returning the fraction consisting chiefly of solvent to the system at a point prior to the first phase separation step.

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