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HIGH QUALITY SEALING WAX

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The present invention is concerned with a new and improved wax composition and, more particularly, relates to the use of such composition in the coating of materials such as paper, which materials are used for the wrapping of foodstuffs such as bread and the like. In accordance with the present invention, a superior sealing wax is formulated by incorporating therein a critical amount of a copolymer of ethylene with fumaric or maleic diesters. Particularly desirable additives are copolymers of ethylene with diethyl, diisooctyl, or di-2-ethyl-hexyl esters of fumaric or maleic acids.

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 mixture of this character, it has been the practice to add the mixture in toto or incrementally to the

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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 oils, 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 a refined paraffin, having an oil content below about .5%, usually below about .3%, various procedures have been proposed and employed.

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 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 crystalline 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 re-centrifuged 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 crude 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 petrolatum 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 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, 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 then further cooled to cause a second crystallization of the wax which is microcrystalline in nature, and of lower melting point than the first wax cut. Waxes in this fraction vary from 125–140° 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 waxes produced by the methods hereinbefore described, may be used for the coating of materials such as paper, which materials are subsequently used for the wrapping of foodstuffs. Thus, these waxes are principally used in packaging because of their ability to resist the passage of water or water vapor. However, in many cases, a very important property of the wax is its ability to form a strong seal between two pieces of paper. Bread wrapping papers and laminated wrappings are typical examples of applications where strong seals are necessary. It therefore follows that the measurement of the strength of wax seals is a very important part of the value of waxes for such uses. In accordance with the present invention, the sealing characteristics of the waxes are materially improved by the incorporation therein of a copolymer of ethylene with fumaric or maleic diesters.

In accordance with the present invention, the polymerization process is conducted in a solvent as, for example, naphthalene or isobutyl alcohol. It is preferred, however, to use a benzene solvent. The initiator comprises any peroxy compound, preferably di-tertiary-butyl-peroxide. The temperature of the copolymerization reaction is in the range from about 265° to 285° F. A very desirable temperature is about 270° F. The pressure is in the range from about 700 to 5000 pounds, preferably about 800 to 2000 pounds. The autoclave or similar equipment containing the solvent, initiator and diester is purged with nitrogen, then with ethylene before charging with a sufficient amount of ethylene to yield the desired pressure when heated to the reaction temperature. During the polymerization, additional ethylene is added to maintain the pressure at the desired level. Polymerization is considered complete when the pressure drops less than 50 p.s.i.g. per hour. The product is stripped free of solvent and unreacted vinyl acetate under vacuum.

A number of operations were carried out wherein copolymers were produced under different pressures and other varying conditions. These copolymers were then tested as seal improvers in wax compositions with the results as shown in the following tables. The improvement in sealing strength was accomplished without any substantial change in the viscosity of the wax. This is very desirable since the blend can then be used in conventional coating machines. The blocking point of the wax was also improved.

TABLE I
Heat Seal Improvers for Petroleum Waxes

Copolymer Ethylene and Diester Component...	I	II	III	IV	V	VI	VII
	Diethyl Fumarate	Diisooctyl Fumarate		Diethyl Maleate	Diisooctyl Maleate		Di-2-ethyl-hexyl Maleate
Diester Content, Wt. percent.....	37.0	30.0	60.8	34.5	24.0	66.5	31.5
Dropping Point, ¹ ° F.....	192	189	(⁶)	189	179	(⁶)	186
Specific Viscosity ²	0.136	0.163	0.094	0.145	0.184	0.088	0.175
20% in Reference Wax ³	Reference Wax						
Blocking Point, ⁴ ° F.....	118	121	107	113	122	104	125
Sealing Strength, ⁵ g./in.....	15	64	40	88	110	28	80
Viscosity at 210° F., SUS.....	46	87	66	91	118	68	112

¹ ASTM D-127-49.² 1 wt. percent copolymer in toluene at 125° F.³ 64% 158/160° F. melting point paraffin wax 31% 140/142° F. melting point paraffin wax, 5% 135° F. melting point microcrystalline wax.⁴ Blocking test, ASTM-D-1465.⁵ Sealing strength—sealed according to proposed method ASTM-1958, page 1094. Pulled apart as described in "The Mechanism of the Fracture of Wax Seals," Roger M. Butler, David M. MacLeod, and Joseph M. Cahill. Published in TAPPI, vol. 41, No. 7, July 1958.⁶ Below room temp.

The sealing strength should be as high as possible, but a value of 80 to 100 gm./inch indicates good quality. The wax without additive has a sealing strength of 15 gm./inch.

The dropping point is the temperature at which the first drop of liquid falls from a thermometer bulb which has been dipped in the melted material, allowed to cool, then slowly heated under controlled conditions. The measurement is a method of determining the melting point of solids which are not crystalline. A dropping point about 150° F. is desired because lower values might lead to low blocking points. In polymers of similar type, the higher the dropping point, the higher the molecular weight.

The blocking point of a wax is the temperature at which sheets of paper coated with the wax will stick together. In practice, large rolls of waxed paper are stored for some time before use, and if the temperature reaches the blocking point, the whole roll is made useless. In ASTM-D-146S, the blocking point is defined as the temperature at which 50% of the surface becomes marred when two sheets of waxed paper are held together under a specified pressure. The copolymers of the present invention consist of ethylene with diethyl, diisooctyl or di-2-ethyl-hexyl esters of fumaric or maleic acids. It is preferred that the alkyl group which is reacted with maleic acid and fumaric acid to form the ester contain from about 2 to 12 carbon atoms, preferably from about 2 to 8 carbon atoms. The ester content of the copolymers range between about 10% to 40%, preferably in the range from about 20 to 30% by weight.

The preferred copolymers have a dropping point of about 179° F. and higher and a specific viscosity (1% in toluene at 125° F.) higher than 0.1.

For example, the addition of 20 wt. percent of the copolymer of test V increases the sealing strength of the wax from 15 to 110 grams/inch and the blocking point from 118 to 122° F. At the same time, the viscosity increased from 46 to 118 SUS at 210° F. This particular copolymer contains 76 wt. percent of ethylene and 24 wt. percent of diisooctyl maleate, and had a dropping point of 179° F. and a specific viscosity of 0.184.

On the other hand, copolymer of test VI which also contained diisooctyl maleate, but at the higher concentration of 66.5% by weight imparted considerably less improvement to the same wax. (Sealing strength 28 grams/inch and blocking point 104° F.)

As pointed out heretofore, the amount of diester present in the copolymer should vary in the range from about

10 to 40 wt. percent, preferably in the range from about 20 to 30 wt. percent. The molecular weights of these polymers should be in the range from about 2000 to 20,000, preferably in the range from about 5000 to 10,000. A preferred wax composition comprises about 50 to 70%, preferably about 55 to 65% by weight of a paraffin wax having a melting point in the range from about 155 to 165° F. and about 25 to 35% by weight of a paraffin wax having a melting point in the range from about 135 to 145° F. and about 2 to 10% by weight, preferably from about 4 to 6% by weight of a microcrystalline wax which has a melting point in the range from about 133 to 137° F.

What is claimed is :

1. Improved wax composition having incorporated therein from about 10% to about 40% by weight of a copolymer of ethylene and a diester of an acid selected from the group consisting of fumaric and maleic acid, said diester containing from 6 to 16 carbon atoms, said copolymer containing from about 25% to 35% by weight of said diester and from about 75% to 65% by weight of ethylene.

2. Composition as defined by claim 1 wherein the molecular weight of said copolymer is in the range from about 5000 to 10,000.

3. Composition as defined by claim 1 wherein said diester comprises a diisooctyl maleate.

4. Improved wax composition of high sealing strength which comprises about 64% by weight of a paraffin wax having a melting point in the range from about 158 to 160° F., about 31% by weight of a paraffin wax having a melting point in the range from about 140 to 142° F. and about 5% by weight of a microcrystalline wax having a melting point of about 135° F., said wax composition having incorporated therein based upon the total wax from about 10 to 40% by weight of a copolymer of ethylene and a diester of an acid selected from the group consisting of fumaric and maleic acid, said diester containing from 6 to 16 carbon atoms, said copolymer containing from about 10% to 40% by weight of said diester and from about 90% to 60% by weight of ethylene.

5. Composition as defined by claim 4 wherein the amount of ester present in said copolymer is in the range from about 25 to about 35% by weight.

References Cited in the file of this patent

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