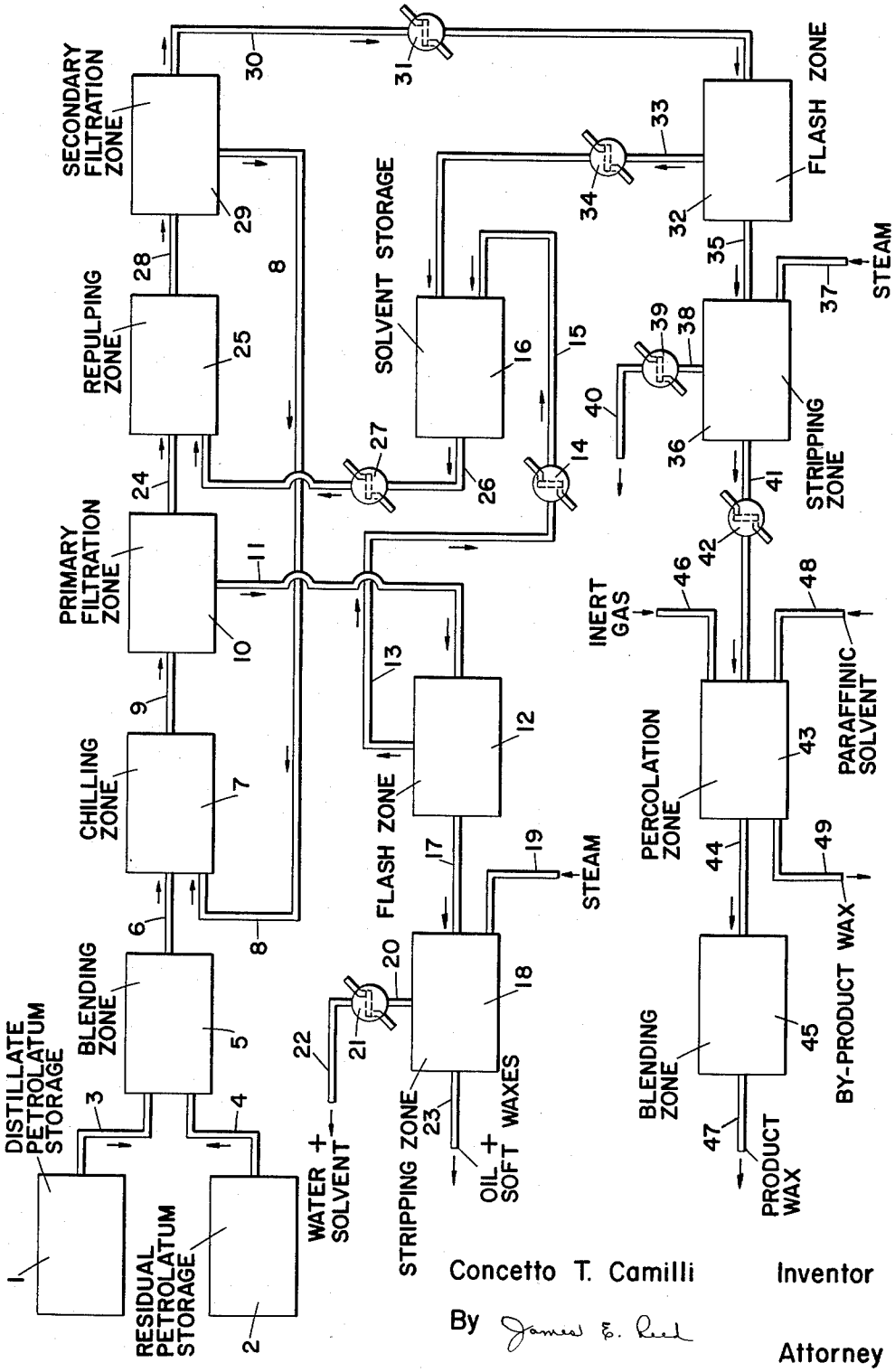
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MICROCRYSTALLINE WAX

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MICROCRYSTALLINE WAX

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The present invention relates to petroleum waxes and more particularly relates to an improved microcrystalline wax having extremely high sealing and laminating strength and other outstanding properties and to a process for the preparation of such a wax from petrolatums derived from mixed base petroleum crude oils.

Waxes are present to some extent in the high boiling distillate and residual fractions of most petroleum crude oils but are found primarily in mixed base and paraffinic crudes. An important step in the refining of such crudes comprises dewaxing the oil in order to improve its low temperature properties and permit recovery of the wax. Normally this is accomplished by first topping the crude in an atmospheric pipe still to remove the naphtha, kerosine and lighter fractions which are essentially free of wax. The topped crude is then generally fed into a vacuum pipe still and the waxy oil is fractionated into an overhead or "paraffin" distillate, a lubricating oil distillate, and a residual fraction. The proportions of these fractions may vary considerably depending upon the particular crude oil being handled but it is general practice to produce these three fractions.

The fractions thus produced are generally dewaxed separately by chilling the oil in the presence of a solvent to crystallize the wax and then separating the wax and oil by filtration or centrifugation. The solvent aids in formation of the wax crystals and reduces the oil viscosity so that rapid separation is possible. Suitable solvents for this purpose include liquefied normally gaseous hydrocarbons such as propane, butane, hexane and the like and aliphatic ketones containing from 3 to 6 carbon atoms, such as methyl ethyl ketone, diethyl ketone, methyl propyl ketone, ethyl propyl ketone, and methyl isobutyl ketone. The lower molecular weight ketones may be used in conjunction with an aromatic solvent such as benzene or toluene. A particularly effective solvent comprises about 50 to 75 volume percent methyl ethyl ketone and about 25 to 50 volume percent of toluene. Following chilling of the oil in the presence of such a solvent, the wax crystals formed are separated from the oil-solvent mixture by centrifugation or by means of rotary filters, plate and frame filter presses or the like. Such dewaxing processes are widely used throughout the petroleum industry and will be familiar to those skilled in the art.

The waxes recovered by dewaxing processes such as those described above fall into two general classes which differ according to the wax crystalline structure. Dewaxing of the overhead fraction from the vacuum still, the

"paraffin" distillate, results in the recovery of a paraffin type wax which is characterized by large well-defined crystals. As recovered from the dewaxing step, it generally contains from about 3 to about 40% oil and is referred to as "slack" wax. Its oil content can readily be reduced to 0.5% or less by sweating or recrystallization to produce a high quality paraffin wax.

Dewaxing of the lubricating oil distillate and residual fractions results in the recovery of petrolatums characterized in that the wax crystals therein are so small that such waxes were at one time thought to be amorphous. These petrolatums contain from about 5 to about 40% or more oil, depending upon the particular dewaxing conditions employed. Such petrolatums may be deoiled to produce microcrystalline waxes melting between about 145° and about 190° F. These waxes are widely used for coating and laminating purposes in the manufacture of paper cartons, food containers, aluminum foil, waxed paper and many other products and are often incorporated in polishes, electrical insulating compositions, explosives and other formulations. It is with waxes of this general type that the present invention is concerned.

In the past, considerable difficulty has been encountered in producing microcrystalline waxes suitable both for coating and for laminating papers and foils. Although high quality microcrystalline waxes useful for these purposes can be derived from paraffinic crude oils such as those found in Pennsylvania and West Virginia, the supply of such crudes is very limited and most petroleum refiners are forced to utilize mixed base crude oils, Panhandle, East Texas and Mid-Continent crudes for example, for their production of waxes. Microcrystalline waxes produced from such mixed base crudes heretofore have either had laminating and sealing strengths greatly inferior to those produced from paraffinic stocks or else have had very bad staining characteristics and therefore have not been suited for coating and laminating purposes. Substantially non-staining microcrystalline waxes derived from mixed base crude oils which are now marketed commercially have laminating strengths ranging up to about 130 grams per inch and sealing strengths ranging from about 20 to about 50 grams per inch, as shown in the following table:

Properties of commercial microcrystalline waxes from mixed base crude sources

Wax	Laminating Strength, gms./in.	Sealing Strength, gms./in.
Commercial Wax A	125	24
Commercial Wax B	130	55
Commercial Wax C	120	44

Such waxes leave much to be desired.

The present invention provides a new and improved microcrystalline wax derived from mixed base petroleum crude oil which is essentially non-staining and has a laminating strength of at least 200 grams per inch and a sealing strength of at least 200 grams per inch. These

properties are unique in microcrystalline waxes produced from mixed base crude oils. Wax having such properties are adapted for use in both coating and laminating applications and thus the invention provides a superior dual-purpose microcrystalline wax.

In accordance with the invention, it has now been found that microcrystalline waxes of greatly improved properties can be produced from mixed base crude oils by deoiling a mixture of residual and distillate petrolatums derived from a mixed base crude and blended in critical proportions. The proportion of the total wax in the blend of petrolatums which is recovered during the deoiling step profoundly affects the properties of the microcrystalline wax product and must be controlled within critical limits if a product having the improved properties of the waxes of the invention is to be obtained.

The mixture of petrolatums which is deoiled in accordance with the invention to produce microcrystalline waxes of superior properties is a mixture of distillate and residual petrolatums containing from 21 to 28 wt. percent, based upon dry wax content, of a microcrystalline wax which is volatile at a temperature of about 650° F. under 1 millimeter of mercury pressure and from 72 to 79 wt. percent, based upon dry wax content, of microcrystalline wax which is nonvolatile under those conditions. Dry wax content of a petrolatum for the purpose of preparing such a blend is defined as being 100 minus the oil content of the petrolatum as determined from the solubility of the petrolatum in secondary butyl alcohol at a temperature of 0° F. It is the wax content determined in this manner which will be referred to hereafter. This method of determining petrolatum dry wax content is widely used throughout the petroleum industry and will be familiar to those skilled in the art.

The distillate petrolatum employed in the mixture of petrolatums is normally produced as a by-product in the dewaxing of mixed base light motor oil distillates boiling at temperatures equivalent to atmospheric pressure boiling points between about 650° F. and about 1100° F. or higher; while the residual petrolatum is the source of conventional microcrystalline waxes derived from mixed base crude oils. The amount of each of these petrolatums which must be blended to produce a mixture containing from 21 to 28 wt. percent of microcrystalline wax which is volatile at temperatures below about 650° F. at 1 mm. of Hg and from 72 to 79 wt. percent of microcrystalline wax which is nonvolatile at temperatures below about 650° F. under 1 mm. of Hg will, of course, depend upon the boiling ranges of the particular distillate and residual petrolatum used. If, for example, the residual petrolatum has an initial boiling point below 650° F. at 1 mm. of Hg, it will probably contain microcrystalline wax which is volatile below 650° F. at 1 mm. of Hg and it will be necessary to take that wax into account in determining the amount of distillate petrolatum to be used in preparing the blend. If, on the other hand, the residual petrolatum has an initial boiling point above 650° F. at 1 mm. of Hg, it will contain no microcrystalline wax which is volatile below 650° F. at 1 mm. of Hg and all of the wax boiling below that temperature will have to be provided by the distillate petrolatum. The amount of dry microcrystalline wax boiling above and below 650° F. at 1 mm. of Hg in any petrolatum may be readily determined by dissolving the petrolatum in secondary butyl alcohol at a temperature of 0° F., separating the undissolved wax from the solvent and oil, and then vacuum distilling the wax in accordance with the procedure set forth in ASTM Method D–1160. Those skilled in the art will be familiar with this procedure. In general it is preferred to employ residual petrolatums boiling wholly above 650° F. at 1 millimeter of mercury in carrying out the process of the invention.

A mixture containing microcrystalline waxes boiling above and below 650° F. at 1 mm. of Hg in the necessary critical ratio cannot normally be produced by merely deoiling a residual petrolatum having a low initial boiling point and hence it is essential that a distillate and a residual petrolatum first be blended and that the blend then be deoiled. Separate deoiling of the two petrolatums followed by blending of the recovered waxes is not feasible. The wax obtained by separate deoiling and subsequent blending contains constituents different from those of the wax obtained by deoiling of the blended petrolatums and does not possess the improved properties of the wax of the invention, even though the two waxes may have the same boiling range. The preparation and subsequent deoiling of a blend of a distillate and a residual petrolatum containing from 21 to 28 wt. percent, on a dry wax basis, of microcrystalline wax volatile at 650° F. and 1.0 millimeter of mercury and from 72 to 79 wt. percent, on a dry wax basis, of microcrystalline wax nonvolatile at 650° F. and 1 millimeter of mercury is thus essential in preparing the improved wax of the invention.

The deoiling of the critical mixture of petrolatums described above in order to produce the improved microcrystalline wax of the invention is a critical step in the process and must be carefully controlled if a product of the requisite quality is to be attained. It has been found that this deoiling step must be carried out so that from about 60 to about 70 weight percent of the total dry wax in the mixture, as determined on the basis of the solubility of the mixture in secondary butyl alcohol at 0° F., is recovered as deoiled wax. This use of a dry wax basis in determining yields compensates for variations in the oil contents of the blended petrolatums.

The amount of wax recovered during the deoiling step of the process may be varied by varying the deoiling temperature, the deoiling solvent, or other variables. A wide variety of deoiling solvents familiar to those skilled in the art may be employed in the deoiling step and with each of these the requisite yield may be obtained by suitably controlling the deoiling temperature. Because the yield is influenced to some extent by factors such as the deoiling equipment employed and the degree to which equilibrium conditions are approached during deoiling, it is generally impractical to attempt to predicate the temperature which will be required to produce the necessary yield with a given solvent. It has been found, for example, that due to a difference in the degree of equilibrium attained, greater yields are obtained with a given solvent in laboratory deoiling than can be obtained with the same solvent at the same temperature in plant scale operation. It is therefore necessary, when using this solvent, to deoil at a lower temperature in the plant than in the laboratory in order to control the yield of deoiled wax between about 60 and about 70 wt. percent. Similar variations have been observed with many other solvents. By basing the deoiling upon yield of deoiled wax as a percentage of total wax content as determined from solubility in secondary butyl alcohol at 0° F., the effect of such variations, as well as variations in petrolatum oil contents, can be eliminated and a product wax of the requisite quality can be assured. The conditions necessary to obtain a yield of deoiled wax within the critical range with any particular solvent and equipment can be readily determined by simple experiments wherein the deoiling temperature is varied and the yield of deoiled wax obtained is observed. With most deoiling

solvents it has been found that the temperatures required for the critical yields will fall between about 20° F. and about 60° F.

A wide variety of solvents conventionally employed in wax deoiling processes are suitable for use in the process of the invention. Such solvents include, for example, acetone, methyl ethyl ketone, secondary butyl acetate, isopropyl acetate, amyl acetate, isopropyl propionate, isopropyl butyrate, hexyl acetate, benzol-ketone mixtures, chlorinated hydrocarbons, hexane, heptane, liquefied propane and the like. A preferred class of solvents is that comprising mixtures of a low molecular weight aliphatic ketone containing from about 3 to about 6 carbon atoms per molecule, methyl ethyl ketone, diethyl ketone, methyl isopropyl ketone, ethyl isopropyl ketone, and the like, with an aromatic hydrocarbon containing from about 6 to 10 carbon atoms per molecule, such as benzene, toluene, xylene and the like. Mixtures of from 65 to 70 vol. percent of methyl ethyl ketone and from 30 to 35 vol. percent of toluene have been found to be particularly effective in the process of the invention and are therefore preferred. As pointed out above, the deoiling temperature to be used with each of these solvents in order to obtain the necessary yield of deoiled wax can readily be determined.

It is preferred to carry out the deoiling step of the process of the invention in two separate stages, the wax being initially separated from a blend of petrolatums and solvent by filtration or centrifugation, being repuddled with fresh solvent, and again being filtered or centrifuged from solution. Filtration is the preferred separation method. In such a two stage system, the filtrate from the second filtration consists primarily of solvent and contains very little oil. This filtrate may be used as the solvent for the initial filtration, thereby permitting more efficient solvent utilization than can otherwise be attained. The quantity of solvent employed in the process may be varied rather widely depending upon the particular solvent and deoiling conditions used. In general solvent-to-petrolatum ratios between about 4 to 1 and about 14 to 1 may be utilized. Ratios of solvent to petrolatum between about 8 to 1 and about 10 to 1 have been found particularly effective and are preferred. In a single stage process the solvent to petrolatum ratio will, of course, normally be somewhat higher than in a two stage system. Use of a two stage deoiling step is not essential to the process of the invention and in some cases it may be advantageous to carry out the filtration in a single step despite the benefits derived from the two stage system.

In mose cases it will be desired to improve the color of the microcrystalline wax prepared by deoiling the critical blend of petrolatum by means of a percolation step designed to remove color bodies from the wax. If such a step is to be employed, the wax may be percolated under controlled conditions through either bauxite or a clay adsorbent. Although bauxite is the conventional adsorbent for improving the color of microcrystalline waxes, it has been found that clay adsorbents are generally somewhat more effective than bauxite in the process of this invention, particularly where the wax to be decolorized is one recovered in the lower part of the 60 to 70% yield range, and therefore the use of a clay adsorbent is preferred. Suitable clays include those of the fuller's earth type such as Attapulgus, Floridex, Standard Utah and the like.

The ratio of wax to adsorbent employed in the percolation step should preferably be not more than about 3 to 1. Somewhat lower ratios are often advantageous. Wax to adsorbent ratios above about 3 to 1 generally do not result in a wax of satisfactory odor and color. The temperature during the percolation step should be at least 40° F. above the melting point of the wax in order to assure complete contact between the wax and adsorbent and to avoid unnecessary holdup of wax in the percolation zone. A percolation temperature of from about 200° to about 300° F. has been found to be particularly effective and is therefore preferred.

The yield of finished wax obtained from the process of the invention and the strength of the wax product can be improved where percolation is employed by purging wax retained by the adsorbent with an inert gas such as carbon dioxide, nitrogen or the like and adding the purged wax to the wax recovered during the percolation step. From about 5 to about 15% of the retained wax can be displaced by the inert gas and it has been found that addition of this wax improves the sealing and laminating strength of the final finished wax product. The wax remaining on the adsorbent after the purging can be recovered by washing the adsorbent with normal heptane or a similar paraffinic containing from about 3 to 30 carbon atoms per molecule. Naphthas consisting predominantly of paraffinic hydrocarbons may also be employed. Such solvents remove the wax from the adsorbent without taking off color bodies and hence the wax thus recovered by solvent washing constitutes a valuable by-product which may be used in a variety of microcrystalline wax applications wherein the superior properties of the product wax of the invention are not required. Wax recovered in this manner may also be recycled to the deoiling step if desired.

In some cases it may be preferred to hydrotreat the wax to improve its color, rather than employing a percolation step. Wax hydrotreating is a well known process and need not be described in detail for purposes of this invention.

The exact nature and objects of the invention can be more fully understood by reference to the following detailed description of a preferred process for producing the improved microcrystalline wax of the invention and to the attached drawing illustrating that process.

Referring now to the drawing, a distillate petrolatum derived from the solvent dewaxing of a light motor oil distillate boiling between about 650° and about 1100° F. and stored in storage zone **1** and a residual petrolatum derived from the solvent dewaxing of a petroleum residua boiling wholly above about 1100° F. and stored in zone **2** are passed through lines **3** and **4** respectively into blending zone **5**. The two petrolatums are introduced into the blending zone at rates to produce a blend containing from 21 to 28%, based upon dry wax content, of microcrystalline wax volatile at 650° F. under 1 millimeter of mercury and from 72 to 79%, based upon dry wax content, of wax which is nonvolatile under those conditions. Since the petrolatums have rather high melting points, it will usually be necessary to provide the storage zones, the blending zone and the interconnecting lines with steam jackets or the like to maintain the petrolatums in the liquid state. The petrolatums are preferably agitated during the blending step in order to assure uniform mixing. The blend thus produced is passed through line **6** into chilling zone **7**. A solvent consisting of a mixture of from about 65 to 70% methyl ethyl ketone and about 30 to about 35% toluene is introduced through line **8** and mixed with the blend of petrolatums introduced into the chilling zone. The amount of solvent added should be sufficient to give a solvent-to-wax ratio of from about 7 to 1 to about 14 to 1. It is particularly preferred to employ a solvent-to-wax ratio of about 9 to 1. The solvent employed is preferably essentially free of water. It has been found that the petrolatum feeds sometimes contain sufficient water to cause a gradual accumulation of water in the solvent employed in the process. In such cases

the solvent may be dried by passing it over a suitable adsorbent or by other conventional methods. Molecular sieve adsorbents having 4 A. pore diameters are particularly effective for this purpose because they remove the water without adsorbing the solvent itself. Such adsorbents are now well known in the art and need not be described in detail here. Other selective adsorbents may, of course, also be used. Chilling zone 7 is of conventional design and is provided with coils through which a suitable refrigerant may be circulated. The solution thus introduced into the chilling zone is chilled to a temperature of 45° F. and is then introduced through line 9 into primary filtration zone 10 where the wax crystals precipitated by the chilling step are filtered from solution.

Filtrate consisting of solvent, oil and soft waxes is withdrawn from the primary filtration zone 10 through line 11 and introduced into flash zone 12. In the flash zone the oil-wax-solvent solution is heated to a temperature of about 300° F. and the solvent is flashed overhead through line 13 to condenser 14. The condensed solvent then passes through line 15 into solvent storage zone 16. The remaining oil and soft wax containing small amounts of solvent are removed as a bottoms product from flash zone 12 through line 17 and passed to stripping zone 18. Steam introduced into the stripper through line 19 strips the residual solvent from the oil and the steam and solvent are taken overhead through line 20 and condensed in condenser 21. This condensate is withdrawn through line 22. Water and solvent in the condensate may be separated and the solvent recycled to solvent storage if desired. Oil containing soft wax flows from the bottom of the stripping zone through line 23 and may be sent to storage or further processed. This oil will normally have too high a pour point to permit its direct use as a lubricant and will most frequently be employed as a cracking feed stock. In some cases, however, it may be desirable to use the oil as a crystal modifier or dewaxing aid in the dewaxing of other stocks.

The wax separated from the solution of solvent and oil in the primary filtration zone is removed therefrom by means of line 24 and introduced into repulping or repuddling zone 25. Fresh solvent is introduced into the repulping zone from solvent storage zone 16 through line 26 and heat exchanger 27 and mixed with the wax. The fresh solvent is introduced at a temperature of about 40° F. The solvent-to-wax ratio in the repulping zone may range from about 2 to 1 to about 6 to 1. A ratio of about 4 to 1 has been found particularly effective and is preferred. A slurry of wax crystals and solvent is produced in the repulping zone 25 and is passed through line 28 to secondary filtration zone 29 where the wax crystals are separated from the solvent. Solvent recovered as filtrate is recycled through line 8 to chilling zone 7. The wax filtered from the solution is transferred through line 30 and heat exchanger 31, where it is melted, into flash zone 32. Sufficient heat is provided in the flash zone to vaporize most of the solvent contained therein. The vaporized solvent is withdrawn overhead through line 33, condensed in condenser 34 and passed to solvent storage zone 16.

Wax from which the major part of the solvent has been removed in flash zone 32 is introduced through line 35 into stripping zone 36. The remaining solvent is stripped from the molten wax by means of steam introduced into the stripping zone through line 37. Steam and solvent are taken off overhead through line 38 to condenser 39. Water and trace amounts of solvent are withdrawn therefrom through line 40. These may be separated and the solvent may be recycled to solvent storage zone 16 if desired. The molten wax is withdrawn from the stripping zone via line 41 and passed through heat exchanger 42 where its temperature is adjusted to a point about 40° or more above the melting point of the wax, preferably to a temperature between about 175° and 300° F. The molten wax is then introduced into wax percolation zone 43. A single percolation zone is shown in the drawing but it will be understood that normally a plurality of suitably manifolded zones will be employed to permit continuous wax percolation. The percolation zone consists essentially of a bed of finely divided Attapulgus clay or a similar clay. Wax percolates through the bed of clay, passes through line 44, and is collected in blending zone 45. When the clay no longer decolorizes the wax to an adequate degree, the flow of molten wax to the percolation zone is discontinued. As mentioned heretofore, normally a second percolation zone will be placed on stream at this point and percolation will be continued therein. After the input of molten wax to the percolation zone is stopped, the zone is purged by introducing nitrogen or a similar inert gas into the zone through line 46. About 5 to 15% of the wax can be displaced from the adsorbent clay by the inert gas and is withdrawn through line 44 into blending zone 45. In the blending zone the percolated wax and the purged wax are mixed to produce the microcrystalline wax product. This product is withdrawn from the system through line 47.

When no more wax can be displaced from percolation zone 43 by the inert gas, purging is discontinued and the bed of clay is washed with normal heptane or a similar paraffinic hydrocarbon containing from about 3 to about 30 carbon atoms per molecule introduced through line 48. This solvent removes most of the remaining wax from the percolation zone, leaving color bodies behind. This wax is discharged through line 49 as a by-product wax. This wax may be employed in a number of applications wherein rigid wax quality is not required. The percolation zone is then regenerated by burning, by washing with dewaxing solvent, or by other conventional means adopted to remove the color bodies remaining on the adsorbent after it has been washed with the paraffinic solvent. Since the spent adsorbent contains only a small part of the wax originally adsorbed thereon, wax losses during regeneration are low and overall wax yields are high.

The wax withdrawn from blending zone 45 through line 47 as microcrystalline product wax will normally have an oil content of less than about 1.5% and will be nonstaining under the standard test carried out at 110° F. after 16 hours. This wax will have a laminating strength in excess of about 200 grams per inch and a sealing strength of at least 200 grams per inch. It is thus superior to conventional microcrystalline waxes produced from mixed base crude oils and may be employed in a variety of applications where excellent laminating and coating properties are required.

The process of the invention may be further understood by reference to the following examples.

EXAMPLE 1

A distillate petrolatum and a residual petrolatum produced by the solvent dewaxing of a Panhandle light motor oil petroleum fraction boiling between about 680° F. and about 1050° F. and a mixed base petroleum residuum having an initial boiling point of about 820° F. respectively were blended to produce a blend containing 24.5 wt. percent, on a dry wax basis as determined from solubility in secondary butyl alcohol at 0° F., of microcrystalline wax volatile at 650° F. under a pressure of 1 mm. of mercury and 75.5 wt. percent, on a dry wax basis, of microcrystalline wax which was nonvolatile at 650° F. and 1 mm. of mercury. The residual petrolatum contained about 3%, on a dry wax basis, of wax volatile at 650° F. and 1 mm. of mercury and hence it was necessary to use 22.2 wt. percent of the distillate-petrolatum and 77.8 wt. percent of the residual petrolatum. Properties of the individual petrolatums and of the blend were as follows:

TABLE I

Properties of petrolatums and blend

Sample	Distillate Petrolatum	Residual Petrolatum	Blend of 22.2% Distillate Petrolatum and 77.8% Residual Petrolatum
Gravity, API	35.4	30.0	
Kinematic Viscosity, cs. @ 210° F.	7.26	24.60	19.58.
Percent Solubility in Methyl Ethyl Ketone:			
70° F.	59.5	41.2	49.4.
90° F.	77.1	56.4	69.7.
Percent Solubility in 75% Methyl Ethyl Ketone/25% Toluene at 50° F.	55.4	54.6	53.7.
Percent Solubility in Secondary Butyl Alcohol at 0° F.	23.3	27.4	26.5.
Distillation @ 1.0 mm. Hg:			
Initial Boiling Point	320° F.	416° F.	380° F.
5% Off	402° F.	544° F.	466° F.
10% Off	437° F.	576° F.	489° F.
20% Off	474° F.	592° F. (14% Off)	534° F.
30% Off	492° F.	Cracked	590° F.
40% Off	508° F.		594° F. (31% Off).
50% Off	522° F.		
60% Off	533° F.		
70% Off	541° F.		
80% Off	560° F.		
90% Off	576° F.		
95% Off	579° F.		
	589° F. (98% Off)		

The blend of petrolatums thus produced was chilled to a temperature of 45° F. in the presence of nine volumes of a solvent consisting of 70% methyl ethyl ketone and 30% toluene. The chilled slurry was filtered at the 45° F. temperature and the wax cake recovered was repuddled by the addition of four volumes of the cold methyl ethyl ketone/toluene solvent. The resulting mixture was then refiltered at about 40° F. The yield of wax recovered in the deoiling step was 63.9%, based upon the total dry wax content of the blend as determined from secondary butyl alcohol solubility at 0° F.

The deoiled wax thus recovered was then melted and solvent was flashed off, after which the melted wax was stripped at a temperature of 450° F. The stripped product was percolated through about 1/3 volumes of Attapulgas clay at a temperature of 275° F. The percolation zone was purged at 180° F. with nitrogen and purged wax was recovered. A yield of wax amounting to 65% of the feed to the percolation step was recovered by percolation. An additional 15 wt. percent of wax was recovered by the purging and blended with the product to give a total finished wax yield of 80 wt. percent based on percolator feed. A yield of about 37% of finished microcrystalline wax, based upon the original blend of petrolatums, was recovered.

EXAMPLE 2

The properties of the microcrystalline wax produced as described in the preceding example were determined. For comparison's sake, the same properties of samples of three leading commercial mixed base microcrystalline waxes purchased upon the open market were also determined. The results of these determinations are shown in Table II below.

From the above table it can be seen that the wax produced as described in Example 1 had properties manifestly superior to those of the commercial microcrystalline waxes. Stain, sealing strength and laminating strength are particularly important properties and largely determine the suitability of a wax for laminating and coating purposes. Since sealing strength and blocking point are particularly important in wax coating applications, these properties were determined for coating blends containing 48.5 wt. percent microcrystalline wax, 48.5% of a 135° F. melting paraffin wax and 3% of polyethylene. Use of microcrystalline waxes in such coating blends is conventional practice. The "paper tear" designation for the sealing strength of the coating blend containing wax of the invention indicates that the paper strip used in the test tore before the seal failed. This means that this coating blend had a sealing strength well in excess of 200 grams per inch, at least 4 times that of the coating blend containing the best commercial wax and about 10 times that of the blend containing the poorest commercial wax. Similarly, the laminating strength of the wax of the invention was nearly twice that of any of the other products. Such properties are outstanding and unique in a microcrystalline wax derived from mixed base petroleum and clearly indicate the surprising superiority of the waxes of the invention.

EXAMPLE 3

Samples of the distillate petrolatum and the residual petrolatum described in Example 1 were individually deoiled and finished by percolating the deoiled wax through 4 volumes of Attapulgus clay at 275° F., purging the percolation zone with nitrogen at 180° F., and adding the purged wax to the percolated wax. The residual and

TABLE II

Properties of finished microcrystalline waxes

Wax	Oil Content, Wt. Percent	Stain, 16 hrs. @ 110° F.[1]	Laminating Strength, gm./in.	Sealing Strength, gm./in.[2]	Blocking Point, ° F.[2]	MEK Solubility, Percent		Kinematic Viscosity @ 210° F.	Melting Point, ° F.	Refractive Index @ 100° C.
						70° F.	90° F.			
Microcrystalline Wax Produced as Described in Example 1	1.07	0	235	Paper Tear	112.5	9.5	28.5	16.3	145.0	1.4409
Commercial Microcrystalline Wax A	4.23	1+	125	24	128	10.8	26.2	17.73	169.0	1.4427
Commercial Microcrystalline Wax B	2.09	0	130	55	117	8.1	21.9	13.98	151.0	1.4513
Commercial Microcrystalline Wax C	2.01	1−	120	44	102	--------	29.2	15.26	136.8	----------

[1] 0–4 debit scale.

[2] Measured for a coating blend of 48.5 wt. percent the microcrystalline wax with 48.5% of 135° M.P. paraffin wax+3% 12,000 M.W. polyethylene.

distillate microcrystalline waxes thus prepared were then blended to produce blends containing 70 and 80 wt. percent of the residual wax and 30 and 20 wt. percent of the distillate wax, respectively. Both of these blends contained between 21 and 28% of wax which was volatile at 650° F. under a pressure of 1 millimeter of mercury. The laminating strengths, sealing strengths and staining properties of the blends were determined and are shown in Table III below.

TABLE III

Properties of microcrystalline wax blends

Blend	Finished Distillate Microcrystalline Wax Content, Wt. Percent	Finished Residual Microcrystalline Wax Content, Wt. Percent	Laminating Strength, gms./in.	Sealing Strength, gms./in.	Stain, 16 Hrs. @ 110° F.
A	20	80	240	110	Trace
B	30	70	235	165	0

From the above table it can be seen that neither of the wax blends prepared by separately deoiling the distillate and residual petrolatums, finishing the waxes and then blending them possessed the improved properties of the waxes of the invention. The sealing strengths were unacceptably low despite the fact that both blends contained above the same proportions of wax boiling above and below 650° F. at 1 millimeter of mercury as do the waxes of the invention. This difference in properties is due to the fact that the distillate and residual wax constituents in the blend influence the solubility of one another during deoiling and hence the material recovered is entirely different from that recovered when separate deoiling steps are employed.

EXAMPLE 4

In order to demonstrate the critical necessity for employing a blend containing from 21 to 28 wt. percent, based upon dry wax content, of microcrystalline wax volatile at 650° F. under 1 millimeter of mercury and from 72 to 79 wt. percent, based upon dry wax content, of microcrystalline wax not volatile at 650° F. under 1 millimeter of mercury in order to produce the improved waxes of the invention, a series of blends of distillate and residual petrolatums similar to those described in Example 1 were prepared. The amount of wax volatile above and below 650° F. at 1 millimeter of mercury was determined for each blend. These blends were then individually deoiled at 50° F. in the presence of a methyl ethyl ketone-toluene solvent and then clay percolated in the manner set forth in Example 1. The properties of the resulting microcrystalline waxes were determined. These are shown in Table IV.

TABLE IV

Effect of amount of volatile wax in blended petrolatums upon properties of finished microcrystalline waxes [1]

Wax	Blended Petrolatums		Stain, 16 Hrs @ 110° F.	Laminating Strength, gms./in.	Sealing Strength, gms./in.
	Wt. Percent Volatile @ 650° F. and 1 mm. Hg [2]	Wt. Percent Nonvolatile @ 650° F. and 1 mm. Hg [2]			
A	31.7	68.3		112	
B	24.5	75.5	0	235	Paper Tear
C	20.2	79.8	0	170	220

[1] All waxes contained wax purged at 180° F. and had oil contents of about 1.0%.
[2] Dry wax basis.

From the above Table IV it can be seen that only the wax produced from the blend containing 24.5 dry wt. percent of wax volatile at 650° F. and 1 mm. of Hg and 75.5 dry wt. percent of wax nonvolatile under those conditions had the outstanding properties of the waxes of the invention. Waxes produced from petrolatum blends containing 20.2 dry wt. percent and 31.7 dry wt. percent of the volatile wax were inferior from the standpoint of laminating strength. Similar experiments carried out at other conditions which produced essentially the same yield of wax during the deoiling step also showed that only blends containing from 21 to 28 dry wt. percent of wax volatile at 650° F. and 1 mm. Hg and from 72 to 79 dry wt. percent of wax nonvolatile at 650° F. and 1 mm. Hg resulted in waxes having the properties of the waxes of the invention. It therefore appears that blending of the distillate and residual petrolatums to produce a blend containing from 21 to 28 dry wt. percent of wax volatile at 650° F. and 1 mm. of Hg and from 72 to 79 dry wt. percent of wax nonvolatile under those conditions is a critical requirement for preparing the improved microcrystalline waxes of the invention.

EXAMPLE 5

The effect of the deoiling yield upon the properties of microcrystalline waxes prepared from the petrolatum blends shown to be critical in the previous example is demonstrated by data obtained in a series of tests wherein samples of blends of distillate petrolatum and residual petrolatum containing between 21 and 28% of wax volatile at 650° F. and 1 mm. of Hg were deoiled under conditions such that the yields of deoiled wax ranged from 45.6 to 82.5 wt. percent, based upon total wax content of the blends as determined from secondary butyl alcohol solubility at 0° F. The waxes thus obtained were tested for their sealing strengths, laminating strengths and staining properties, with the following results.

TABLE V

Effect of deoiling yield on finished microcrystalline wax properties

Blend	Oil Content of Blend, Wt. Percent Based on SBA solubility @ °F.	Total Wax Content of Blend	Deoiled Wax Yield Wt. Percent Based On Blend	Deoiled Wax Yield Wt. Percent Based on Wax Content of Blend	Stain, 16 Hrs. @ 110 ° F.	Laminating Strength, gms./in.	Sealing Strength gms./in.
A	36.4	63.6	29.0	45.6	0	105	270.
B	36.4	63.6	33.0	51.9	0	170	250.
C	36.8	63.2	34.0	53.8	0	160	250.
D	36.8	63.2	34.4	54.5	0	150	90.
E	36.8	63.2	35.2	55.7	0	170	220.
F	36.8	63.2	37.7	59.7		112	
G	36.4	63.6	39.0	61.3	1−	215	200.
H	36.8	63.2	39.6	62.7	1−	215	300.
I	30.2	69.8	44.5	63.6	0	210	Paper Tear.
J	26.5	73.5	47.0	63.9	0	235	Do.
K	26.5	73.5	48.0	65.3	0	260	Do.
L	26.5	73.5	48.4	65.8	0	270	
M	32.3	67.7	44.8	66.2	0	200	Paper Tear.
N	32.3	67.7	48.5	71.6	1+	285	145.
O	32.1	67.9	56.0	82.5	3	215	

The data of Table V clearly demonstrate that the deoiling yield has a critical effect upon the properties of microcrystalline wax produced from blends of distillate and residual petrolatums. The waxes recovered in yields of from about 60 to about 70 wt. per cent, based upon total dry wax contents of the petrolatum blends as determined by their solubility in secondary butyl alcohol at 0° F., were all essentially non-staining and had sealing and laminating strengths in excess of 200 grams per inch. The waxes produced by deoiling the blended petrolatums to recover yields greater than about 70% or less than about 60% were unsatisfactory.

EXAMPLE 6

In further tests, samples of unfinished wax produced by deoiling a blend of distillate and residual petrolatums as described in Example 1 were separately percolated through equal volumes of Attapulgus clay and bauxite at temperatures of 210° F. The percolation column was purged with nitrogen and the purged wax was added to the percolated wax in each case. The color of the finished waxes on the Tag-Robinson Scale and the laminating strengths of the waxes before and after nitrogen purging were determined. These are set forth in Table VI.

TABLE VI

Effect of adsorbent and purging on properties of finished microcrystalline wax

Wax	Adsorbent	Color, TR	Laminating Strength of Percolated Wax, gms./in.	Laminating Strength of Percolated Wax + Purged Wax, gms./in.
A	Attapulgus Clay	9.25	225	265
B	Bauxite	7.0	220	275

As shown by the above data, the wax samples finished through bauxite and Attapulgus clay were both acceptable from the standpoint of color. Percolation through either adsorbent results in some loss in laminating strength but this loss is generally offset by the increase in laminating strength which occurs when wax is purged from the adsorbent and blended with the percolated wax. This increase is also shown by the data in Table VI. Further experiments have shown, however, that waxes produced by deoiling the blended petrolatums to a yield in the lower part of the 60 to 70% range undergo a much greater loss in laminating strength when percolated through bauxite than they do when percolated through a clay such as Attapulgus clay. For this reason it is preferred to employ a clay adsorbent in the percolation step of the process.

EXAMPLE 7

The effectiveness of normal heptane and similar paraffinic solvents for removing wax retained upon the adsorbent clay following purging with an inert gas in accordance with the invention can be seen from the following data obtained by washing Attapulgus clay spent in preparing the improved dual purpose microcrystalline waxes of the invention with various solvents and then testing the color of the recovered wax.

TABLE VII

Effectiveness of solvents for recovering wax from spent adsorbent clay

Treatment	Solvent	Total Wax Recovered, Wt. Percent	Wax Color, Tag-Robinson
Percolation	None	65	11-12
Percolation + Solvent Washing:			
A	N-Heptane	96	11-12
B	Naphtha	96	8
C	Benzene	96	1.5
D	Toluene	96	1.5
E	Acetone	96	1.5
F	Methyl Ethyl Ketone	96	1.5
G	68% Methyl Ethyl Ketone—32% Toluene.	96	1.5

The above data show that paraffinic solvents such as normal heptane and naphtha remove essentially all of the wax retained upon adsorbent clays without seriously affecting the color bodies adsorbed by the clay. Other solvents remove both the wax and color bodies and hence do not permit the recovery of wax having good color characteristics. The use of such a paraffinic solvent containing from 3 to 30 carbon atoms per molecule to recover the wax remaining in the adsorbent clay used in the process of this invention, after inert gas purging, permits recovery of a substantial amount of by-product wax suitable for use in various applications wherein quality requirements are not as rigid as those applicable to the improved microcrystalline wax product of the invention.

From the foregoing description and examples it can be seen that the deoiling of a critical mixture of distillate and residual petrolatums containing from 21 to 28 dry wt. percent of microcrystalline wax volatile at 650° F. and 1 mm. of Hg and from 72 to 79 dry wt. percent of microcrystalline wax nonvolatile under those conditions to obtain a yield of from about 60 to 70 wt. percent of deoiled wax, based upon the total wax content of the blended petrolatums as determined from the solubility of the blend in secondary butyl alcohol at 0° F., results in an essentially non-staining microcrystalline wax having surprisingly high sealing and laminating strengths. A finished wax of particularly outstanding properties is obtained when this wax is percolated through a clay adsorbent, the adsorbent is purged with an inert gas, and the purged and percolated waxes are blended. The preferred process of the invention therefore includes these percolation, purging and blending steps.

It will be appreciated that the process of the invention as described above may be modified in certain respects without adversely affecting the quality of the microcrystalline wax product. It has been found, for example, that phenol extraction of the critical blend of petrolatums prior to deoiling permits a reduction in the oil content of the blend without any detrimental effect upon the wax. In some cases such a step may be desirable to facilitate handling of the blend and reduce the amount of oil which must be removed in the deoiling step. Other modifications will be familiar to those skilled in the art.

In the following claims, the term "dry wax content" is used to denote the amount of wax present as calculated by subtracting the oil content as determined from solubility in secondary butyl alcohol at 0° F. from 100 in the conventional accepted manner. This usage of this term is commonplace and will be readily understood by those skilled in the wax and dewaxing art.

What is claimed is:

1. A process for the production of an improved dual-purpose microcrystalline wax which comprises blending a distillate and a residual petrolatum derived from a mixed base crude oil in proportions to produce a blend

containing from 21 to 28 wt. percent, based upon dry wax content, of microcrystalline wax volatile at 650° F. and 1 mm. of Hg and from 72 to 79 wt. percent, based upon dry wax content, of microcrystalline wax nonvolatile at 650° F. and 1 mm. of Hg; diluting the blend of petrolatums with a wax deoiling solvent; chilling the diluted blend until from about 60 to about 70 wt. percent of the wax present therein, based on dry wax content, has precipitated; and recovering a microcrystalline wax having a sealing strength in excess of 200 grams per inch, a laminating strength in excess of 200 grams per inch, and an oil content of less than 1.5 wt. percent.

2. A process as defined by claim 1 wherein said diluted blend of petrolatums is chilled to a temperature of from about 20 to about 60° F.

3. A process as defined by claim 1 wherein said recovered wax is percolated through an adsorbent clay at a temperature of from about 175 to about 300° F. to remove color bodies from said wax.

4. A process as defined by claim 3 wherein wax adsorbed upon said clay during percolation is purged therefrom with an inert gas and the purged wax is added to the percolated wax.

5. A process as defined by claim 1 wherein said wax deoiling solvent comprises a mixture of from about 65 to 70 vol. percent methyl ethyl ketone and from about 30 to 35 vol. percent toluene.

6. A process for preparing an improved dual-purpose microcrystalline wax which comprises blending a distillate petrolatum derived by the dewaxing of a light motor oil distillate from a mixed base crude oil and a residual petrolatum derived by the dewaxing of a mixed base petrolatum residual fraction in proportions to produce a blend containing from 21 to 28 wt. percent, based upon dry wax content, of microcrytsalline wax volatile at 650° F. and 1 mm. of Hg and from 72 to 79 wt. percent, based on dry wax content, of microcrystalline wax nonvolatile at 650° F. and 1 mm. of Hg; diluting the blended petrolatums with from about 4 to about 14 volumes of a wax deoiling solvent comprising from 50 to 75 vol. percent of an aliphatic ketone containing from 3 to 6 carbon atoms per molecule and from 25 to 50 vol. percent of an aromatic hydrocarbon containing from 6 to 10 carbon atoms per molecule; chilling the diluted blend until from about 60 to about 70 wt. percent of the wax present therein, based upon dry wax content, has precipitated; filtering the precipitated wax from solution and removing solvent therefrom; percolating the filtered wax through from about ⅓ to about 1 volume of an adsorbent clay; purging adsorbed wax from said clay with an inert gas; blending the purged wax with the percolated wax; and recovering a finished microcrystalline wax having a sealing strength in excess of 200 grams per inch, a laminating strength in excess of 200 grams per inch, and an oil content of less than 1.5 wt. percent.

7. A process as defined by claim 6 wherein said blended petrolatums are diluted with from about 8 to about 10 volumes of said wax deoiling solvent.

8. A process as defined by claim 6 wherein said deoiling solvent comprises a mixture of from about 65 to 70 vol. percent of methyl ethyl ketone and from about 30 to 35 vol. percent of toluene.

9. A process as defined by claim 6 wherein said adsorbent clay is Attapulgus clay.

10. A process as defined by claim 6 wherein from about 5 to about 15 wt. percent of the wax adsorbed by said clay is purged therefrom with said inert gas.

11. A process as defined by claim 6 wherein said wax is percolated through said clay at a temperature of from about 175 to about 300° F.

12. An improved dual-purpose microcrystalline wax having a sealing strength in excess of 200 grams per inch, a laminating strength in excess of 200 grams per inch, and an oil content of less than 1.5 wt. percent; said wax being produced by blending a mixed base distillate petrolatum and a mixed base residual petrolatum in proportions to produce a blend containing from about 21 to 28 wt. percent, based upon dry wax content, of microcrystalline wax volatile at 650° F. and 1 mm. of Hg and from about 72 to 79 wt. percent of microcrystalline wax nonvolatile at 650° F. and 1 mm. of Hg; chilling the blended petrolatums in the presence of a wax deoiling solvent until from about 60 to about 70 wt. percent of the wax present in the blend, based upon dry wax content, has precipitated; recovering said precipitated wax from solution; percolating the recovered wax through a decolorizing adsorbent; and recovering a finished microcrystalline wax.

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