

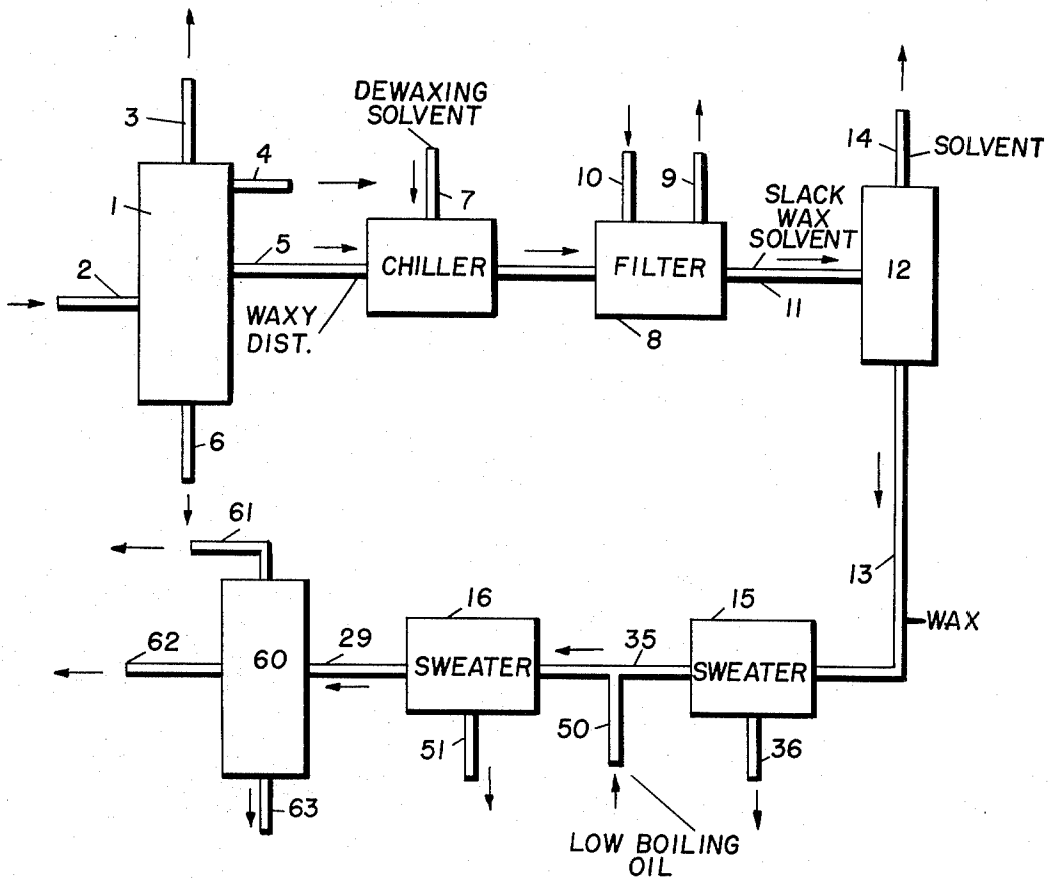
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MANUFACTURE OF REFINED WAX

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MANUFACTURE OF REFINED WAX

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The present invention is concerned with the production of a high quality paraffin wax. The invention is more specifically directed toward the more efficient removal of small traces of oil by an improved sweating operation. In accordance with the present invention, a small quantity of a relatively low boiling oil is added to the wax prior to sweating the same under conditions to secure substantially complete and efficient removal of the undesirable oil constituents.

In the refining of hydrocarbon oils such as petroleum oils, it is known to segregate paraffin waxes from so-called paraffin distillates, waxy lubes and the like. The segregation of these waxes is secured by a number of processes. For example, it is known to chill the selected wax-containing fraction in order to secure crystallization of the wax and to remove the wax crystals from the oil by filtering, centrifuging and the like. It is also known to use various dewaxing solvents such as liquid normally gaseous hydrocarbons, such as propane, butane, as well as other solvents, such as methyl-ethyl ketone and the like. It is also known to utilize in dewaxing operations solvent mixtures wherein one solvent comprises a wax precipitating solvent while the other comprises a solvent having a high solubility for oil. A solvent mixture of this character, for example, comprises about 60% by volume of methyl-ethyl ketone and about 40% by volume of toluene. In utilizing a solvent mixture of this character, it has been the practice to add the mixture in toto or incrementally to the waxy distillate as it is being chilled. In dewaxing operations, it is also known to use various filter aids and other agents in order to render the dewaxing and filtering operations more efficient.

The wax segregated from the hydrocarbon oil, usually termed, "slack wax," contains from about 10% to 40% of oil. The slack wax is refined usually by conventional sweating to produce "crude scale wax" in a manner to reduce the oil content to less than about 5% by weight. The slack wax may be distilled to obtain the desired boiling range prior to sweating, if desired. This "crude scale wax" generally has an oil content of about 2% to 3% by weight.

At the present time two major methods are employed for producing refined paraffin wax (0.2% or less oil content) from scale wax (2 to 3% oil content). The older of these, the sweating process, has been used for many years without important modifications. This process is suitable only for refining the waxes present in relatively low viscosity stocks. The newer deoiling process utilizes a suitable selective solvent which dissolves the oil and does not dissolve the wax. This method may be employed in crystallizing wax from both low and high viscosity stocks.

The older sweating method of deoiling consists of chilling the warm, liquid scale wax in pans until it is solid, then slowly raising the temperature, during which time the entrained oil drains away first, followed by lower melting point waxes as the temperature rises, leaving the desired product. In general, sweating is a rather inefficient method in the utilization of heat, time required to complete the cycle, and degree of fractionation ob-

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tained per cycle. Although sweating separates waxes by melting point, the major factor to be considered when sweating scale to refined wax is the oil content of the refined sweater product. If the oil present is over the amount allowed, the sweating is continued even though much wax of the desired melting point runs into intermediate cuts which must be recycled.

It has now been found that the addition of a small percentage of a lower boiling hydrocarbon to scale wax will greatly accelerate the removal of oil in the sweating operation and give a product of lower oil content without any loss in yield of wax or sweater capacity. Melting point separation is also improved. In commercial practice it is contemplated that a heavy naphtha or kerosene fraction be employed. This technique is applicable only where a subsequent stripping or distillation step is used, which will remove any traces of the added light oil from the final wax product and thus prevent an odor problem.

The lower wax oil content readily obtained by the practice of this invention results in improved color, stability and tensile strength, and eases the load on any treating step and on the bauxite filtration step employed for final purification of the wax. Furthermore, an additional 10-15% increase in yield and plant capacity is realized with the present technique as compared to conventional sweating when sweating to the same oil content of about 0.2%.

In the manufacture of refined paraffin wax from the wax-bearing petroleum distillates, conventional processing sequence calls for an initial dewaxing step to remove the bulk of the oil from the wax-bearing stream, deoiling the resultant wax to a suitable oil content, chemical treating the low oil content wax in order to stabilize the oil, and finally bauxite or clay filtering to improve color, odor and taste. One of the quality tests that the finished paraffin wax product is required to meet is the U. S. Pharmacopeia (U. S. P.) Acid Test.¹ This test, designated as A. S. T. M. D612-45, is a measure of purity and determines the relative amounts of carbonizable material in the wax. By spectroscopic studies it has been determined that the oil remaining in the wax contains the constituents responsible for the paraffin wax passing or not passing the U. S. Pharmacopeia (U. S. P.) Purity Test. Therefore, any treatment given the oil, per set, will be reflected in the quality of the finished refined wax. Further spectroscopic studies have indicated that the 2 and 3 ring aromatic constituents in the oil contained in the wax are responsible for the failure of the wax to pass the U. S. P. Acid Test for purity. In fact, optical density or absorptivity at 330 millimicrons wavelength, in the ultraviolet region, which is a reflection of condensed aromatic content, has been found to correlate with U. S. P. Acid Test in a straight line relationship described by the following formula:

U. S. P. Acid Test = 7650 times K_{330} , when K_{330} is the optical density in units of liters/gm.-cm.

Acid treating the wax, as expected, does improve the U. S. P. Acid Test on refined wax due to the acid reacting

¹ "Paraffin" is listed in the U. S. Pharmacopeia with specifications which include that it must pass the U. S. P. Acid Test. This test is applicable to paraffin wax to ascertain whether it conforms to the standard of quality required for pharmaceutical, food and drug uses.

The test procedure is as follows: 5 ml. of wax and 5 ml. of 94.7% (± 0.2) sulfuric acid are contacted at 157° F. for six minutes with intermittent mixing and settling intervals. The resultant color of the acid layer is compared with a standard color system. An arbitrarily chosen color standard of 5 or less is considered satisfactory. A color darker than 5 is considered not passing. If not passing the paraffin wax contains carbonizable material making it unfit for use in connection with cosmetics, foods and drugs. This is the same test formerly listed in the National Formulary and called the N. F. Acid Test.

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with the 2 and 3 ring aromatics. The reaction products are removed by neutralization and water washing. Deoiling and melting point separation by sweating will also reduce the 2 and 3 ring aromatics in the paraffin wax as the oil content is reduced. However, sweating alone will not reduce the aromatic content sufficiently low enough for the wax to pass the U. S. P. Acid Purity Test without a further chemical treatment unless the sweating is carried to an uneconomical extreme. The final percolation step through bauxite or clay also reduces the U. S. P. Acid Test indication but only approximately 50% under normal conditions. This alone is not sufficient for obtaining a paraffin wax of the desired purity as measured by passing the U. S. P. Similarly, the constituents responsible for the poor heat stability of certain waxes have been isolated in the aromatic portion of the oil content of the wax.

In accordance with the present invention, instead of acid treating the wax, which requires large quantities of chemicals, extraneous equipment, and also presents sludge disposal problems, the scale wax prior to sweating is blended with a small quantity of a low boiling oil such as a heavy naphtha fraction (boiling range 230-430° F.), a kerosene fraction (boiling range about 350-500° F.) or with constituents such as toluene and heptane. In general, the final boiling point of the low boiling oil added should be at least 100° F. and preferably 150° F. lower than the initial boiling point of the wax fraction being deoiled.

In general, wax fractions boil at atmospheric pressure in the range from about 600° F. to 950° F. However, these waxes are normally distilled at about 10 mm. pressure wherein the initial boiling point is about 370° F., 90% at about 550° F. and final boiling point at about 600° F. Thus, it is desirable that the final boiling point of the added oil not exceed about 500° F.

By this procedure the concentration of undesirable, reactive constituents in the oil contained in the wax is materially reduced. Furthermore, the viscosity of the oil is lowered, which improves the efficiency of sweating. In the subsequent sweating operations the bulk of the added low boiling oil together with the native oil is removed in the initial sweater cuts and the sweater yields for a given native oil content is materially improved.

The process of the present invention may be fully understood by reference to the drawing illustrating one embodiment of the same. Referring specifically to the drawing, a waxy crude oil is introduced into distillation zone 1 by means of feed line 2. Temperature and pressure conditions in zone 1 are adapted to remove overhead by means of lines 3 and 4 the low boiling hydrocarbon fractions. A waxy distillate fraction is removed as a side stream by means of line 5, while a residual oil is removed by means of line 6.

The waxy distillate flows through a chilling zone 7 which may comprise a plurality of chilling stages wherein the temperature of the waxy distillate is progressively reduced. A typical operation is to introduce the feed oil into an initial chilling stage at a temperature of about 130° F.; to introduce the feed oil into the second chilling stage at a temperature of about 90° F.; to introduce the feed oil to the third chilling stage at a temperature of about 60° F.; to introduce the feed oil to the fourth chilling stage at a temperature of about 25° F. and to chill the same in the fourth chilling stage to a temperature in the range from about -10 to +10° F. The operation of the respective chilling stages may be varied appreciably and either direct or indirect chilling means utilized. For purposes of illustration, it is assumed that a solvent mixture is used and that the wax-precipitant comprises methyl-ethyl ketone and that the aromatic solvent having a high solubility for oil comprises toluene. It is also assumed that 3 to 4 volumes of total solvent mixture is utilized per volume of waxy oil being dewaxed. The solvent mixture comprises 75% by volume of methyl-ethyl ketone and 25% by volume of toluene.

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The entire mixture comprising oily constituents, crystallized wax constituents, toluene and methyl-ethyl ketone, after chilling is held at the filtering temperature and passed to filtering zone 8 wherein the solid wax particles are segregated from the oily constituents by any suitable filtering or separation means. The filtering zone may comprise drum filters, plate and frame presses, centrifuges or suitable equivalent equipment for the separation of the precipitated waxy constituents from the oily constituents. The oil and a portion of the solvent are removed from zone 8 by means of line 9 and the wax cake washed with a wash solvent introduced into filtering zone 8 by means of line 10. Slack wax and solvent are removed from zone 8 by means of line 11 and passed to a distillation zone 12 wherein a separation is made between the wax and the solvent. It is to be understood that other means of separating the solvent from the wax may be utilized if desirable.

The wax substantially free of solvent is removed from separation zone 12 by means of line 13. The solvent mixture comprising methyl-ethyl ketone and toluene is removed overhead from zone 12 by means of line 14 and preferably recycled to the system. The oil-solvent mixture removed from filtering zone 8 by means of line 9 is introduced into a distillation zone wherein a separation is made between the oily constituents and the solvent mixture.

While the drawing illustrates a solvent dewaxing operation with respect to the production of the slack wax, it is to be understood that the waxy constituents may also be separated in a conventional plate-and-frame pressing operation. The slack wax may be further refined to crude scale wax in zone 15, which comprises a conventional sweating operation, or solvent deoiling operation, or the like. The oil removed from zone 15 by means of line 36 may preferably be recycled to zone 7. The scale wax is removed from zone 15 by means of line 35 and may be further refined by treatment with sulfuric acid or fuller's earth, bauxite or other absorbent materials, or by hydrogenation under mild treating conditions.

However, in accordance with the present invention, a low boiling oil is added to the scale wax by means of line 50. The mixture is passed to sweating zone 16 wherein the same is solidified by cooling and then exposed to progressively higher temperatures. By this procedure the quantity of 2 and 3 ring aromatics in the wax product is materially reduced. The bulk of these compounds is removed from the sweated wax by means of line 51. Wax fractions of desirable quality are removed from zone 16 by means of line 29.

The fraction removed by means of line 29 is then passed into a distillation zone 60 wherein temperature and pressure conditions are adjusted to remove overhead by means of line 61 the low boiling oil and to remove by means of lines 62 and 63 high quality wax fractions.

The invention is broadly concerned with the more complete removal of oily constituents from scale wax in order to improve the quality of the wax. This is secured by adding to the wax from 1 to 5, preferably from 2 to 3 volumes of a lower boiling oil per volume of oil remaining in the scale wax, and then subjecting the same to a sweating operation. Since the oily constituents of the scale wax amount to from 1% to 5% by volume thereof, the amount of lower boiling oil added is therefore broadly from 1% to 25% by volume based on the scale wax.

As pointed out heretofore, preferred oils to be added comprise individual hydrocarbons such as toluene and heptane. However, it is within the concept of the present process to employ heavy naphtha fractions and kerosene fractions. In general a spread of at least 100° F. should exist between the final boiling point of the oil added and the initial boiling point of the wax fraction to be deoiled.

The process of the present invention may be more fully understood by the following example illustrating the same.

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EXAMPLE

Operations were conducted wherein 4 parts of toluene and 4 parts of heptane (based on original oil) were added to a conventional wax and sweated. The results of these operations are illustrated in the following table:

Table

SWEATING OF CRUDE SCALE TO REFINED WAX WITH AND WITHOUT LOWER BOILING HYDROCARBON DILUTION

Dilution	None	4 Parts Toluene to 1 Part Original Oil	4 Parts Heptane to 1 Part Original Oil
Sweater Charge:			
Melting Point, ° F.....	133	125.5	128.5
Percent Oil, ASTM.....	3.5		
Color, TR.....	10 $\frac{1}{2}$		
U. V. Absorption (K ₂₅₀).....	0.0607		
Refined Wax (Sweated, stripped to remove diluent and Bauxite filtered 25 T/T):			
Yield Based on Sweater Charge, Wt. Percent.....	33.5	33.8	34.9
Yield Based on Wax Charge, Wt. Percent.....	33.5	38.6	39.8
Melting Point, ° F.....	138.5	140.5	140.5
Percent Oil, ASTM.....	0.23	0.08	0.05
Color, Saybolt.....	+30	+30	+30
U. V. Absorption (K ₂₅₀).....	0.0036	0.0018	0.0017
U. S. P. Acid Test ¹	29	14	13
Tensile Strength, p. s. i.....	300	400	450

¹ Calculated from K₂₅₀. A value of 5 or less is satisfactory. Chemical treatment (omitted in this workup) will improve the U. S. P. Acid Test. A milder treatment would suffice when using a diluent in sweating and in many cases could be omitted altogether.

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What is claimed is:

1. Process for the production of a high quality paraffin wax of improved stability, which comprises segregating a molten scale wax comprising about 1-5% by volume of oil, adding to said molten scale wax a hydrocarbon oil having a final boiling point at least 100° less than the initial boiling point of said scale wax in an amount of from about 1% to about 25% by volume of said scale wax, thereafter solidifying the resultant mixture of said molten wax and said hydrocarbon oil and subsequently sweating the solidified mixture to produce a wax of reduced oil content, and thereafter distilling said wax of reduced oil content to completely remove said lower boiling hydrocarbon oil.

2. Process according to claim 1 wherein said mixture of said wax and said hydrocarbon oil is sweated to an oil content of less than 0.2% by volume of oil.

3. Process according to claim 1 wherein said mixture of said hydrocarbon oil and said wax is sweated to an oil content of less than about 0.1% by volume of oil.

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