PROCESS FOR THE PREPARATION OF PARAFFIN WAX PRODUCTS

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The present invention relates to improvements in processes or preparation of paraffin wax products. More particularly, the invention pertains to an improved method of solvent dewaxing and deoiling at relatively low deoiling temperatures whereby paraffin waxes having improved low temperature properties are obtained.

The method of the present invention is superior to various processes heretofore proposed for the preparation of paraffin waxes especially suitable for use as milk can-
ton waxes and the like. Paraffin waxes prepared by prior processes normally exhibit poor low temperature proper-
ties, especially with respect to flexibility as evidenced by both bending and fracture-resistance tests at relatively low temperatures or, at least, by having poor properties in one of these respects.

Paraffin waxes are normally a mixture of hydrocarbons predominating in those having substantially straight-chain configurations together with minor amounts of materials having branched chains and naphthenes with only minor portions of olefins (if any). They are to be differentiated in properties and in predominating configurations from the so-called microcrystalline or amorphous waxes nor-

mally obtained from residual oil fractions. The latter type of waxes predominate in highly branched configura-
tions, as well as, cyclic or poly cyclic molecules which impart to the microcrystalline wax a structure which is apparently non-crystalline to the naked eye. These microcrystalline waxes may be combined with paraffin waxes to impart certain desirable properties thereto but it is necessary to employ relatively large amounts in the order of 35-40% of a microcrystalline wax in order to impart improved low temperature properties to paraffin waxes. In utilizing such large proportions of microcrystalline waxes, the blocking point of the wax composition is undesirably depressed. Moreover, as data given later in this disclosure show, the low temperature properties of such wax blends are not satisfactory with respect to flexi-
bility and fracture, especially when normal (i. e., at least 40° F. or higher) deoiling temperatures are employed.

The low temperature properties of paraffin waxes may be improved according to prior art processes by utilizing variations of complicated alternatives to the basic step of dewaxing a waxy lubricating oil. The effort in the past has been to isolate a whole paraffin wax from a rela-
tively low-boiling lubricating oil fraction and combine it with a desired fraction of a higher boiling wax fraction obtained from another lubricating oil cut and thereafter deoiling the mixture at relatively high deoiling temperatures. The process involved in isolating a particular por-
tion of a paraffin wax is undesirable due to the fact that numerous processing steps and equipment are involved.

While the waxes so produced may be desirable with re-
spect to one function or another, the benefit so gained is counterbalanced by the complication of the defining pro-
cess and the low temperature properties possessed by wax products obtained by the process of the present inven-
tion have not thereby been attained.

It is an object of the present invention to provide a process for the preparation of improved paraffin wax products. It is a further object of this invention to pro-
vide paraffin wax products having improved low tempera-
ture properties. It is a particular object of this invention to provide a process for the preparation of wax products having improved low temperature properties. It is a special object of this invention to provide a process for the isolation of paraffin waxes having improved flexibility characteristics at low temperatures. Other objects will become apparent during the following discussion.

Now, in accordance with the present invention, it has been found that paraffin wax products have having greatly im-
proved low temperature properties may be obtained by the following process: A waxy lubricating oil is frac-
tionated into waxy lubricating oil fractions such that the waxes contained therein have a carbon atom content per molecule varying no more than about 15 carbon atoms. At least two of these fractions are separately subjected to dewaxing operations whereby substantially wax-free lubricating oil fractions are obtained from each, together with at least two asphalt wax fractions. Substantial portions of each of these asphalt wax fractions as defined hereafter are combined and then subjected to deoiling at relatively low deoiling temperatures. The product so ob-
tained comprises a substantially purified, i.e., deoiled, paraffin wax product having improved low temperature properties not obtainable by other methods known in the art. By “a low deoiling temperature” is meant a tem-

perature below about 33° F. and preferably in the order of about 15-30° F. The use of the low deoiling tem-

perature combined with the specified relationship of the wax cuts as defined more fully hereinafter for the pur-
pose of purifying the particular mixture of paraffin waxes appears to be the key to obtain the improved products having excellent low temperature flexibility characteristics. Alternatively, the slack waxes may be deoiled separately at the low deoiling temperatures and thereafter com-
bined. The waxes to be combined are to be chosen so that the wax having the higher melting point has an average molecular weight from about 50 to 150 higher than that of the lower melting waxes.

For the purpose of this invention, a waxy oil is defined as a high viscosity index solvent-extracted 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 2 to 20% in waxy raffinates obtained from solvent treating distillate fractions or residua. It is preferred that waxy raffinates obtained from solvent treating distillate lubricating fractions be utilized.

The slack waxes obtained by dewaxing usually contain between about 10 and about 60% of a 0° F. pour point lubricating oil, although the oil content may be as low as 2-5%. In its preferred version, the present process is applied especially to full-range paraffin waxes having a relatively low average melting point modified with full-range waxes from higher boiling waxy lubricating oils, the latter waxes having an average molecular weight be-
tween about 60 and about 100 greater than that of the lower melting point wax cut. By “full-range waxes” is meant the entire wax mixture separated by dewaxing of a waxy lubricating oil substantially without any of the wax members having been later segregated from said mixture. Preferably, these paraffin waxes are obtained from low-boiling and intermediate boiling waxy lubricating oils. The waxes in the low boiling distillates as well as in the intermediate distillates of full-range fractions but predominate in both cases in normal or straight-chain paraffinic hydrocarbons with minor proportions of slightly branched hydrocarbons and naphthenes or other config-

urations. Consequently, it will be understood that the
combination of low melting paraffin wax obtained from relatively low boiling waxy lubricating oils with fractions of slack wax obtained from intermediate boiling waxy lubricating oil distillates results in a full range of all of the wax configurations involved and is not "unbalanced" with respect to one configuration or another.

The exact proportion of each of these configurations has not been determined to date. Therefore, it can only be said at the present time that the configurations appear to be balanced by the method of preparation in such a manner as to result in obtaining improved low temperature flexibility and other properties. A secondary advantage, which is nonetheless an important commercial consideration, is the fact that the waxes so produced do not inherently entail the production of other less desirable wax products which must be worked off, or disposed of, in other means such as by being sent to a cracking unit or the like. There is no necessity, furthermore, for increasing lubricating oil manufacture to any extent for the purpose of improving the waxes by the present process. The process entails, on the contrary, the full utilization of waxes in products bearing a premium price rather than necessitating a dispersal of undesirable fractions into channels bearing no appreciable cost advantage.

In carrying out the improved process of the present invention, the dewaxing and deoiling operations are accomplished by chilling the waxy lubricating oils, preferably in the presence of oil solvents or diluents including, for example, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone, etc.; alcohols, such as ethyl alcohol, isopropyl alcohol, normal propyl alcohol and the like; petroleum naphthas, higher paraffin 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, propylene, propylene, butane, isobutane, etc. Other normally gaseous diluents, such as methanol, toluene, methyl chloride and dichloromethane, or mixtures thereof. The normally gaseous diluents serve to dilute and dissolve the oil and also to chill the mixture when the diluent is evaporated under reduced pressure. Ordinarily, mixtures of solvents or diluents, such as benzene, containing known proportions of methyl ketones and other diluents are employed.

Solvant 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 of the wax material in the original charge in admixture with certain proportions of 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, that is, between about 0° F. and about —15° F. Thereafter, the dewaxed oil is segregated from the precipitated waxy material in a suitable manner such as by means of a filter as described in U. S. Patent 2,107,664.

As stated hereinbefore, each of the waxy oils should contain waxes having a range of no more than about 15 carbon atoms between the wax molecules having highest and lowest molecular weights.

The dewaxing step is still more preferably carried out on fractions of waxy lubricating oil distillates having a relatively narrow boiling range, such that the major proportion of paraffin hydrocarbon waxes contained therein have a range of carbon atoms per molecule of not more than about 4 and preferably not more than 2 or 3, such that the melting point of the highest melting isomeric paraffin wax in said fraction is lower than the melting point of the lowest melting normal paraffin wax therein. In general, it will be satisfactory if at least 90% of the isomeric paraffin waxes therein melt below the melting point of the lowest melting normal paraffin wax therein.

In accordance with a particular phase of the present invention, the lower melting component employed as the wax to be modified by addition thereto of other slack waxes comprises about 50% of waxes contained in the intermediate boiling lubricating oil containing waxes having an average melting point particularly in the range of 120-125° F. AMP (American melting point, as defined in ASTM D87-42). The preferred higher melting wax component has an average of 135-140° F. AMP, while the products most suitable for wax news are those having higher melting point of about 130-135° F. AMP. More generally, the present process may be applied to any paraffin wax obtained from the lubricating oil distillates but the maximum effect is found when employing waxes having the above average melting point as a major component.

Wax isolated from a waxy lubricating oil of intermediate boiling range is preferably utilized in conjunction with the lower molecular weight waxes, although higher boiling range material may be so employed. The cut utilized preferably has the narrow boiling range (less than 15 carbon atoms spread) similar in range to that of the lower boiling waxy lubricating oil and containing paraffin waxes exhibiting the same spread in carbon atom content as detailed above. For the purpose of obtaining wax products having optimum low temperature properties, it is preferred that the slack waxes obtained from two or more lubricating oil distillates be combined so that the proportion of lower boiling paraffin waxes obtained from the lower boiling lubricating oil distillate after the deoiling operation following the combination of the slack waxes is between about 30 to about 50 weight percent of the higher boiling paraffin waxes present in an amount between about 70 and about 50 weight percent.

For deoiling the slack wax combinations, it is essential to employ relatively low deoiling temperatures if wax products having optimum low temperature properties are desired. Preferably, the slack wax charge prior to cooling is admixed with at least a substantial portion of the solvent or diluent, such as at least 1 volume of solvent to 4 volumes of waxy material up to about 10 volumes of solvent for each volume of slack wax. Then the mixture is preferably heated to about 20-50° F. above the average melting point of the waxy material in order to dissolve the oil at least a substantial proportion of the wax in the deoiling solvent. During the subsequent chilling of the waxy solvent-oil mixture, additional solvent, such as 1-5 or more volumes per volume of wax charge, may be added, as desired. After the mixture has been cooled to the proper relatively low wax deoiling temperature, the oil mixture, preferably in the order of 10-30° F., the oil-free wax is separated from the foot oil in a suitable manner, such as by a continuous filter. The wax product contains less than about 1% and preferably less than 0.5% oil. In accordance with this invention, it has been found to be essential to deoil the slack waxes, either before or after their combination, at temperatures below about 32° F., since higher deoiling temperatures provide oil-free waxes having poor flow and shatter resistance. The reasons for this are not clear, but it is to be emphasized that low deoiling temperatures alone are not sufficient to provide the desirable capability for use at low temperatures; it is necessary to utilize the two types of wax fractions defined hereinbefore, combined in the ratios already specified, and deoiled as just stated.

Referring to the drawing, the waxy lubricating oil is drawn through pump 2 from tank 1 into a distillation column 3 wherein the waxy oil is split by distillation into a plurality of boiling fractions of waxy lubricating oil. A low boiling fraction A is passed through pump 4 and mixed in line 5 with an aromatic solvent of the phenol
The binary liquid mixture is then sent to separator 7, from which the solution of aromatics and solvent therefrom is withdrawn and the remaining high viscosity index wax lubricating oil is passed through line 8 and mixed therein with the dewaxing solvent obtained, for example, from the solvent recovery area 9. This mixture is then passed through a heater 10 and warmed to such a point that homogeneous solution is obtained. The latter is then subjected to a chilling operation in chiller 11 for the purpose of precipitating slack wax and obtaining a solution of dewaxed lubricating oil. This mixture is separated in filter 12, the solution of dewaxed oil being pumped by pump 13 to a stripping column or similar piece of apparatus for the recovery of solvent in solvent recovery area 9. The solvent so recovered may be returned to the system, for example, into line 8. The dewaxed oil isolated during solvent recovery is sent by means of pump 14 to storage 15.

At least one other wax lubricating oil cut from the distillation column 3 is processed through a similar series of steps in the same or a parallel set of apparatus in order to isolate a slack wax to be combined with the slack wax from cut A. This set of apparatus need not be detailed since the steps are substantially identical to those carried out on cut A and are shown in the figure as area 16. The slack wax so derived is pumped to the blend tank 17 together with a substantial portion of the slack wax obtained from cut A. Dewaxing solvent from solvent recovery 18 is inserted in the lines to the blend tank or in the blend tank itself. The mixture is then pumped by means of pump 19 through heater 20 for the purpose of forming a homogeneous single phase system which is then conducted by means of line 21 to chiller 22 wherein the system is cooled to the relatively low dewaxing temperature as specified hereinafter.

The chilled mixture is passed to filter 23 wherein the dewaxed purified wax product is separated from the solution of foot oil. The latter solution is passed by means of pump 24 to solvent recovery area 18 wherein the solvent is recovered and recycled to the system and the foot oil sent for further processing. The dewaxed wax is sent by means of pump (or conveyer) 25 to the solvent recovery area where residual amounts of the dewaxing solvent are removed in the area 26 to separate both the solvent and wax product.

Having described a general but preferred set of apparatus and operating steps for the preparation of the subject wax products, the following specific example constitutes a utilization of the general process:

**Example I**

Distillation of a Texas crude oil resulted in Cuts A and B, each comprising wax and oil. A lube oil of 100 SSU at 100° F. would finally be obtained from Cut A and a lube oil of 250 SSU at 100° F. would be obtained from Cut B. Both streams were mixed with solvents (2 parts of methyl ethyl ketone and 1 part of benzene to 1 part by volume of oil), cooled to 0° to +10° F. and filtered. The slack waxes from each were combined in a 60% of A and 40% of B ratio, redissolved in the same solvent mixture, cooled and subjected to dewaxing at +30° F. The resulting product passed bend and fracture tests described heretofore and had a melting point of 126 to 128° F. This wax was flexible enough to be satisfactory for milk containers and was obtained in 12% higher yield than by usual operations.

In contrast to the above described process, a method of manufacture that consisted of following the same procedure described above to produce a substantially wax-free lubricating oil but from then on dewaxed at 35° F. in one case and 45° F. in another case produced two wax products which would not pass the bend test and were unsatisfactory for milk containers. The "Bend Test" recognized by milk carton manufacturers as one of the two tests of a wax satisfactory for coating of milk cartons is conducted as follows: A sample of the wax is cast into a cake 0.5 inch thick and is bent at a temperature of 77° F. In order to pass the test, the cake of wax must bend noticeably before breaking at this temperature.

The "Fracture Test" which is recognized by carton manufacturers as the second basic criterion, requires that of ¼ inch film of the wax not crack when chilled from 104° F. by plunging into 40° F. water.

**Example II**

The following table illustrates the benefits of the present invention and the necessity for avoiding the normal dewaxing temperatures. It also shows that combined (Sample G) or separate (Sample F) low temperature dewaxing does not affect the quality of the eventual product.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wax Source</th>
<th>Dewaxing Temp., ° F.</th>
<th>Bend Test</th>
<th>Fracture Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Slack wax from intermediate lube oil cut.</td>
<td>45</td>
<td>Fail</td>
<td>Pass</td>
</tr>
<tr>
<td>B</td>
<td>Slack wax from intermediate lube oil cut.</td>
<td>35</td>
<td>Fail</td>
<td>Pass</td>
</tr>
<tr>
<td>C</td>
<td>Slack wax from low viscosity lube oil cut.</td>
<td>45</td>
<td>Fail</td>
<td>Pass</td>
</tr>
<tr>
<td>D</td>
<td>Slack wax from intermediate lube oil cut.</td>
<td>35</td>
<td>Fail</td>
<td>Pass</td>
</tr>
<tr>
<td>E</td>
<td>60% slack wax from intermediate lube oil cut.</td>
<td>15</td>
<td>Fail</td>
<td>Pass</td>
</tr>
<tr>
<td>F</td>
<td>60% slack wax from intermediate lube oil cut.</td>
<td>15</td>
<td>Fail</td>
<td>Pass</td>
</tr>
<tr>
<td>G</td>
<td>60% slack wax from low viscosity lube oil cut.</td>
<td>30</td>
<td>Pass</td>
<td>Pass</td>
</tr>
</tbody>
</table>

I claim as my invention:

1. The process of segregating a substantially oil free paraffin wax having improved low temperature flexibility which comprises distilling a solvent extracted wax lubricating oil into a plurality of high viscosity index lubricating fractions wax lubricating oil fractions, dewaxing one of said fractions to produce a substantially wax-free lubricating oil and a first slack wax which on dewaxing would yield a first lower melting point wax, separately dewaxing a second of said wax high viscosity index fractions to produce a substantially wax-free lubricating oil and a second slack wax which on dewaxing would yield a second higher melting point wax with an average molecular weight from about 50 to about 150 units higher than that of said first wax, and solvent dewaxing the slack waxes at a temperature below about 32° F. and above 10° F. to produce a paraffin wax product having an average melting point in the range of 120-140° F. and improved low temperature flexibility properties, the product containing 30-50% of wax from the first slack wax and 50-70% of wax from the second slack wax, said waxes being combined together subsequent to the separate dewaxing steps.

2. The process of segregating a substantially oil free paraffin wax having improved low temperature flexibility which comprises distilling a wax lubricating oil into a plurality of wax lubricating oil fractions, solvent extracting said fractions to produce wax high viscosity index lubricating oil fractions, dewaxing one of said fractions to produce a substantially wax-free lubricating oil and a first slack wax, which on dewaxing would yield a wax with an average melting point in the range of 120/125° F. AMP, separately dewaxing a second of said wax high viscosity index fractions immediately above the boiling range of the first fraction so treated to produce a substantially wax-free lubricating oil and a second slack wax which on dewaxing would yield a wax with an average melting point in the range of 130/135° F. AMP, combining substantial proportions of the slack waxes so produced and solvent dewaxing the combined slack waxes at a temperature below about 32° F. and above 10° F. to produce a paraffin wax having an average
2,761,814 melting point in the range of 125/130° F. AMP and improved low temperature flexibility properties.

3. The process of segregating a substantially oil free paraffin wax having improved low temperature flexibility which comprises distilling a waxy lubricating oil into a plurality of relatively narrow boiling waxy lubricating oil fractions, solvent extracting said fractions to produce waxy high viscosity index lubricating oil fractions, dewaxing one of said fractions to produce a substantially wax-free lubricating oil and a first slack wax which on deoiling would yield a wax with an average melting point in the range of 120/125° F. AMP, and improved low temperature flexibility properties.

4. The process of segregating an improved oil free wax having improved low temperature flexibility comprising the steps of fractionating a waxy oil stock into a plurality of relatively narrow boiling waxy lubricating oil fractions, solvent extracting said fractions to produce high viscosity index waxy lubricating oil fractions, separately dewaxing at least two of said fractions to produce substantially wax-free lubricating oils and slack waxes from each fraction so treated, combining at least substantial portions of the slack waxes from at least two of such fractions, and solvent deoiling the mixture so formed at a temperature below about 32° F. and above 10° F. to produce a paraffin wax having improved low temperature flexibility properties.

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