

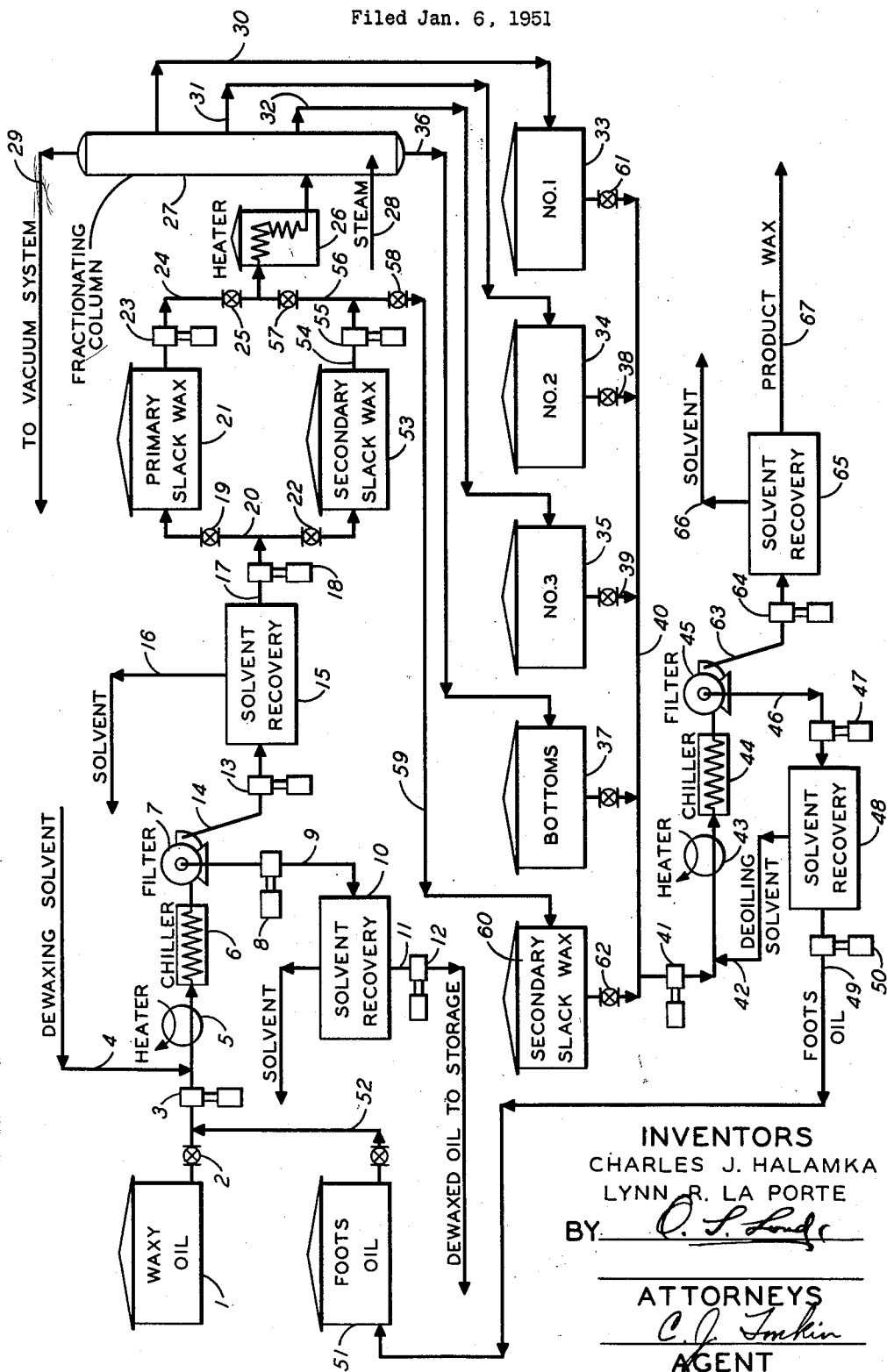
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WAX-OIL SEPARATION PROCESS

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WAX-OIL SEPARATION PROCESS

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4 Claims. (Cl. 196—17)

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The present invention relates to improvements in processes for separating wax-oil mixtures into valuable lubricating oils and superior wax products. More particularly, the invention pertains to an improved method of solvent dewaxing and deoiling whereby the desired high quality is obtained for both the lubricating oil products and the wax products.

The method of the present invention is superior to various processes heretofore proposed for separating wax-oil mixtures. Whereas prior methods usually give dewaxed lubricating oils of satisfactory properties, they do not at the same time yield the desired high quality wax products without employing special treatments or additives or the like.

It is therefore an object of this invention to provide an improved process for efficiently separating wax-oil mixtures into lubricating oils and waxes of high quality.

A particular object of this invention is to provide an improved process for obtaining relatively low melting point wax of superior characteristics.

A further object of this invention is to recover a greater amount of low melting point oil-free waxes than heretofore recovered in deoiling operations.

Further objects and advantages of my invention will appear from the following description taken in connection with the attached drawing which is a schematic flow diagram of a preferred embodiment.

Briefly stated, the present process involves the following steps: A waxy oil is first separated by solvent-dewaxing into dewaxed oil and primary slack wax. The primary slack wax is then fractionated into primary wax distillates of relatively narrow boiling point ranges including a low-boiling fraction which on deoiling yields waxes having an average melting point in the range of 127–140° F. AMP (i. e., American Melting Point, as defined in ASTM D87-42). Preferably, these low-boiling distillate cuts are such that the waxes produced on deoiling can be classified as 125/127, 128/130, 133/135 AMP grades or combinations of two of these such as an 125/130 AMP grade. Likewise produced is a higher-boiling primary slack wax distillate, which yields by deoiling, a wax having an AMP of 135–160° F., preferably having an AMP at least 5° F. higher than the wax resulting from normal solvent deoiling of the low-boiling primary slack wax distillate selected. Thereafter a primary wax distillate of such higher average boiling point is solvent-deoiled to product a wax product

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and a foots oil. While the fraction boiling next above said selected low-boiling fraction is preferred, other higher primary wax distillates up to those which, on deoiling, give waxes with a maximum of about 160° F. AMP can be used. The foots oil so obtained is then solvent-dewaxed to obtain a high quality lubricating oil component and a secondary slack wax. At least a portion of the secondary slack wax is then combined with the selected low-boiling primary wax distillate in a ratio of 20–35 volumes of secondary slack wax to 80–65 volumes of said primary wax distillate. This wax mixture is then subjected to solvent-deoiling to produce a wax product of the desired high quality.

For purposes of this invention, a waxy oil is defined as an oil derived from crude petroleum containing paraffinic compounds which are normally solid at room temperature. The percentage of such petroleum paraffin wax may vary from 1 to 25% in a virgin crude oil, or from 2 to 50% in topped crude oil or distillate fractions or in waxy raffinates obtained from solvent treating or deasphalting distillate fractions or residua. The slack waxes obtained by dewaxing usually contain about 10–60% of a zero ° F. pour point oil, although the oil content can be as low as 2–3%. The wax in the low-boiling distillates of primary slack wax is substantially all (i. e., more than about 90%) normal or straight chain paraffinic compounds. In the secondary slack waxes as obtained by solvent-dewaxing a foots oil resulting from deoiling a primary slack wax distillate, the wax is predominately (i. e., more than about 75%) non-straight chain paraffinic compounds. Both of these petroleum paraffin waxes are to be distinguished from petroleum microcrystalline or amorphous wax; for example, the paraffin waxes, which are obtained from distillates, have low melting points and low tensile strengths, whereas microcrystalline waxes which are obtained from residuum are relatively high melting and have high tensile strengths. Thus, although the low melting point paraffin wax products of the present invention have surprisingly good tensile strength, they are not the same as the products obtained by incorporating a high tensile strength petrolatum (i. e., slack microcrystalline wax) into paraffin wax, as described in Adams Patent 2,127,668.

In some instances it is most advantageous to distill the secondary slack wax to produce a lower boiling fraction and a higher boiling fraction in which case the higher boiling fraction, comprising about 30–80%, preferably 30–60%,

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of the secondary slack wax, is combined with the low-boiling primary wax distillate. Sometimes it is preferable to use the whole of the secondary slack wax in combination with the low-boiling primary wax distillate together with the whole (preferably the higher-boiling 30-60%) of the secondary slack wax produced by solvent dewaxing the foots oil derived from solvent deoiling wax mixtures containing said lower primary wax distillate. Another preferred embodiment of the present invention utilizes the secondary foots oil resulting from deoiling an admixture containing at least the low-boiling primary slack wax distillate and secondary slack wax. In such embodiment, the secondary foots oil is solvent dewaxed to produce a third low pour point oil and a third slack wax. Thereafter an admixture for subsequent deoiling to a superior low melting wax contains 20-35 volumes of the secondary slack wax, 75-50 volumes of low boiling primary wax distillate and 5-15 volumes of the third slack wax. When the low-boiling primary slack wax distillate is combined with the higher-boiling fraction of the secondary slack wax with or without the higher-boiling fraction of the third slack wax, the product contains about 20-35% non-straight chain paraffin wax and about 80-65% of normal or straight-chain paraffin wax, which composition is claimed in the copending application of Melvin V. Hunter and John R. Segesser, Serial No. 204,316, filed January 6, 1951.

These especially preferred variations, as well as the more general process of the present invention, are particularly effective in producing waxes of improved properties when the initial or primary slack wax is derived from petroleum residua. Such petroleum residua include viscous lubricating oil stocks and may be pretreated such as by deasphalting or refining with aromatic-removing solvents or the like.

By means of the present invention, high quality lubricating oil material and wax products of improved characteristics are obtained in an efficient and economical manner. The lower melting point wax products which result from the present method are superior to the comparable grades of waxes obtained from processes heretofore used. As compared to the products of known dewaxing and deoiling operations, the new wax products have increased tensile strength, are less brittle and have improved adhesiveness towards paper products. In particular, the relatively low-melting grades such as the 125/130 grade wax as produced by the present process are excellent for coating paper cartons such as those used for milk. With these waxes, strong and waterproof films are obtained with a minimum amount of wax and the resultant coating has less tendency to crack off. Thin films of these waxes are flexible and have high resistance to fracture on sudden chilling. In storage of milk cartons coated with the present waxes, less bulging occurs and fewer leakers are found. In addition to improved wax products, the present process yields a primary dewaxed oil and a secondary dewaxed lubricating oil component, both oils being of high lubricating oil quality.

Further, the present invention results in numerous processing advantages. For example, the production of low melting waxes which are most in demand is increased without having to increase lubricating oil manufacture to an appreciable extent or without having to reduce the quality of the desired wax product. By incorpo-

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rating the secondary slack wax in the deoiling feed the length of the primary slack wax distillate can be increased to the extent that separate deoiling of the longer slack wax distillate would yield a wax of about 5-10° F. higher AMP, but without increasing the AMP of our new product. For example, whereas according to prior practices the low boiling primary wax distillate is adjusted to yield by deoiling a wax having an AMP of 125-130° F., our new wax product of the same AMP utilizes a broader primary wax distillate which, if separately deoiled, would yield a wax having an AMP of 130-140° F. The inventive process yields deoiled low-melting wax products without filtering difficulties as generally is found when separately deoiling the secondary slack wax. Also, the low melting paraffin wax products are readily obtained with the desired low oil contents.

In carrying out the improved process of the present invention, the dewaxing and deoiling operations are accomplished by chilling the oil-wax mixtures in the presence of solvents or diluents including, for example, ketones such as acetone, methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, etc.; aromatic hydrocarbons such as benzene and toluene; alcohols such as ethyl alcohol, isopropyl alcohol, normal propyl alcohol and the like; petroleum naphthas; halogenated hydrocarbons such as ethylene dichloride and trichloroethylene; esters such as ethyl acetate; ethers such as diethyl ether and isopropyl ether; liquefied normally gaseous hydrocarbons such as ethane, ethylene, propane, propylene, butane, isobutane, etc.; other normally gaseous diluents such as methyl ether, methyl chloride and dichloro difluoro methane; or mixtures thereof. The normally gaseous diluents serve to dilute and also to chill the mixture when the diluent is evaporated under reduced pressure. Ordinarily, mixtures of solvents or diluents such as benzene plus methyl ethyl ketone are employed.

The solvent dewaxing step can be carried out by the various known methods wherein the primary object of the step is to obtain a substantially-completely dewaxed lubricating oil with a low pour point. Such processes also yield a so-called slack wax containing substantially all the waxy material in the charge in admixture with oil, the slack wax usually containing 10-60% oil. Preferably the oil-wax charge is admixed with solvent or diluent prior to cooling. The solvent-wax-oil mixture is chilled to the dewaxing temperature, i. e., about 0° F. to -15° F. Thereafter the dewaxed oil is segregated from the precipitated waxy material in a suitable manner, preferably by means of a filter like that described in U. S. Patent 2,107,664.

For deoiling the slack wax or distillate fractions thereof, or admixtures of primary slack wax distillate and secondary slack wax, the several solvent-treating processes which segregate the slack wax into foots oil and oil-free wax can be employed. Preferably, the wax charge prior to cooling is admixed with at least a substantial portion of the solvent or diluent, such as at least 1-4 volumes of solvent to 4 volumes of wax. Then the mixture is preferably heated to about 20-50° F. above the average melting point of the waxy material. During the subsequent chilling of the solvent-wax-oil mixture, additional solvent, such as 1-2 or more volumes per volume of wax charge, can be added, as desired. After the mixture has been cooled to the proper wax de-

oiling temperature, i. e., about 35–55° F., the oil-free wax is separated from the foots oil in a suitable manner; such as by means of a continuous filter. The wax product contains less than 1%, preferably less than 0.5%, oil.

For fractionating the primary slack wax into relatively narrow boiling distillates, it is preferable to employ a fractionating column operating under a low vacuum sufficient to avoid appreciable cracking of the paraffin wax. If desired, steam may be introduced into the column to assist the distillation. While the fractions are separated ordinarily on the basis of the average melting point of the waxes produced by deoiling the distillates, it is generally desirable to obtain at least three fractions with average boiling points (atmospheric pressure basis) of about 800° F., 900° F. and 1050° F., which can be designated as cuts No. 1, No. 2 and No. 3. Cut No. 1 on deoiling yields a wax having an AMP of about 133–138° F., and deoiling of No. 1 and No. 2 cuts together yields a wax with an AMP of 143–150° F.

While for the purpose of carrying out the process of the present invention, separate facilities can be provided for dewaxing and topping or fractionating the foots oil, these facilities can be used intermittently for different feed stocks. Likewise, where in the hereinbelow detailed description one device for chilling the solvent-wax-oil mixtures is shown or referred to, the operation can be carried out in several stages.

Since the present invention is especially applicable to the production of a superior wax product melting at 125–130° F. AMP, which product is known as 125/130 grade wax, the process will be described in relation thereto. Referring to the drawing, the waxy oil in feed tank 1 can be, and preferably is, a solvent-refined lubricating oil stock such as a long residuum (20–30% from crude) from a California waxy crude (which is classifiable as "intermediate" by the Bureau of Mines Gravity Classification described by Love & Garton in Bureau of Mines Report of Investigations No. 3279, 1935). The waxy oil is taken from the feed tank 1 through valved line 2 by means of pump 3 and admixed with dewaxing solvent introduced through line 4. The solvent-waxy oil mixture passes through heater 5 which is maintained at a temperature sufficiently high to insure complete solution of the waxy oil in the solvent. Thereafter the mixture is introduced into a chiller 6 for chilling the solvent-wax-oil mixture to the dewaxing temperature such as about –10° F. The chilled mixture is introduced into filter 7 wherein lubricating oil of low pour point is separated from the waxy material. The filtrate is taken from the filter by means of pump 8 via line 9 and introduced into a solvent recovery system 10 for separation of the solvent from the dewaxed oil which passes to storage through line 11 and pump 12. The wax cake produced in the filter is taken by pump 13 through line 14 to solvent recovery system 15 in which the dewaxing solvent is removed via line 16. The solvent-free waxy material passes via line 17 and pump 18, open valve 19 and line 20 into primary slack wax storage tank 21. During this operation, valve 22 in line 20 remains closed.

The primary slack wax is taken from storage tank 21 by means of pump 23 and passed through line 24, open valve 25 and a suitable heater, such as fired heater 26, into vacuum fractionating column 27. Preferably, steam is introduced through

line 28 into the lower portion of fractionating column 27 to assist the distillation. A sufficiently low pressure is maintained in column 27 by means of a vacuum system (not shown) connected to the column through line 29 to permit the distillation to proceed without appreciable cracking of the waxy material. In the fractionating column 27 the primary slack wax is separated into the desired number of relatively narrow boiling primary slack wax distillates. As indicated in the drawing, three distillate cuts can be taken and passed from the column 27 via lines 30, 31 and 32 to the respective distillate storage tanks 33, 34 and 35. Line 36 is provided for passing the primary slack wax bottoms to storage tank 37.

In one preferred embodiment of the present invention, an admixture of No. 1 and No. 2 primary slack wax distillates are taken from their respective storage tanks 34 and 35 via valved lines 38 and 39 and header 40 by means of pump 41, mixing with deoiling solvent introduced through line 42. The resultant solvent primary slack wax distillates are passed first through heater 43 and chiller 44 and thence into deoiling filter 45. The wax cake so obtained in filter 45 is removed through line 63 by means of pump 64 in the solvent recovery system 65 from which solvent passes via line 66 and by-product wax is discharged through line 67. From the deoiling filter 45 is taken a filtrate comprising solvent and foots oil which passes via line 46 and pump 47 into solvent recovery system 48. The deoiling solvent which is thus recovered may be recycled through line 42. The solvent-free foots oil is conducted via line 49 and pump 50 to foots oil storage tank 51.

Foots oil is then treated in the solvent dewaxing system to obtain a secondary slack wax and an oil of low pour point. For this purpose the foots oil passes from storage tank 51 via valved line 52, and the effluent of pump 3 is admixed with dewaxing solvent introduced through line 4, the solvent foots oil mixture passing through heater 5, chiller 6 and into filter 7. The secondary slack wax, i. e., the wax so obtained in the filter 7, passes through line 14, solvent recovery system 15, line 17, pump 18, line 20 and open valve 22 into secondary slack wax storage tank 53.

The secondary slack wax is taken from tank 53 via line 54 and pump 55 and can be passed through line 56 and open valve 57 into fractionating column 27 for obtaining the desired distillate fraction of the secondary slack wax. Alternatively, the whole secondary slack wax may be taken via line 56 and open valve 58 (valve 57 being closed) and through line 59 into secondary slack wax storage tank 60. When the secondary slack wax is fractionated, the desired distillate cut or cuts issuing from the fractionating column 27 may be introduced into secondary slack wax storage tank 60 through suitable conduit lines not shown.

Thereafter the admixture of the selected low-boiling primary slack wax distillate, such as cut No. 1 from storage tank 33 and secondary slack wax from storage tank 60 are passed through the respective valved lines 61 and 62 into header 40, from which pump 41 takes suction to pass the admixture together with deoiling solvent introduced from line 42 through heater 43, chiller 44 and into filter 45. From the filter is obtained as filtrate a secondary foots oil which, after removal of the deoiling solvent in solvent recovery system 48, may be discarded or returned

to foots oil storage tank 51 through line 49. The wax cake obtained in the filter is removed through line 63 by means of pump 64 and is introduced into solvent recovery system 65; there in the deoiling solvent is removed from the wax and discharged through line 66. The desired low-melting product wax is discharged through line 67.

Where in the above-described operation the low-boiling No. 1 cut primary slack wax distillate yields, on normal deoiling (i. e., separate deoiling, without admixture with secondary slack wax) a wax having an AMP of 133-138° F. and the by-product wax produced incident to obtaining the foots oil from which is derived the secondary slack wax has an AMP of 143-150° F., and where the deoiling charge contains about 30 volumes of the secondary slack wax and 70 volumes of said No. 1 cut primary slack wax distillate, the volume of wax produced having an AMP of 125-130° F. is 50 to 150% greater than that produced by deoiling alone a primary slack wax distillate of suitable low boiling range to give a comparable melting point wax product. Further, the product of our new process has improved properties as compared to the old product, and the following data is illustrative:

	Properties of Deoiled Wax			
	Melting Point, ° F., AMP	Oil Content, Wt. Percent	Tensile Strength, p. s. i.	
			at 70° F.	at 40° F.
Wax from Old Process.....	128.9	0.37	80	325
Wax from New Process.....	127.9	0.42	275	325

The tensile strength was determined by the Perkins method. (Paper Trade Journal 122, No. 19, pp. 201, May 9, 1946) modified to the extent that the shape of the test pieces were changed from rounded ends to tapered or wedge-shaped ends.

While the process is exemplified by the passing of foots oil to an intermittently-operated dewaxing section, the mixture of solvent and foots oil obtained as a filtrate in the separation of oil-free wax product can be passed directly to a separate section substantially the same as the chilling and filtering portion of the dewaxing section. Thus, it will be convenient at times to take the cold solvent-foots oil filtrate without allowing its temperature to rise appreciably and then to chill it to dewaxing temperatures after adding, if desired, further quantities of solvent or diluent.

The solvent recovery systems are schematically illustrated in the drawings and may consist of a flash column or tank or the like to remove at least a substantial portion of the solvent from the various wax filter cakes and oily filtrates. The solvent, if any, remaining in the products can be removed by steam stripping, and the stripped material thereafter dehydrated, if required.

Various modifications of the above-described specific embodiment of the present invention can be made without departing from the spirit of the invention, which is merely illustrated by the preferred embodiments.

We claim:

1. The process of segregating a waxy lubricating oil stock into dewaxed lubricating oil components of low pour point and improved oil-free

waxes comprising the steps of solvent dewaxing said waxy oil stock to produce a substantially wax-free oil and a primary slack wax; fractionating said primary slack wax into a plurality of relatively narrow-boiling primary wax distillates including a low boiling distillate which on deoiling yields a wax with an average melting point in the range of 125-140° F. AMP; solvent-deoiling a primary wax distillate of intermediate boiling range to produce a substantially oil-free wax and a foots oil, solvent-dewaxing said foots oil from the intermediate wax distillate to produce a secondary dewaxed lubricating oil component and a secondary slack wax; combining at least a substantial portion of said secondary slack wax with said low boiling primary wax distillate in a ratio of 20 to 35 volumes of said secondary slack wax to 30 to 65 volumes of said primary wax distillate; and solvent-deoiling said mixture of secondary slack wax and primary wax distillate to produce a low melting wax of superior properties.

2. In the process of segregating waxy lubricating oil stock into dewaxed oil components of low pour point and oil-free wax comprising the steps of solvent-dewaxing a waxy lubricating oil stock under conditions to produce a dewaxed oil of low pour point and a slack wax, fractionating said slack wax into a plurality of relatively narrow-boiling range wax distillates including a low-boiling primary distillate which on deoiling yields a wax of average melting point within the range of 125-140° F. AMP; and solvent-deoiling each of said wax distillates separately under conditions to produce a substantially oil-free wax and a foots oil, the improvement which comprises solvent-dewaxing the foots oil derived from the wax distillate immediately above the selected low-boiling primary distillate to produce a secondary dewaxed lubricating oil component of low pour point and a secondary slack wax, combining at least a substantial portion of said secondary slack wax with said primary wax distillate in a ratio of 20 to 35 volumes of secondary slack wax to 30 to 65 volumes of said primary wax distillate; and subjecting the combined waxy material to solvent-deoiling to produce a substantially oil-free low melting wax of superior properties.

3. A process of producing from waxy lubricating oil stock both lubricating oil of low pour point and a low melting refined paraffin wax having an AMP in the range of 125-135° F., which comprises solvent-dewaxing said waxy oil to produce a low pour point lubricating oil and a primary slack wax, fractionating said slack wax into primary wax distillates including a low-boiling fraction yielding by solvent-deoiling a paraffin wax having an AMP of up to 10° F. higher than that of the desired final product and a higher-boiling fraction yielding by solvent-deoiling a paraffin wax having an AMP within the range of 135-160° F. and at least 5° F. higher than the wax derived from the low-boiling fraction selected; solvent-deoiling said higher-boiling primary wax distillate to produce a relatively oil-free wax and a foots oil, solvent-dewaxing said foots oil to produce a low pour point lubricating oil and a secondary slack wax, admixing 20 to 35 volumes of at least a substantial portion of said secondary slack wax with 30 to 65 volumes of said selected low-boiling primary slack wax distillate, and solvent-deoiling the resultant admixture to produce a substantially oil-free, low melting wax of superior properties.

4. The process of claim 3 wherein the foots oil

resulting from deoiling the admixture of secondary slack wax and low boiling primary wax distillate is subjected to solvent-dewaxing to produce a third low pour point oil and a third slack wax, and 5 to 15 volumes of said third slack wax are combined with 20 to 35 volumes of said secondary slack wax and 75 to 50 volumes of said low boiling primary, slack wax distillate to form an admixture for subsequent solvent-deoiling.

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