

1

3,214,365

**STRENGTH PROPERTIES OF MICROCRYSTALLINE
WAXES WITH AROMATIC EXTRACT OILS****Herman J. Zoeller, Union, N.J., assignor to Esso Research
and Engineering Company, a corporation of Delaware
No Drawing. Filed Aug. 25, 1961, Ser. No. 133,782
3 Claims. (Cl. 208—21)**

The present invention is concerned with a high quality wax particularly with respect to its laminating strength as well as its sealing strength. The invention is more particularly concerned with the manufacture of a high quality microcrystalline wax as, for example, a residual microcrystalline wax having improved laminating and sealing characteristics. In accordance with the present invention, this wax having these improved characteristics is secured by utilizing in conjunction with the wax as, for example, a residual microcrystalline wax, a critical amount of a particular oil as, for example, an aromatic extract oil.

The hydrofining or adsorbent percolation of residual microwax improves color, reduces aromatics and also laminating strength. This loss in laminating strength due to a reduction in aromatic concentration can be regained and brought up to the original strength value by incorporating aromatic components. Aromatic extract oils from solvent extraction of petroleum fractions are an excellent product for this purpose. However, the crude aromatic extracts have a high concentration of color bodies and their use as laminating strength improvers would necessarily reduce the color of the finished microwax. Aromatic extract oils have been hydrofined separately to improve color and color stability for such use. It is now possible to add these hydrofined, color stable aromatic extract oils to the good color microwax and obtain a marked improvement in strength properties without loss in color. Previous to this it was not possible to accomplish both simultaneously.

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 overhead or "paraffin distillate" fraction, for example, has a boiling range of about 580° F. to 850° F. and a viscosity of about 80 S.U.S. at 100° F. A heavy lubricating oil distillate side stream, for example, has a boiling range of about 800° F. to 1000° F. and a viscosity of about 50–70 S.U.S. at 210° F. The residuum comprises all the hydrocarbons boiling above this range and, for example, has a viscosity from about 150 to 200 S.U.S. at 210° F. Crystalline or paraffin wax produced from the paraffin distillates have melting points which range from about 120° F. to 150° F. This type of wax is characterized by large well-formed crystals that can be readily separated from the oil. Furthermore, this type of wax generally contains a relatively small amount of oil and can be refined with comparative ease.

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, as well as other solvents, such as methyl ethyl ketone, methyl isobutyl 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 40% by volume of toluene and 60% by volume of methyl ethyl ketone. In utilizing a mix-

2

ture 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 wax prior to sweating, if desired. This "crude scale wax" generally has an oil content of about 2% to 3% by weight. In order to remove this oil from the scale wax to produce a refined wax, such as refined paraffin wax having an oil content below about .5%, usually below about .3%, various procedures have been proposed and employed. One procedure may be to simply continue the sweating operation to lower the oil content of the crude scale wax.

Alternatively, the slack wax may be processed by a solvent deoiling process, to remove oil from the wax. In this, the wax is dissolved in such solvents as methyl isobutyl ketone, methyl ethyl ketone, or mixtures of methyl ethyl ketone and toluene in a ratio of approximately 75 to 25 respectively. The wax solution is cooled to produce crystallization and the crystallized wax is removed by a process such as filtration. The filter cake of crystallized wax may be washed with cold solvent to remove occluded oil solution. The wax so produced may be an unfinished refined paraffin wax or an unfinished microcrystalline wax, depending on the nature of the slack wax feed and on the selection of crystallization conditions. After oil removal from the wax, it is subjected to a finishing process such as clay percolation or hydrofining. In the latter, the process involves treating the unfinished wax with hydrogen gas at a rate of about 0.5–1.0 volume per volume of wax per hour, at 500–800 p.s.i., at 500–600° F., in contact with cobalt molybdate catalyst. Or, at lower pressures such as 200 p.s.i., a nickel catalyst may be used. The hydrogen treated wax product is greatly improved with respect to color, odor and purity.

It is also known in the art to segregate microcrystalline waxes from residual oils. As pointed out heretofore, these waxes are normally produced from residuums which boil above about 1000° F. and have viscosities in the range from 150 to 200 S.U.S. at 210° F. These microcrystalline waxes are characterized by very minute crystalline forms and which melt in the range from about 145° F. to 190° F. These microcrystalline waxes from residual oils are of a relatively high melting point and of different crystalline structure. The microcrystalline waxes may be prepared from any of the paraffin or mixed base crude oils. The undistilled residue may be treated with sulfuric acid and neutralized to remove the tarry matter and unsaturated hydrocarbons. The undistilled residue also may be deasphalted. The treated stock, containing a fairly high percentage of wax as evidenced by a very high pour point, may be dewaxed by blending with a dewaxing solvent, such as propane, methyl ethyl ketone-benzol, or petroleum naphtha and chilled, and filtered or centrifuged to separate the waxy fraction from the residual lubricating oil solution.

This dewaxing operation produces a wax fraction containing some oil and solvent. The wax after removal of the solvent has a melting point of from about 130 to 180° F. The wax may be again put in solution with more solvent or naphtha and chilled and filtered or recentrifuged to further reduce the oil content. The wax which separates in either of these operations is referred to as crude

microcrystalline wax. The wax separated in the second crystallization process after stripping to remove solvent is fairly dry and of a low oil content. This wax should not be confused with petroleum jellies which contain large amounts of oil. The microcrystalline wax may be again put into solution with naphtha and filtered through clay or an equivalent material in order to improve its color. The clay filtered solution is distilled to remove the naphtha, the residue being a refined microcrystalline wax having a melting point within the range of about 140° to 180° F. Alternatively, the microcrystalline wax may be hydrogen treated to improve its color and odor, such as by hydrofining at about 600° F., 600 p.s.i. of hydrogen, using cobalt molybdate catalyst. The source of the crude oil and the oil content of the refined microcrystalline product will affect the melting point of the final wax product. The refined microcrystalline wax, sometimes called amorphous wax, is as pointed out of a very small crystal structure.

It is also known in the art to segregate microcrystalline waxes from distillate lubricating oils. These distillate type microcrystalline waxes differ in characteristics from the residual type microcrystalline waxes hereinbefore described. Thus, the distillate waxes are lower in viscosity and are generally finished to a higher degree of purity, such as freedom from color and odor. Furthermore, the distillate microcrystalline waxes have two advantages over the residual microcrystalline waxes from the standpoint of ease of manufacture. Namely, first, the distillable nature of the wax makes it possible to manufacture specific microcrystalline wax fractions for use in specific product applications; and, second, the distillate waxes can be more readily and more economically refined with respect to color and odor than can the residual microcrystalline waxes. These features of distillate microcrystalline wax (low viscosity, high purity, select fractionation, economy of finishing), have been found to be of particular value in one phase of the present invention.

The distillate microcrystalline waxes are manufactured from distilled waxy lubricating oil fractions from crude oil. These fractions will vary with regard to distillation range, depending upon the desired viscosity grade of the lubricating oil ultimately produced. Thus, a number of fractional cuts may be taken across the lubricating oil distillation range, to produce different lubes. The entire range may cover a distillation from about 650–1180° F. (760 mm. basis). Each of the fractional waxy lubricating oil cuts are processed to remove the waxy components by a process such as dewaxing by solvent crystallization. As hereinbefore described, this comprises dissolving the waxy distillate in such solvents as methyl ethyl ketone, methyl isobutyl ketone and mixtures of methyl ethyl ketone and toluene, propane, etc., cooling the solution to cause crystallization of the wax, then filtering to separate the lubricating oil and the slack wax. The slack wax is then processed to further remove oil from it by a procedure such as solvent deoiling. In this operation, the excess oil is removed from the slack wax, by the solvent crystallization technique, while at the same time the solvent and temperature conditions are controlled to achieve a fractional crystallization of the wax fraction. Thus, a slack wax may be crystallized first at a relatively high temperature, to separate the most crystalline, paraffinic and high melting wax components present in the slack wax as the solid phase. The melting point may range from 140° to 190° F., depending on the properties of the slack wax feed and the crystallization temperature. The filtrate phase is further cooled to cause a second crystallization of wax which is microcrystalline in nature, and of lower melting point than the first wax cut. Waxes in this fraction vary from 125 to 140° F. melting point. By selection of the solvent composition and crystallization temperature, the exact properties of the separated wax can be controlled. The filtrate from the second crystallization contains the oil which was removed from the wax

fractions. Both the first and second fractions of wax contain about 0.2 to 1.5% oil, this generally being 0.3 to 1.0% oil. These deoiled wax fractions may then be finished to the desired degree of purity with respect to color and odor by one of several methods, such as the hydrogen treating (hydrofining) or adsorption (clay percolation) methods previously described. As a final manufacturing operation, the paraffin or microcrystalline wax may be distilled again, to further separate specific wax fractions.

The particular hydrofined extract oils used in conjunction with the present invention are secured as follows: In the manufacture of medium viscosity index lube oils from naphthene type crudes, for example, Coastal (Texas) crude, the raw lube distillates are extracted to improve viscosity index, color, and reduce organic acidity (neutralization No.). Any one of the known solvents can be applied, such as furfural, chlorex, nitrobenzene or phenol. The last mentioned solvent was utilized in segregating the aromatic feed stocks used in the manufacture of aromatic oils in the present invention. The low viscosity index material known as extracts are removed by the solvent and contain most of the aromatic components in the original raw lube distillate. The extracts are dark color, low V.I. and very viscous. Previously the extracts were discarded as fuel. Quite recently these aromatic concentrates have become important feed sources for making selective aromatic chemicals, i.e. as components in manufacture of plastics, rubber extenders, roofing material and vinyl base tile.

In the present invention where color of product is one important property, the dark color, aromatic extract cannot be used directly without further color improvement. This is accomplished by Hydrofining. The physical properties of the hydrofined aromatic extracts are shown in the following table.

TABLE I
Inspections of hydrofined aromatic oils¹

	Extract I	Extract II
Gravity, ° API	13.7	12.0
Flash ° F., COC	430	440
Viscosity, SSU/210° F.	96	226
Pour Point, ° F.	20	60
Sulfur, Wt. Percent	0.15	0.23
Color, Robinson	17½	9¼
Color Hold Robinson (16 Hrs. at 212° F.)	11½	9
Aniline Point, ° F.	126	123
Refractive Index, DC 67° C. (167° F.)	1.5212	1.5338
Aromatics (Silica Gel) Wt. Percent	71.8	76.4
Neutralization No. MgKOH/100 ml.	0.00	0.006
Average Molecular Weight	362	420

¹ Process conditions:

Pressure, p.s.i.g.	750
Temperature, ° F.	625
Oil charge rate, v./v./hr.	1.0
Hydrogen rate, s.c.f./bbl.	1000
Catalyst, cobalt molybdate (Nalco Esso, ½/16")	

In determining the desirability of a wax composition it is very essential that it have a high laminating strength as well as a high sealing strength. In general, these characteristics are determined by the following tests.

SEALING STRENGTH TAPPI¹—TENTATIVE TEST T-642M

Sample specimens of sulfite paper are waxed (blend of microwax-paraffin-polyethylene) sealed and conditioned. Five sample strips 4.5 in. long and 1 in. wide are tested. Weights are attached to bottom of strip. Top is peeled apart smoothly by adjusting weight and pull. Results are reported as grams/in. width (Reference: Tappi Publication, vol. 37, No. 3, March 1954).

LAMINATING STRENGTH TAPPI¹—TENTATIVE TEST T-642M

Substitute glassine for sulfite paper and 100% microwax for three-component blend. Results are reported as grams/in. width.

¹ Technical Association of Pulp and Paper Industry.

The desirability of the wax composition of the present invention may be readily understood by the following examples wherein a number of wax compositions were prepared.

ufacture of a residual microcrystalline wax of improved laminating and sealing strength characteristics. The main objective is to replenish the loss in laminating strength on decolorization by hydrofining or adsorbent percolation.

TABLE II

Improvement in strength properties of microcrystalline waxes with aromatic extract oils

Composition.....	A	B	C	D	E	F	G	H
Hydrofined Microwax, Wt. Percent.....	100	95	90	95	90	-----	-----	-----
Hydrofined Extract I, Wt. Percent.....	-----	5	10	-----	-----	-----	-----	-----
Hydrofined Extract II, Wt. Percent.....	-----	-----	-----	5	10	-----	5	10
Un-Hydrofined Microwax, Wt. Percent.....	-----	-----	-----	-----	-----	100	95	90
Congearing Pt., ° F.....	144.5	142.5	144.0	144.0	143.0	142.5	143.0	143.5
Oil Content SBA at 0° F.....	1.1	6.1	15.5	6.2	11.0	0.2	4.8	9.8
Laminating Strength.....	85	235	235	270	280	60	235	375
Sealing Strength.....	120	65	15	75	75	110	130	140
Penetration at 77° F.....	24	29	38	28	36	19	23	32
Penetration at 100° F.....	50	101	147	94	103	38	51	76
Penetration at 110° F.....	129	212	250+	201	240	58	113	168
Color T.R.....	13	13 1/4	13 1/4	12	12	1/4	1/4	1/4
P+N+R,* Wt. Percent.....	98.78	97.57	96.47	96.56	94.88	98.08	95.67	94.01
2R, Wt. Percent.....	1.03	2.03	2.89	2.84	4.16	1.55	3.43	4.88
3R, Wt. Percent.....	0.19	0.40	0.64	0.60	0.96	0.37	0.90	1.11
Silica Gel:								
P+N, Wt. Percent.....	96.0	94.0	90.4	93.4	90.8	91.9	91.5	88.6
Arom., Wt. Percent.....	3.6	5.9	9.4	6.6	9.1	8.2	8.2	11.1

Extract I, 17 1/2 T.R. Color. Extract II, 9 1/4 T.R. Color.

*R=1 Ring Aromatic. 2R=2 Ring Aromatic. 3R=3 Ring Aromatic. P=Paraffin. N=Naphthene.

The addition of light color aromatic-extracts to Hydrofined microwax definitely improves laminating strength without loss in color. However, at levels of 5-10% extract concentration in microwax, the final product is somewhat softer and oilier. This is illustrated with increased penetration and oil content values. As a result, the extract lowers the sealing strength. The Extract II oil is more effective as a laminating strength improver than the Extract I oil. These data are shown in columns A, B, C, D, and E in the foregoing table.

The increase in oil content accompanied by the addition of Hydrofined extract oil to the microwax can be controlled by producing a low oil content microwax initially and reducing the concentration of extract oil in the blend. An Un-Hydrofined microwax (column F) of 0.2% oil content was fortified with 5 and 10% of extract oil. The oil content increased, but not to as high a level as that encountered with similar concentrations in the 1.1% oil content microwax. Both laminating and sealing strengths increased due to the addition of extract oil. Concentrations below 5% extract were not investigated (columns G and H).

Thus, the addition of Hydrofined light color aromatic extract to a low oil content Hydrofined microwax improves its laminating and sealing strengths. Normally, these strength properties are reduced as the microwax oil content is reduced and the color improved on hydrofining. The Hydrofined aromatic extract concentrates renew these lost properties in the microwax.

The amount of hydrofined oil used is preferably in the range of about 0.1 to 15.0, particularly in the range of about 2.0 to 5.0 wt. percent based upon the amount of wax present. The pour point of the oil should be in the range from about 15 to 90, preferably 50 to 80, while the viscosity S.S.U. at 210° F. in the range from 80 to 300, preferably in the range from 210 to 230. The molecular weight of the oil should be in the range from about 300 to 500, preferably in the range from about 400 to 450.

Thus, the present invention is concerned with the man-

This is accomplished by the addition of high color aromatic extract oil. In some cases there is an improvement in sealing strength as well. However, whether the sealing strength is improved or not, there are distinct requirements wherein the superior microwaxes of the present invention are needed. For instance, there are several types of microcrystalline waxes present and utilized in the market which are classified as, namely, hard coating; soft coating and laminating or dual-purpose; and laminating only. The waxes of the present invention particularly satisfy the latter two classifications as, for example, wherein it is desirable to improve the sealing strength in bread wraps, frozen food wrappers and cheese wraps; and to laminate or seal combinations of paper, paperboard, foil and film.

What is claimed is:

1. Improved wax composition of increased laminating strength which consists essentially of a hydrofined residual microcrystalline wax having a melting point in the range from 145° to 190° F. containing from about 0.1 to 15 wt. percent of a hydrofined aromatic extract oil having a molecular weight in the range from about 300 to 500 and a viscosity in the range from about 80 to 300 S.S.U. at 210° F.

2. Composition as defined by claim 1 wherein the amount of extract present is in the range from about 2.0 to 5.0 wt. percent.

3. Composition as defined by claim 2 wherein the viscosity of the extract is in the range from 210 to 230 and the molecular weight is in the range from 400 to 450.

References Cited by the Examiner

UNITED STATES PATENTS

1,949,231	2/34	Young	-----	208-87
2,848,385	8/58	Arabian et al.	-----	208-21
2,915,448	12/59	Annable et al.	-----	208-27
3,014,002	12/61	Beggs	-----	208-21

ALPHONSO D. SULLIVAN, *Primary Examiner.*