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3,170,864

HIGH QUALITY DAIRY WAX

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No Drawing. Filed June 27, 1961, Ser. No. 119,790

2 Claims. (Cl. 208-21)

The present invention is concerned with a high quality dairy wax, particularly with respect to its flaking characteristics. In accordance with the present invention, a superior coating wax particularly a superior high quality dairy wax composition is formulated utilizing a base paraffin wax and at least one microcrystalline wax in combination with a critical amount of a neutral oil. In essence, this neutral oil is relatively low in aromatic content and relatively high in paraffinic content and has a critical pour point. In accordance with a preferred adaptation of the present invention, a superior dairy wax composition is formulated utilizing microwaxes secured from distillates in conjunction with a critical amount of neutral oil of specific characteristics. By utilizing the waxes of this character, greater flexibility and better wax distribution is secured, thereby producing a high quality waxed container. The wax composition of the present invention is secured by utilizing a conventional refined paraffin wax in conjunction with critical quantities of particular microcrystalline waxes which have been produced from various distillates and a critical amount of a neutral oil of specific characteristics.

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 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 waxy distillate as it is being chilled.

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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, 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 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.

In the preferred compositions of the current invention, microcrystalline waxes of the distillate type are preferred for their comparatively better purity and lower viscosity. However, the residual type microcrystalline waxes may also be employed as components in the dairy wax coating formulations.

The particular neutral oil used in conjunction with the wax formulations of the present invention is one that has a relatively low aromatic content below about 12%, has a high paraffinic content above about 30%. The pour point of the oil is -10 to +10° F., while the viscosity is in the range from 60 to 80 Saybolt seconds at 100° F. The flash point of the oil is in the range from 340 to 380° F. as, for example, 360° F.

It is also known in the art that the wax formulations used for milk carton coating are among the most critical of all wax applications from a quality standpoint. The quality of the wax coating is under continuous close scrutiny by the dairy operators, milk distributors, retail stores, and the ultimate users. For example, it is known that waxes exist on the market which have good performance quality in one or two aspects, but which also have certain quality weaknesses. The overall quality for dairy waxes is controlled by a number of rigid tests. One test is the flaking test which measures the degree to which wax particles will flake off the carton and adulterate the milk. Other rigid tests for wax for milk coating cartons are the bottom wax accumulation test, the bottom wax flowing test, the cold flexibility test, the consumption test, as well as the appearance of the coating, the dye coverage, and the rub-off.

However, the most important factors are those that concern the very undesirable flaking, since the excessive wax floats in the milk and is of immediate deep concern to the users. Flaking is a prime cause of customer complaint. The flaking test procedure is as follows for waxed milk cartons after passing through the waxing machine and after filling with a liquid at 38° F., the normal filling temperature. The flaking test is conducted as follows. Five to ten filled test cartons are each dropped eight times from a height of 7 inches onto a rail frame, i.e., a group of 3/32" rods spaced 3/4" apart, 4" long for 1/2 gallon cartons and 3" long for quart cartons. The displaced flakes are filtered out, washed, dried and weighed.

The Bottom Wax Accumulation Test is a visual rating of the relative amount of wax that has run down the sides of the carton and has gathered inside of the carton at the bottom. The accumulation is rated as light, moderate, or heavy. Greater accumulation tends to lead to more flaking.

The Bottom Wax Flowing Test determines the amount of molten or semi-molten wax that flows across the bottom of the carton due to the vigorous motion of the carton as it travels through the cooling or wax hardening section of the dairy machine. The molten lava-like flow does not re-fuse with the main body of wax, but tends to solidify separately from the main coating, in the form of a thin sliver or overlayer on the bottom, in the corners, or "washed" up the sides. This overlayer is very readily displaced if the carton receives a mechanical

shock due to rough handling. Flowing is a phenomenon depending very much on the machine type, and on the routing of the carton within the cooling chamber. In some machines flowing does not occur and is not contributory to flaking. In other machines where flowing can occur, it becomes an extremely serious problem. Flowing is evaluated by visual observation of the inside coating of the carton and the displaced flakes.

The Cold Flexibility Test determines cold flexibility rather than brittleness. Cold flexibility is desired in the wax coatings in order to resist mechanical shock. The cold flexibility is evaluated by cutting off the bottom of a test carton which has been filled with liquid at 38° F., and rapidly flexing the bottom through an angle of about 90 degrees. The rating of poor to very good is made on the basis of audible brittleness, the degree of cracking and the separation of ruptured flakes from the bent paperboard.

Consumption is the rate of wax usage per thousand cartons, measured by weighing cartons before and after waxing. High wax consumption generally tends to produce high wax accumulation and flowing and high flaking. Also, a reasonable amount of consumption must always be maintained in order to achieve a uniform protective covering of the paperboard.

In accordance with the present invention, a conventional refined paraffin wax is used in conjunction with critical amounts of distillate or residual microcrystalline waxes and in conjunction with a critical amount of a neutral oil of specific characteristics.

A satisfactory neutral oil for utilization in the wax compositions of the present invention has the following inspections:

	Effective agent solvent 75 neutral	
Specific gravity, 60/60	-----	0.8493
Flash point, ° F.	-----	360
Pour point, ° F.	-----	0
Viscosity @ 100° F., SUS	-----	73.8
Viscosity @ 210° F., SUS	-----	37.0
Percent aromatics	-----	11.1
Mass spec., wt. percent paraffins	-----	30.8
Non-condensed naphthenes	-----	25.3
Other naphthenes	-----	32.8

One method of producing this oil is as follows: A paraffinic crude oil is distilled, solvent extracted and solvent dewaxed to produce a neutral oil of about 100 S.U.S. at 100° F. and having about a +20° F. pour point. This fraction is run through a vacuum pipe still and various fractions are taken off. A fraction having a viscosity of 65-75 S.U.S. at 100° F. and other properties similar to the "Solvent 75 Neutral" is preferred for this application.

In the broad adaptation of the present invention, the neutral oil will improve the flaking characteristics of all wax formulations as, for example, a wax formulation comprising a conventional paraffin wax used in conjunction with a residual microcrystalline wax and a distillate wax. A typical formulation of this character is as follows:

TABLE I

Constituents	Percent By Weight	
	Range	Preferred
Refined paraffin wax X	72-87	80.0
Residual microcrystalline wax Y	3-8	5.4
Distillate wax Z	10-16	13.6
Polyethylene (7,000 molecular wt.)	.1-2	.5
Polyethylene (12,000 molecular wt.)	.1-2	.5
Oxidation inhibitor	.0003-.001	.0005

Typical inspections of wax X, wax Y and wax Z in the above formulation are as follows:

	Refined Paraffin Wax X	Micro-crystalline Wax Y	Distillate Wax Z
Congeeing pt., ° F. (ASTM D 938)	128	163	151.
Viscosity at 210° F., cs. (D 445)	3.8	20.6	5.7.
Oil content, percent (D 721)	0.2	0.8	0.2
Color	+30 (D 156)	1.9 (D 1500)	+25 (D 156)
ASTM (D 1160)	Distillation at 10 mm.	Distillation at 1 mm.	Distillation at 10 mm.
Boiling pt., ° F.:			
Initial	404	438	464.
2%	450	531	510.
5%	463	565	524.
10%	470	585	534.
20%		609	
30%		628	
40%		648	
50%	508	669, F.B. Pt.	559.
60%			
70%			
80%			
90%	570		586.
95%	586		600.
Final	630, 98% recovered.		611, 98% recovered.

However, as pointed out heretofore, the preferred wax formulations of the present invention comprise a base paraffin wax in conjunction with critical amounts of distillate microcrystalline waxes in conjunction with the neutral oil.

These waxes of the present invention have outstanding and unusual advantages over other commercial dairy waxes. The waxes of the present invention avoid or minimize the bottom accumulation and flowing, and impart desirable cold flexibility, leading to an overall reduction in the level of the flaking. The wax of the present invention will also have better performance by reason of better cold flexibility characteristics.

Thus, a very important part of the preferred adaptation of this invention is that these characteristics are achieved utilizing distillate or residual microwaxes and a neutral oil of specific characteristics. Advantages are thereby realized with regard to purity, availability and cost. In cases where control of accumulation and flowing are desired or necessary, it is seen further that the congealing point of the preferred dairy wax should be about 138° F. minimum, and preferably about 140° to 145° F.

The preferred base wax formulations of the present invention are characterized by having the following constituents.

TABLE II

Constituents	Percent By Weight	
	Range	Preferred
Refined paraffin wax (about .3% oil)	70-90	79
Microcrystalline A	8-12	10
Microcrystalline B	3-12	5
Microcrystalline C	3-7	5
Polyethylene (7,000 molecular wt.)	.1-2.0	.5
Polyethylene (12,000 molecular wt.)	.1-2.0	.5
Oxidation inhibitor	.0003-.001	.0005

The refined paraffin wax is secured as described heretofore and comprises a deoiled slack wax to produce a refined wax having an oil content less than about .3% by weight.

The microcrystalline waxes A, B, and C are secured from distillate lube oil petrolatums by recrystallization techniques utilizing a solvent comprising methyl ethyl ketone and methyl isobutyl ketone.

Microcrystalline wax A was secured by treating a distillate waxy lubricating oil stream of about SAE 30 with a solvent at a temperature of 20° F. with approximately 3 volumes of solvent to one volume of oil. Under these conditions, a slack wax was produced and separated from

the lubricating oil. The slack was then redissolved in about 6 volumes of solvent to one volume of wax and cooled to 65° F. to achieve crystallization. Under these conditions, 155-160° F. melting point paraffin wax was removed. The filtrate was further cooled to a temperature of 51° F. with treatment of 8 volumes of solvent to one volume of wax, to crystallize microcrystalline wax A.

Microcrystalline wax B was secured by treating a waxy lubricating oil distillate of SAE 60 with 5 volumes of solvent to one volume of waxy lubricating oil distillate at a temperature of 25° F. Under these conditions, a slack wax was produced which was then redissolved with heat in about 6 volumes of solvent to one volume of wax plus oil feed and cooled to about 96° F. The wax fraction precipitated comprised crude microcrystalline wax B.

The filtrate was further cooled with 7 volumes of sol-

The high quality of the wax composition of the present invention may be readily appreciated by the following examples wherein the various wax compositions were tested utilizing several field tests and full-scale machines.

Various tests were conducted to determine the effect of the added neutral oil of specific characteristics. The tests were carried out in Model Q (quart) and S (half-gallon) full-scale dairy machines and the effect of the added neutral oil of specific characteristics is clearly shown in the test data of Table IV. The base case is wax I which, in essence, comprises 79% of a refined paraffin wax containing less than about 0.3% oil, 10% of microcrystalline wax A, 5% of microcrystalline wax B, and 5% of microcrystalline wax C. The base wax also contained .5% of polyethylene 7,000 molecular weight and 0.5% of polyethylene 12,000 molecular weight.

TABLE IV

Machine	Wax	Composition	Viscosity at 210° C.	Cong. pt., ° F.	Field Flaking, gms./1000 cartons	Wax Consump., lbs./1000		Cold Flexibility	Flowing	Bottom Wax Accum.
						Quart	½ gal.			
Model Q—Quart..	I	79% paraffin wax 10% microcrystalline A 5% microcrystalline B 5% microcrystalline C 0.5% polyethylene 7000 M.W.+0.5% polyethylene 12,000 M.W.	5.48	140	24.0	24.3	-----	Very good..	No.....	No.
Model Q—Quart..	II	Wax I+1% neutral oil	5.44	139	1.7	23.1	-----	Excellent....	No.....	No.
Model S—½ gal..	III	79% paraffin wax 5.4% wax X 13.0% wax Y 0.5% polyethylene 7000 M.W.+0.5% polyethylene 12,000 M.W.	5.62	140	36.6	-----	40-51	Fair.....	No.....	Very little.
Model S—½ gal..	IV	Wax III+1% neutral oil	5.64	142	9.6	-----	46-52	Very good— excellent.	No.....	Very little.

vent to one volume of wax plus oil feed. At the temperature of 48° F., the crude microcrystalline wax C was collected.

The crude microcrystalline waxes were finished by hydrogen treating at 600° F. and 600 p.s.i., using cobalt molybdate catalyst, to improve their quality with respect to color, odor, and purity. The inspections of the respective wax fractions are listed in Table III.

TABLE III

Typical wax component inspections

Identity.....	Microcrystalline			Refined base wax
	A	B	C	
Description.....	Second crystallization from Ketone (MIBK) deoiling of SAE 30 slack wax	First crystallization from MIBK deoiling of SAE 60 slack wax	Second crystallization from MIBK deoiling of SAE 60 slack wax	
Congeaing point, ° F.....	130	182	136	128
Viscosity at 210° F., cs.....	6.5	11.0	11.4	3.8
Distillation, ° F. at pressure.....	10	1	1	10
2%.....	472	480	400	453
5%.....	490	409	436	458
10%.....	410	529	471	466
50%.....	602	610	610	502
90%.....	688	648	656	566
95%.....	706	659	661	584
98%.....	714	688	698	621
Width of distillation at 5-95%, ° F.....	1 216	2 150	2 225	1 135

1 At 10 mm. 2 At 1 mm.

From the above, it is apparent that 1% neutral oil appreciably reduced the flaking characteristics and produced a very high quality wax. The amount of neutral oil utilized should vary in the range from about .2 to 3% by weight, preferably in the range from about .75 to 1.5% by weight based upon the total composition.

What is claimed is:

1. Improved wax coating composition which comprises a refined paraffin wax having a typical congealing point of about 128° F., a typical viscosity of about 3.8 cs. at 210° F. and an oil content below about 0.5% by weight present in a concentration from about 70 to 90% by weight; a microcrystalline wax having a melting point in the range of about 125 to 190° F. present in a concentration from about 10 to 30% by weight; and a neutral oil present in a concentration from about 0.2 to 3% by weight, said neutral oil being characterized by having an aromatic content below about 12%, a paraffinic content greater than about 30%, a pour point in the range from about -10 to +10° F. and a viscosity in the range from about 60 to 80 Saybolt seconds at 100° F.

2. Composition as defined by claim 1 wherein said microcrystalline wax is a distillate microcrystalline wax.

References Cited by the Examiner

UNITED STATES PATENTS

2,773,812	12/56	Tench	208-21
2,808,382	10/57	Jakaitis	208-21
2,885,341	5/59	Tench	208-21
3,023,156	2/62	Podlipnik	208-21