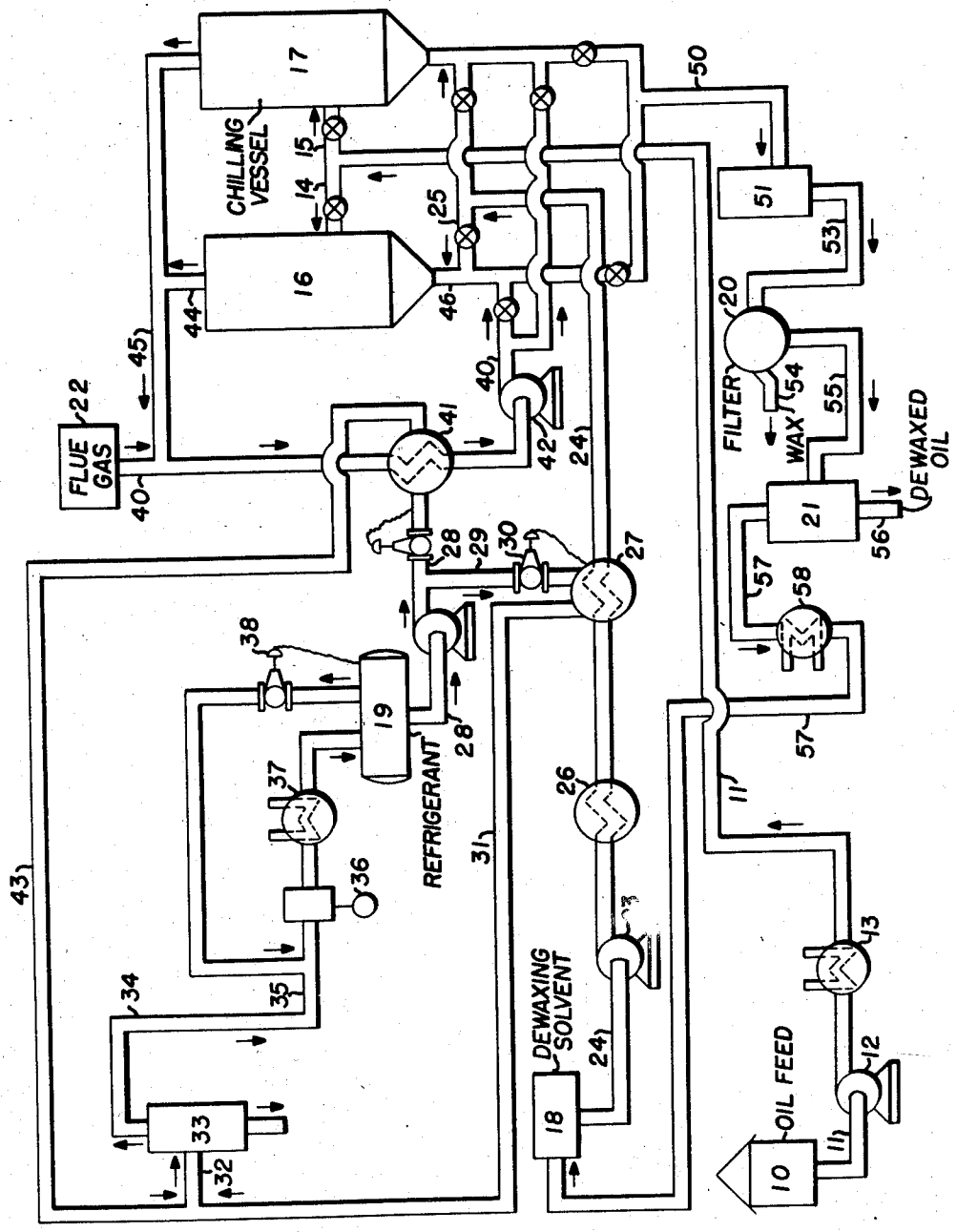
March 31, 1959 J. G. LIVINGSTONE ET AL 2,880,159

SOLVENT DEWAXING OF PETROLEUM OIL

Filed July 20, 1955



James G. Livingstone
Alfred George Moreton Inventors
John L. Tiedje

By J. A. Reilly Attorney

United States Patent Office 2,880,159 Patented Mar. 31, 1959

2,880,159

SOLVENT DEWAXING OF PETROLEUM OIL

James G. Livingston, Toronto, Ontario, and Alfred G. Moreton and John L. Tiedje, Sarnia, Ontario, Canada, assignors to Esso Research and Engineering Company, a corporation of Delaware

Application July 20, 1955, Serial No. 523,314

12 Claims. (Cl. 208—31)

The present invention is concerned with a process for dewaxing waxy mineral oils and especially petroleum lubricating oil fractions. It further relates to a process for reducing the oil content of slack waxes by recrystallization. The invention especially relates to a process in which a waxy mineral oil or slack wax is diluted with a dewaxing solvent and chilled to a temperature such that wax is crystallized and precipitated from the oil. The precipitated wax is thereafter separated from the solvent and oil mixture by conventional separation and washing procedures. The invention is particularly characterized by a process wherein a waxy oil or slack wax is simultaneously diluted and chilled to the desired dewaxing temperature by mixing the oil continuously with a dewaxing solvent that has been precooled to a temperature below the dewaxing temperature.

The dewaxing of mineral oils is a procedure that is well known to the petroleum industry. It finds particular application in the removal of wax from waxy lubricating oil fractions. These fractions generally range in boiling point from about 580° F. up to fractions that are residudal in character. Fractions that boil from about 580° F. to 850° F. are generally referred to as paraffin distillates; fractions that boil from about 800° F. to 1000° F. are generally designated as heavy lubricating oil distillates; and fractions that boil above 1000° F. are generally characterized as residua.

In accordance with existing dewaxing procedures, a petroleum fraction such as one of the three types described in the preceding paragraph is diluted with a dewaxing solvent and is then chilled to a temperature such that wax is crystallized and precipitated from the fraction. Thus, the general technique of dewaxing a lubricating oil fraction consists basically in lowering the solubility of the wax in the oil. This is achieved by chilling the oil to a low temperature with or without the use of a solvent, although it is generally preferred to employ a solvent.

Solvents that are conventionally employed at the present time for solvent dewaxing operations serve three main functions: first, they lower the solubility of the wax in the oil; second, they form a wax precipitate of a structure such that the precipitate can be removed from the oil by filtration or other means; and third, they lower the viscosity of the oil sufficiently to make rapid separation possible.

Solvents that are used for dewaxing petroleum fractions fall into three main categories: the so-called single solvents, the dual solvents, and the auto-refrigerant solvents. The single solvents include materials such as petroleum naphthas, aliphatic ketones, halogenated low molecular weight hydrocarbons, etc. Dual solvents include mixtures of aromatic hydrocarbons such as benzene or toluene and ketones such as acetone, methyl ethyl ketone, normal propyl ketone, etc. The refrigerant solvents include liquefied normally gaseous hydrocarbons such as propane which serve simultaneously as dewaxing solvents and also as auto-refrigerants. The dual functions of a refrigerant solvent are realized by merely allowing a part of the solvent to evaporate after the solvent and the waxy oil have been admixed.

The present invention has application to all of the types of dewaxing solvents mentioned above. It has particular application, however, to the single and dual solvents wherein the solvent and oil mixtures are cooled by passing the mixtures through heat exchangers in indirect heat exchange with standard refrigerants. Thus, the invention has particular application to solvent dewaxing processes which employ aliphatic ketones, mixtures of certain ketones and aromatic hydrocarbons, and halogenated solvents such as dichloroethylene.

In addition to dewaxing processes, the present invention also has application to recrystallization processes wherein the slack wax from a dewaxing and/or deoiling operation is liquefied, admixed with one of the aforementioned dewaxing solvents, and then cooled to recrystallize the wax. As in the case of the dewaxing processes, the invention is especially concerned with recrystallization processes that emplay a single or dual type solvent. In any case the solvent functions in the recrystallization process substantially as it functions in the dewaxing process.

In a conventional solvent dewaxing or recrystallization process which utilizes a single or dual-type dewaxing solvent, a waxy oil or slack wax is diluted with the solvent and is thereafter passed through a heat exchanger where it is cooled by indirect contact with a refrigerant. A very common practice consists in passing the mixture of waxy oil and solvent through a double-pipe heat exchanger wherein the solvent and waxy oil mixture flows through the inner pipe of the exchanger and a refrigerant such as propane, sulfur dioxide or other suitable material flows in the annular space between the two pipes. The inner pipe is provided with rotating blades or scrapers which continually remove any wax which adheres to the interior surface of the pipe and causes the wax to move through the pipe along with the oil and solvent.

Upon leaving the double pipe heat exchanger, the chilled oil and solvent mixture including the crystallized precipitated wax is conducted through suitable conduits to a separation device, preferably a rotary filter, where the crystallized wax is separated from the oil and solvent. The wax is thereafter washed and may be recrystallized further in order to remove oil from the wax and to separate the wax into melting point fractions. The solvent and oil mixture, on the other hand, is conventionally conducted to a fractionation train where the solvent is separated from the oil and returned to the dewaxing or recrystallization operation. The oil, of course, may be subjected to further processing in any manner desired.

The conventional dewaxing or recrystallization procedures just described, although widely accepted and practised by the petroleum industry, have several major disadvantages. In the first place, it is extremely difficult to obtain satisfactory heat transfer conditions through the walls of a double pipe heat exchanger for the reason that the wax on the wall surfaces is a very poor conductor of heat. Attempts have been made to remedy this condition by the use of scrapers and the like, but in spite of these techniques, relatively poor heat transfer conditions prevail and the use of scrapers greatly increases the cost of this equipment. A second disadvantage which characterizes the presently conventional procedures is that relatively low yields of dewaxed oils are obtained as a result of the operations. These low yields are in a measure caused by the fact that large amounts of solvent and oil are retained in the filter cakes.

In an effort to improve upon the yield and quality of the waxes and dewaxed oils that are obtained in conventional dewaxing and recrystallization operations, various techniques have been employed to date, including the use of crystal modifiers, critical chilling rates, and the like. In general, all of these techniques are intended to cause the wax to precipitate in the form of large crystals, since it has been observed that large

crystals tend to occlude smaller amounts of oil than do small crystals. These techniques, however, have not been entirely successful, and, accordingly, a continuing search for better procedures has been maintained.

In view of the shortcomings that characterize the presently conventional dewaxing and recrystallization procedures, it is an objective of the present invention to improve generally upon the same. For example, in the case of dewaxing procedures it is an objective of the invention to improve upon these procedures by providing a dewaxing process wherein improved yields of dewaxed oil are obtained. With respect to both dewaxing and recrystallization procedures, it is another objective of the invention to eliminate the expense and the poor heat transfer conditions that characterize double pipe heat exchangers and other presently conventional chilling means by permitting complete elimination of the use of the devices themselves. It follows, therefore, that it is an additional objective of the invention to achieve economic gains over presently conventional dewaxing and recrystallization procedures by eliminating the costly scraped surface chillers and double pipe heat exchangers that are now employed to chill solvent and waxy-oil mixtures. With respect to recrystallization operations, it is still a further objective of the invention to provide a procedure whereby wax products of markedly reduced oil contents are obtained.

These and related objectives are attained in accordance with the present invention by adjusting the temperature of a hydrocarbon mixture containing waxy constituents and oily constituents to a value such that all of the constituents are in a liquid condition. The liquid mixture is then blended with a dewaxing solvent in an amount and prechilled to a temperature such that the resulting hydrocarbon-solvent blend reaches a predetermined temperature at a predetermined solvent dilution. The new temperature is intermediate in value between the temperature of the original hydrocarbon mixture and the temperature of the solvent, and is low enough to crystallize at least a portion of the waxy constituents present. The solvent is preferably added to the hydrocarbon mixture in a continuous manner and at a rate such that the temperature of the mixture drops an average of 2°–5° F. per minute. The precipitated or crystallized waxy constituents are then separated in a conventional manner from the solvent and the hydrocarbons that are still in a liquid condition.

Referring now specifically to dewaxing operations, the objectives of the invention are achieved by adjusting the temperature of a waxy petroleum fraction to a value substantially at the cloud point of the oil and thereafter chilling the oil by adding a prechilled dewaxing solvent continuously to the oil with suitable agitation. The solvent must be prechilled to a point below the desired dewaxing temperature and to a temperature such that the solvent upon being incorporated within the oil to a predetermined desirable dilution causes the resulting solvent and oil mixture to be at the dewaxing temperature. In other words, the entire body of solvent must be initially at a temperature such that it not only dilutes the oil eventually to the desired extent, but it must upon diluion also chill the oil to the desired dewaxing temperature. Thus, the solvent acts not only as a dewaxing diluent, but also as a refrigerant.

As stated earlier, the amount of solvent that is added to a waxy oil feed in the present dewaxing process must be such that the desired degree of dilution of the oil occurs at the dewaxing temperature. In line with this requirement, it has been found that the desired dilution ratio varies slightly, depending largely upon the character of the waxy oil feed. Thus, it has been observed that waxy oils corresponding in viscosity to an SAE 10 grade motor oil are preferably diluted with about 1½ to 2½ volumes of solvent per volume of oil at the desired dewaxing temperature. Dewaxing

temperatures for such oils range from about 0° F. to +20° F. when using ketones as solvents. More viscous oils such as would correspond to about SAE 30 grade motor oils, on the other hand, have been found to require about 2.5 to 3.5 volumes of solvent (again ketones) per volume of oil at the dewaxing temperature. In short, the more viscous the oil feed to the process, the generator is the amount of solvent desired. In general, however, it has been observed that solvent to oil ratios of from about 1½ to 1 to 4 to 1 embrace substantially the entire range of oils that are dewaxed in the petroleum industry.

The rate at which the prechilled solvent is added to the waxy oil may be adjusted to produce any desired rate of chilling. Generally slower chilling rates produce larger wax crystals which are more easily separated from dissolved wax or oil by filtration. However, very low chilling rates tend to result in excessive holdup of waxy oil in the process. It has been found that very good results are obtained with average chilling rates in the range of 2°–5° F./minute.

In so far as chilling rates are concerned, it is an important feature of the present invention that it gives much better control of the chilling conditions than is possible with conventional scraped surface chillers. The rate of chilling can be varied as desired over the entire temperature range. Although chilling at a constant rate of 2° F./minute will give a better filter rate than chilling at 5° F./minute, still better results can be obtained at an average chilling rate of 2° F./minute by chilling at a very much slower rate initially and gradually increasing the rate as the temperature decreases and the concentration of wax crystals increases. By maintaining the rate of wax deposition on crystal faces constant in this manner, the formation of additional small crystals is discouraged. This result can be readily obtained by this invention by starting at a low rate of addition of cold solvent and increasing the solvent rate as chilling progresses. No such exact control of chilling is possible when using conventional scraped surface chillers.

During the chilling period in the present process, it has further been observed that it is necessary and highly desirable to provide a critical degree of agitation to the mixture of solvent and oil. Specifically, it has been found that the agitation must be sufficient to prevent the formation of lumps of wax in the immediate vicinity of the point where the solvent enters the oil or solvent-oil mixture.

The agitation which is provided to the oil or solvent and oil mixture must also be sufficient to distribute the added solvent throughout the mixture and to thereby maintain the entire bulk of hydrocarbons and solvent at a substantially uniform temperature. This is important, since shock chilling occurs at the point where cold solvent and warm oil first come in contact. In the present process, however, the small undesirable crystals formed by this initial contact redissolve and are replaced by larger better formed crystals as the shock chilled zone is slowly digested in the bulk of the oil.

In mixing the oil and solvent during the chilling period, it is additionally necessary to avoid mixing intensities so great that gelling and improper crystallization of the wax particles occurs. Excessive mixing can result in breakdown of otherwise satisfactory wax crystals. This condition can be avoided by merely meeting the two requirements just mentioned.

A particularly preferred procedure to follow in mixing the oil and solvent during the chilling step consists in providing a localized degree of agitation in the immediate vicinity of the point where the fresh solvent enters the chilling zone and in providing additional mixing means for establishing uniform mixing of the entire body of liquid. This may be achieved, for example, by employing two propeller mixers—a small one being provided at the point of entry of the fresh solvent, and a larger

slower rotating mixer at a point within the main body of liquid. Equivalent mixing means, of course, may be employed in place of propellers.

A preferred method of agitating the body of solvent and oil during the chilling step consists in bubbling a non-condensing and non-soluble gas up through the body of liquid. The gas necessarily must be chemically inert toward the oil and solvent and should be prechilled to substantially the same temperature that exists within the chilling zone. It is contemplated that the volume of gas that must be employed for this purpose should constitute about 2 volumes of gas per minute per volume of liquid in the chilling zone. Gas rates between 0.5 and 3.0 volumes of gas per minute per volume of liquid have proven to be extremely effective in this regard; and a gas rate of about 2 volumes of gas per minute per volume of liquid is especially preferred. Gases that are suitable for this purpose include flue gas, the inert gases such as nitrogen, helium, etc. The gas must be free of water vapor and therefore must be dried or otherwise in a dry condition before entering the mixing zone. A gas that is especially preferred for this purpose is dry flue gas, since it is readily available, is inexpensive, and can be easily adapted to the purposes of the invention.

It has been mentioned earlier that a wide variety of dewaxing solvents may be employed in the practice of this invention. It will be noted, however, that ketone solvents are especially preferred. In this connection, aliphatic ketones or mixtures of such ketones that contain from 3 to 6 carbon atoms and particularly 4 to 5 carbon atoms are preferred. Solvents that are especially preferred include methyl ethyl ketone and toluene or benzene and methyl n-propyl, methyl isobutyl and diethyl ketones.

The principles and basic features of a dewaxing embodiment of the invention having been generally described, attention is now directed to the attached figure, which illustrates the best mode contemplated for carrying out this embodiment. Turning to the figure, it will be observed that the apparatus illustrated there includes an oil feed tank **10**, chilling vessels **16** and **17**, a dewaxing solvent feed tank **18**, a refrigerant supply tank **19**, dewaxing filter **20**, a solvent recovery unit **21**, and a source of dry flue gas **22**.

A waxy oil feed, as, for example, a Mid-Continent type lube oil distillate, corresponding to an SAE 30 grade, is withdrawn from supply tank **10** by means of pump **12** and is passed through line **11** and line **14** or **15** into one of the chilling vessels. At this point it will be noted that the apparatus in this figure utilizes a batch-type chilling operation and that chilling vessels **16** and **17** are therefore continuously alternated between a chilling cycle where wax is precipitated from the oil and a filtering cycle where the crystallized wax is separated from the oil. Accordingly, for the purposes of the present description, it will be assumed that chilling vessel **16** is being utilized in the chilling cycle of the process and that vessel **17** is being utilized in the filtration or separation stage of the process.

As the oil from tank **10** flows through line **11**, it will be noted that it may be cooled if necessary as by means of a cooling coil **13** to a temperature just above the cloud point. In most instances ordinary cooling water may be supplied to the heat exchanger **13** for this purpose.

As stated above, the oil feed passes from line **11** to line **14** and thence into chilling vessel **16**. When a sufficient change of oil has thus been placed within vessel **16**, dewaxing solvent (i.e., dewaxing diluent) is introduced within the vessel from supply tank **18**. In the present instance it will be assumed that the solvent is actually methyl n-propyl ketone. The solvent is removed from tank **18** by means of pump **23** and transmitted through lines **24** and **25** to a point near the bottom of the vessel **16**. Suitable manifolding, such as is illustrated in the figure, prevents the solvent from passing into vessel **17**.

As the solvent flows through line **24**, it is chilled in one or more heat exchangers such as exchangers **26** and **27** illustrated in the figure to a temperature below the desired dewaxing temperature of the oil. As explained earlier, the dewaxing solvent must be prechilled such that upon being mixed with the waxy oil to the proper dilution it brings the oil down to the dewaxing temperature.

As illustrated in the figure, the prechilling of the dewaxing solvent is achieved by means of heat exchangers **26** and **27**. Exchanger **26**, as depicted, illustrates how cooling water or a liquid such as the dewaxed oil and solvent stream from the filter **20** may be utilized to initially and partially reduce the temperature of the solvent. Final chilling of the solvent, however, is preferably achieved by passing it in indirect heat exchange with a refrigerant, preferably liquefied propane, ammonia, or ethane. Thus, in the figure it will be observed that a refrigerant in the form of liquefied propane is withdrawn from supply tank **19** through line **28** and is passed thence to line **29** and a suitable expansion valve **30** into the heat exchanger **27**. Here, evaporation of the propane causes the temperature of the dewaxing solvent to be decreased to the desired level.

The vaporized propane from the exchanger **27** flows through lines **31** and **32** into a knock-out drum **33** and thence to lines **34** and **35** to compressor **36**. The compressor reliquefies the propane, and its liquid condition is maintained by passing it through a suitable cooler **37** into the supply tank **19**. The supply tank **19** is maintained under suitable pressure as by means of control valve **38** so as to retain the propane within the tank **19** in the liquefied state. A convenient pressure for storing the propane in a liquefied condition at substantially atmospheric temperature is of the order of about 180 p.s.i.g.

As stated earlier, the dewaxing solvent enters the charge of oil within the chilling vessel **16** at a rate such that the oil experiences an average drop in temperature of between 2° F. and 5° F. per minute during the chilling process. As further stated earlier, the solvent may be introduced into the waxy oil continuously at a constant or variable liquid rate. If the liquid is added at a constant rate, chilling is very rapid to begin with, but decreases to a very low rate towards the end. If the liquid is added at a variable rate, this variation may be selected to give a constant rate of chilling or any variable chilling rate desired. For example, a variable rate of solvent addition might be selected to give a variable chilling rate such that a constant rate of wax deposition on crystal surfaces would be obtained.

During the chilling process that is illustrated in the figure, pre-dried flue gas from a suitable source **22** is passed through line **40** and chiller **41** into the bottommost portion of the chilling vessel **16**. As in the case of the dewaxing solvent and also the oil feed, the flue gas supply system is manifolded such that the gas passes either into vessel **16** or **17** of both vessels simultaneously. In the present instance is will be assumed that the flue gas flows through line **40** and line **46** upward into vessel **16**.

A suitable device such as blower **42** is provided to drive the flue gas into the vessel **16**, and heat exchange means such as coil **41** is employed in order to cool the flue gas down to a temperature substantially equal to that of the oil charge within the vessel **16**. Thus, the flue gas is conveniently chilled in the range from 100° F. to 0° F. The actual cooling of the flue gas is preferably achieved by indirect heat exchange with vaporizing propane which passes through exchanger **41** by means of lines **28** and **43**. Line **43** also serves to convey the vaporized propane back to the knockout drum **33** and thence to the compressor **36** and the storage tank **19**.

The amount of flue gas that is forced into the oil

charge in the vessel 16 should be such as to constitute about 2 volumes of flue gas per minute per volume of total liquid within the vessel. Uuon leaving the vessel 16, the flue gas passes through lines 44 and 45 back to the flue gas transfer line 40. Thus, all or a portion of the flue gas may be recycled to the chilling vessel. If necessary, the flue gas which exits from the top of the vessel may be further chilled or otherwise treated to remove solvent or hydrocarbons from the gas.

When the oil and solvent charge within the vessel 16 has been brought down to the proper dewaxing temperature, the flow of solvent and flue gas into the vessel 16 may be curtailed and the liquid charge then conducted via lines 46 and 50 to a filter tank 51. Once again, vessels 16 and 17 should be manifolded in a manner as illustrated in the figure in order to permit independent handling of the charges from the two vessels.

Waxy oil and solvent slurry within tank 51 is then conducted through line 53 to suitable means for separating the precipitated wax from the slurry. The means illustrated in the figure is a rotary filter 20, but other devices such as filter presses and centrifuges may also be employed for this purpose.

Wax and solvent is removed from the filter and is recovered at point 54 for subsequent separation of solvent and wax by distillation, while the dewaxed oil is conducted as by means of line 55 to a zone 21 where the dewaxed oil is separated as by distillation from the dewaxing solvent. The dewaxed oil is actually recovered at point 56, and the solvent vapors are condensed in condenser 18 and returned by means of line 57 to the solvent storage tank 18.

It will be noted that numerous variations and conventional practices may be incorporated within the dewaxing procedure that has just been described and illustrated. For example, solvent may be employed to wash the filter cake as it forms on and travels around the periphery of the rotary filter 20. Furthermore, the dewaxed oil may be separated from the dewaxing solvent by any one of the distillation procedures or the like that are conventionally employed for this purpose. Again, a plurality of chilling vessels greater in number than that illustrated may be employed, if necessary, so as to attain substantially continuous operation of the filter 20. Also, filter aids, crystal modifiers, etc., may be utilized.

The present invention may be even better understood by reference to the following examples, which illustrate actual operations that have been employed utilizing the principles of the invention.

EXAMPLE I

In a first series of tests, a phenol treated Mid-Continent type grade 30 lube oil distillate having a viscosity at 210° F. of 61 SSU and boiling between 820° F. and 990° F. at atmospheric pressure was dewaxed at a temperature of 25° F. with methyl n-propyl ketone as the dewaxing solvent. The distillate was charged to a laboratory-scale insulated mixing vessel which was provided with two propeller type mixers. One of the mixers was immersed well within the liquid in the vessel so as to impart uniform movement and distribution of liquid throughout the vessel. The second mixer was positioned at the point within the vessel where the ketone actually entered the waxy oil charge. The agitation conditions were adjusted so that there was no visual evidence of lumps of wax forming within the vessel, but not sufficiently violent as to break up crystals formed.

The distillate was heated slightly to a temperature of about 125° F. so that it entered the chilling vessel at a temperature of about 5°–10° F. above its wax cloud point. The ketone, on the other hand, was prechilled to a temperature of —15° F. so that it would provide the resulting waxy oil and solvent mixture with a final temperature of +25° F. and a solvent to oil dilution ratio of 3:1. In other words, the final mixture of solvent and oil contained three volumes of solvent per volume of oil.

In different runs of this type, the ketone was added either at a constant rate so as to give an overall average chilling rate or at a variable rate so as to afford a constant chilling rate. In both types of runs, however, the average chilling rate was from 2°–5° F. per minute. Upon reaching the dewaxing temperature of +25° F., the wax, solvent and oil slurry was passed through a leaf-type filter in a manner corresponding to the filtering action experienced in rotary wax filters. Thus, each batch of slurry was filtered and dried for substantially equal periods of time, and when wash solvents were utilized, each batch was washed for the same period of time as was used for filtration. Times for the filtering, washing, or drying operations were 50 seconds in all cases.

In making these runs, comparisons were made of the filtering rates, the yields of dewaxed oil, and the oil contents of the wax products at various chilling rates. The data obtained by these observations are presented in the following table, where they in turn are compared with results obtained in the same apparatus utilizing conventional chilling techniques. In the conventional type operations the lube oil distillate was diluted with the complete charge of solvent at a temperature of about 110° F., and the entire solvent and oil charge then chilled at a rate of about 5° F. per minute to the dewaxing temperature of 25° F.

Table I

BATCH DILUTION CHILLING (LABORATORY)

[M.C.T. 30 distillate dewaxed at 25° F. using methyl N-propyl ketone. Laboratory filtration equivalent to rotary filter turning at 150 seconds/rev. (50 sec. filtering, 50 sec. wash or dry, 50 sec. cake discharge and blocked off).]

Chilling Rate, ° F./min.	Solvent Ratios by Vol.			Filter Rate, USG/sq. ft./hr.		Dewaxed Oil		Cake Thickness [1]	Wax	
	Dilution	Wash	Cake	Waxy Oil	D.W. Oil	Yield, Vol. Percent	Solid, ° F.		M.P., ° F.	Percent Oil
Conventional Chilling:										
5	3.15	-------	2.2	7.1	4.2	58.6	32	11	130	68
	3.15	0.87	4.1	7.1	4.8	67.0	28	13	133	59
Dilution chilling:										
5 average [2]	3.22	-------	2.0	3.4	2.3	68.5	25/20	3	131	60
	3.22	0.81	5.1	3.4	2.6	77.7	25/20	4	138	56
5 constant	3.16	-------	2.0	3.9	2.6	67.3	32	4	131	57
	3.16	0.96	5.5	3.8	3.0	80.2	32	5	139	22
2 average [2]	2.86	-------	1.7	4.5	3.1	68.8	30	4	132	53
	2.86	1.04	5.3	4.7	3.9	84.0	30	5	142	11
2 constant	3.14	-------	2.0	5.0	3.3	66.2	15/10	6	131	58
	3.14	1.02	5.3	5.0	4.0	80.5	15/10	7	138	25

[1] Sixteenths of inch.
[2] Solvent was added at a constant rate to give the overall average rates of chilling shown.

The data in the above table are particularly interesting since they indicate that the wax cakes which are formed by the present process are much more susceptible to solvent washing than are the wax cakes produced by conventional chilling techniques. This results in the present process (i.e., employing dilution chilling) providing markedly greater yields of dewaxed oil and lower oil content waxes than do conventional chilling procedures.

It will be noted in the table that the filter rates obtained with the present procedure were somewhat less than the rates obtained using the conventional chilling technique. It will further be noted, however, that these data were obtained with laboratory scale apparatus. Additional data have conclusively shown that in commercial scale apparatus the filter rates with the two types of procedures are substantially identical and that the other advantages of the present technique are retained.

The table also indicates that constant chilling rates are to be preferred over constant solvent rates which give very high initial and low final chilling rates.

EXAMPLE II

In a second series of runs, the same lube oil distillate was dewaxed in a large scale plant by contacting it with one of two dewaxing solvents. In some instances the solvent was methyl propyl ketone and in other instances a blend consisting of 45 volume percent diethyl ketone and 55 volume percent methyl propyl ketone.

In this series of runs, dried flue gas was employed to agitate the oil and solvent contained within the chilling vessel. The actual flow rate of flue gas varied from about 0.5 to 1.0 volume of gas per minute per volume of oily wax charge.

In each run the oil was adjusted to a temperature of about 125° F. and then introduced within the chilling vessel. Once the entire charge of oil was in the vessel, prechilled ketone was thereafter introduced within the vessel in a continuous flow either at a constant rate or at a variable rate so as to provide constant chilling rates of about 1.3° F. to 2° F. per minute throughout the chilling cycle. In all of these runs the waxy slurries from the chilling vessel were filtered at temperatures of about 37°–43° F. The filtration in each instance was carried out utilizing a conventional rotary filter designed to provide suitable periods for filtering, washing, or drying and discharging of the wax cake. The results obtained with these runs are presented in the following table along with runs of a comparable nature from Table I.

Table II

DILUTION CHILLING—LARGE SCALE v. LABORATORY SCALE

[M.C.T. 30 distillate dewaxed with methyl propyl ketone or 45/55 blend of diethyl and methyl propyl ketone.[1] Laboratory filtration equivalent to rotary filter turning at 150 seconds/rev. (50 sec. filtering, 50 sec. wash or dry, 50 sec. cake discharge and blocked off).]

Run No.	Chilling Rate, ° F./min.	Temp., ° F.	Solvent Ratios		Filter Rate, USG/sq. ft.		Dewaxed Oil Yield, Percent	Cake Thickness [2]	Oil in Wax, Percent
			Dilution	Wash	Waxy Oil	D.W. Oil			
	Laboratory Scale:								
10	2 (average)[4]	25	2.8	1.04	4.7	3.9	84.0	5	10.6
4	2 (constant)	25	3.1	1.02	5.0	4.0	80.5	7	25
23	2 (constant)	40	3.1	1.3	5.6	4.8	86	6	6.4
	Large Scale [3]:								
5	2	43	3.0	0.78	5.0	4.1	82	6	32.3
6	1.7	37	3.5	1.1	5.4	4.6	85	6	24.7
7	1.3	37	3.3	1.2	4.9	4.1	83	6	26.0

[1] Runs 10 and 4 with methyl n-propyl ketone, runs 23, 4, 5, 7 used 45% diethyl ketone, 55% n-propyl ketone.
[2] Sixteenths of an inch.
[3] Runs were made at 37°–43° F. because of difficulties in maintaining solvent at the required —15° F.
[4] Constant solvent rate.

It is apparent from the above table that the filter rates that are attainable with large size equipment are substantially identical with the rates that are attainable with the laboratory apparatus of Example I. It has further been demonstrtaed that these filter rates are equivalent to the rates that are presently attainable by conventional commercial apparatus which utilize conventional chilling procedures and scraped double-pipe chillers. Expressed otherwise, the process of the present invention is capable of providing filter rates that are substantially equivalent to the rates that are obtainable with present commercial apparatus. The data, however, furthermore demonstrate that the process affords substantially improved yields of dewaxed oil as well as wax products that contain less than the usual amounts of oil. Accordingly, the process possesses distinct advantages over presently conventional methods.

Having demonstrated the superiority of the present invention in so far as dewaxing procedures are concerned, it will also be noted (as stated earlier in this description) that the superiority also extends to wax recrystallization procedures. In these latter procedures, substantially the same forms of apparatus and operating techniques are employed as having been described earlier in connection with the dewaxing embodiment of the invention. Thus, a wax to be recrystallized is heated just above its melting point and thereby completely liquefied. The liquefied wax is then diluted with a prechilled dewaxing solvent—the solvent being at a temperature and in an amount such that the wax when cooled to the desired recrystallization temperature is at the desired solvent dilution.

As in the case of the dewaxing embodiment of the invention, the solvent in the recrystallization embodiment acts as both a diluent and a refrigerant. Furthermore, the solvent is added in the form of a continuous stream to provide an average chilling rate of between about 2° F. and 5° F. per minute. Again, the same solvent dilutions may be employed in the recrystallization embodiment as are employed in the dewaxing embodiment, but somewhat higher dilutions of the order of about 5/1 to 10/1 are preferred. In short, the recrystallization embodiment of the invention is preferably carried out in substantially the same manner as the dewaxing embodiment except for the degree of solvent dilution.

As an indication of the superiority that the present invention affords over conventional procedures in the realm of wax recrystallization, attention is directed to the following example.

EXAMPLE III

In this example a slack wax derived from the dewaxing of a Mid-Continent type, SAE 30 grade, phenol-treated waxy distillate (same as in Examples I and II) was recrystallized in accordance with both conventional practice and also the process of the present invention.

In each conventional run the oily wax feed was dissolved in warm ketone and the resulting solution chilled

in scraped surface chillers to the required filtering temperature. In each run using the present process the oily wax feed was liquefied and thereafter blended with the prechilled ketone solvent in the proper amount and at the proper temperature to reach the desired temperature and dilution. In each case the resulting slurries of wax, oil and solvent were then filtered using a rotary type filter to separate the crystallized waxes from the remaining liquid components. The data that were obtained are as follows:

Table III

DILUTION CHILLING FOR FRACTIONAL CRYSTALLIZATION OF WAXES

[M.O.T. 30 slack wax; 145.5° F. melting point; 11.0% oil; 48 S.S.U. at 210° F.; filtered at 90° F.]

Filtering Cycle (secs.)			Wax Loading [1] #sq.ft./hr.	Cake [2] Thickness	Solvent Ratios [4]			Wax Yield, Percent	Oil Content, Percent	Melting Point, °F.
Filter	Wash	Dry			Dilution	Wash	Cake			
Conventional Chilling 7°F./minute [3]										
10	-------	30	44	11	5.2	-------	2.9	74	6.1	150.4
10	30	-------	39	14	5.2	2.6	5.9	55	2.1	153.9
Dilution Chilling 2° F./minute [3] (oily wax at 150° F., ketone 75° F.)										
10	-------	30	44	9	5.8	-------	2.5	60	4.3	152.7
10	30	-------	39	10	5.8	4.8	4.0	50	0.3	157.0

[1] Assuming filter drum speed of 48.5 seconds/revolution.
[2] Sixteenths of an inch.
[3] Chilling rates adjusted to give comparable filter rates and wax loadings.
[4] Solvent employed.

It is apparent from the above table that, for comparable wax loadings, the chilling procedure of the invention produces filter cakes that dry better and also allow much higher wash penetration than does conventional chilling. Both of these factors contribute to the lower oil contents shown for the waxes produced by the present process. It will be noted that a flue gas blow was used for obtaining agitation of the wax and solvent in this example in the same manner as described for the solvent dewaxing examples.

At this point it will also be noted that numerous variations may be incorporated within the examples and embodiments presented above without departing from the spirit or scope of the invention. Thus, refrigerants other than those specifically mentioned may be employed. Furthermore, several wax fractions may be crystallized from the same oily wax feed stock, and the dewaxing and recrystallization steps may be carried out either as separate operations or as one integrated process. Again, a wide variety of pumps, instruments, and the like may be utilized as will be apparent to those skilled in the art. Crystal modifiers may be added as desired to promote filtration, and the various wax and oil products may be further refined as desired.

With respect to the recrystallization embodiment of the invention, it is also contemplated that an oily wax may be merely melted to place it in a liquid condition prior to chilling, or it may be dissolved in a small amount of heated dewaxing solvent. The amount of solvent employed for this purpose, however, must constitute no more than a small proportion of the volume of solvent subsequently employed for the dilution and refrigeration purposes.

What is claimed is:

1. In a method of separating a hydrocarbon wax from a hydrocarbon wax-oil mixture wherein the mixture is chilled in the presence of a ketone dewaxing solvent to a temperature sufficient to crystallize the wax and the wax is thereafter separated from the oil and solvent, the improvement which comprises chilling the mixture by the addition of solvent which has been prechilled to a temperature sufficiently below the separation temperature to cause the resulting blend of solvent and mixture to reach the desired separation temperature when the amount of solvent necessary to provide the desired solvent dilution has been added, the rate of solvent addition being continuous and sufficient to provide an average chilling rate of between 2° F. and 5° F. per minute.

2. In a method of dewaxing a waxy mineral oil wherein the waxy oil is chilled in the presence of a ketone dewaxing solvent to a temperature sufficient to crystallize the wax and the crystallized wax is thereafter separated from the oil, the improvement which comprises adjusting the temperature of the waxy oil to a value just above its cloud point, thereafter blending the waxy oil with the dewaxing solvent in an amount sufficient to provide the desired solvent dilution at the wax separation temperature, the solvent having been prechilled to a temperature sufficiently below the separation temperature that the solvent provides substantially all of the refrigeration necessary to reach the separation temperature, the addition of the solvent being continuous and at a rate sufficient to provide a chilling rate of between about 2° F. and 5° F. per minute.

3. A process as defined in claim 2 in which the dewaxing solvent is an aliphatic ketone containing from 3 to 6 carbon atoms.

4. A process as defined in claim 2 in which the dewaxing solvent is methyl n-propyl ketone.

5. A method of recrystallizing an oily hydrocarbon wax that has been derived from the dewaxing of a waxy petroleum fraction which comprises liquefying the wax and thereafter blending the liquefied wax with a ketone dewaxing solvent, the amount of solvent being sufficient to provide the desired solvent dilution and the solvent having been prechilled to a temperature sufficiently below the separation temperature to provide substantially all of the refrigeration necessary to chill the oily wax to the separation temperature, the solvent being added to the wax continuously and at a rate sufficient to chill the oily wax at a rate between 2° F. and 5° F. per minute.

6. A method of separating the waxy constituents from a hydrocarbon mixture of waxy and oily constituents which comprises adjusting the temperature of the mixture to a value such that all of the waxy and oily constituents are in liquid form, blending the liquid mixture with a prechilled ketone dewaxing solvent in an amount sufficient to form a solvent to oil ratio of from 1½ to 1 to 10 to 1, the solvent having been prechilled to a temperature sufficiently below the separation temperature to reduce the temperature of the mixture to the separation temperature, and thereafter separating the crystallized waxy constituents from the blend.

7. A method as defined in claim 6 in which the solvent

is added continuously to the hydrocarbon mixture at a rate such that the mixture is cooled at between about 2° F. and 5° F. per minute.

8. A process as defined in claim 6 in which the hydrocarbon mixture is continuously agitated to break up lumps of wax within the mixture.

9. A process as defined in claim 6 in which a non-condensing gas that is substantially insoluble in and chemically inert toward the hydrocarbon mixture is blown up through the mixture to agitate the mixture.

10. A process as defined in claim 9 in which the gas is blown at the rate of about 0.5 to 3 volumes of gas at standard conditions per volume of liquid.

11. A process as defined in claim 6 in which the solvent is an aliphatic ketone containing from 3 to 6 carbon atoms.

12. A process as defined in claim 6 in which the solvent is an aliphatic ketone of 4 to 5 carbon atoms.

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