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3,048,551

POLYETHYLENE-WAX COMPOSITIONS**Robert G. Lutz, Houston, Tex., assignor to Shell Oil Company, a corporation of Delaware****No Drawing. Filed Nov. 19, 1959, Ser. No. 854,013**
4 Claims. (Cl. 260—28.5)

This invention relates to improved wax compositions. More particularly, the invention relates to wax compositions containing a combination of particular polyethylenes or polypropylenes and having special utility as dairy carton wax coatings.

Waxes are broadly divided into several well established groups. These include paraffin waxes (normally obtained from petroleum oil lubricating distillates), microcrystalline wax (usually obtained from residual lubricating oil fractions), soft waxes which include isoparaffinic and naphthenic waxes usually obtained during the deoiling of paraffin waxes, and the so-called high melting point waxes normally obtained by fractionating microcrystalline wax. Each of these wax types has been found to have specific physical properties making them especially attractive for particular utilities. For example, many of these waxes are used either alone or in combination for the waterproofing of food cartons and particularly for the preparation of dairy food cartons. Such waxes must have critically limited properties due to the handling which such cartons are subjected to during their manufacture, storage and transportation as well as the temperatures which they encounter during these stages of use. The problem is complicated also by the specific size of the container since many smaller containers are not as critically demanding in the properties of the wax used to waterproof them as are the larger containers such as half-gallon size milk cartons. It is normally the practice to combine several waxes having different properties in order to attain an optimum combination of properties including melting point, shock resistance, blocking point, resistance to flaking, and other properties which will be more fully discussed hereinafter. Certain non-wax components are often added to wax compositions and particularly to food wax coating compositions. These include especially hydrocarbon polymers such as polyethylene. The subject of wax compositions containing a variety of polyethylenes has been treated in numerous patents as well as in the technical literature. For the most part, polyethylenes employed have had average molecular weights in the range of about 1500 to about 20,000. Certain combinations of polyethylenes have been shown to have certain advantages. The combinations have included a mixture of low and high average molecular weight polyethylenes in order to obtain an optimum combination of physical properties in the wax compositions. While these various additives and their combinations have been found to have beneficial results, they by no means have completely cured the objectionable features encountered in food carton coatings.

One of these aspects is especially apparent in the coating and use of half-gallon size milk cartons. These carton blanks, previously scored by a particular mechanism at the folding edges, are shaped into the carton, glued, and then dip-coated with a wax blend. It has been found that the wax contained in the interior of the folded edges tends to break off in "strings." This is not cured by the use of any particular polyethylene or previously disclosed combination thereof. In addition to this, flaking of the wax coatings still continues particularly after the carton has been subjected to mechanical shock such as occurs in moving and transporting the cold cartons containing dairy foods, such as milk. Another problem which the previous disclosures in this art have not fully satisfied is that of wax consumption, by which is meant the amount of wax

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composition found to be necessary for satisfactory coating of the wax carton. Since these cartons are utilized on a large scale for low priced products, it is essential to provide satisfactory coatings using a minimum amount of the composition for this purpose. Consumption is a function of wax actually absorbed into the carton board, wax viscosity and its solidification characteristics.

It is an object of this invention to provide improved wax compositions. It is another object of the invention to provide improved wax compositions especially useful for food carton impregnation. It is a particular object of the invention to provide improved dairy carton wax compositions. Other objects will become apparent during the following description of the invention.

Now, in accordance with the present invention, improved wax compositions are provided comprising a major amount of a petroleum wax having a melting point within the range from about 125 to about 145° F., the wax containing a combination of two types of polyalkene, one type being a low density polyalkene while the other is a relatively high density polyalkene. More particularly, dairy food wax compositions are provided having improved properties relative to their shock resistance at cold temperatures combined with relatively lower wax consumption and reduced wax adsorption, said compositions comprising 40–60% by weight of a distillate paraffin wax having a melting point between about 122 and 142° F.; 5–20% by weight of a heavy distillate paraffin having a melting point between about 145 and 175° F.; 10–20% by weight of a residual microcrystalline wax; 25–40% by weight of an isoparaffinic-naphthenic plastic distillate wax having a melting point between about 102 and 115° F.; and a polyalkene, preferably polyethylene in an amount between about 0.25–5% (preferably 0.35–1.5%) having a density between about 0.870 and 0.900 at 20° C. as well as 0.05–0.75% by weight of a higher density polyalkene, preferably polyethylene, having a density between about 0.915 and about 0.960, the average molecular weights of each of the polyalkenes being between about 1000 and about 12,000. Best results are obtained if the high density polyethylene has a cloud point above 165° F.

One of the unexpected features of this invention is that these compositions exhibit a substantial (4–15° F.) difference between the "congealing point" (ASTM Test D 938) and the "melting point" (ASTM Test D 87). The usual waxes, containing a single polyethylene, show little if any difference between these two values. The difference indicates that the composition will "set up" sooner in the carton coating machine, thus aiding in reducing wax consumption.

Another of the unexpected aspects of the present invention as it relates to prior art compositions is the finding that the combination of high and low density polyalkenes in wax provide compositions having properties not obtainable by the use of either of these polyalkenes alone. The principal advantage gained by the presence of the relatively lower density polyalkene is that of shock resistance at food storage temperatures while the principal advantage of the relatively high density polyalkene is to reduce the wax consumption (while maintaining good coverage). Each of these features is desirable and even essential for the satisfactory operation of the wax composition when utilized for the purpose of coating food cartons.

Another distinct advantage in the use of combinations of the two types of polyethylenes is the greater latitude of waxes which may then be employed for such purposes as dairy food cartons. If only a single type of polyethylene is employed, it is necessary to so process the wax that a relatively low blocking point wax is produced. With the combination this is unnecessary.

The polyalkenes, as indicated, comprise one or more lower density materials and one or more higher density materials. The densities at 20° C. of the materials as described herein are obtained by a hydrostatic method in air and kerosene. Preferably these polyalkenes have molecular weights within the range from 1,000 to about 12,000 and more particularly from about 1,500 to about 6,000. However, the effects of the combination of polyalkenes as described appear to be largely independent of the average molecular weight of each of the two polyalkenes. The polyalkenes may be either polyethylene or polypropylenes and may be prepared by any of the well known methods, such as those described in the book "Polyethylene," by Raff and Allison, Interscience Publishers Incorporated (1956). Table I below gives typical examples of polyethylenes regarded as having low densities according to the range of densities recited herein.

TABLE I
Low Density Polyethylenes

Sample	Density	Cloud Point, ° F.	Avg. Molecular Weight
A-----	0.880	160	4,000
B-----	0.880	160	4,000
C-----	0.890	171	7,000
D-----	0.910	180	10,000
E-----	0.907	173	8,000

Table II lists a number of relatively high density polyethylenes suitable for use in the compositions of this invention. The density of the polyethylene is governed to a large extent by its method of manufacture but may be largely affected by after-treatment of the polyethylene such as by irradiation. Irradiation is also beneficial with respect to other properties of polyethylenes which may be utilized and particularly with respect to their improvement in modulus of elasticity which in turn beneficiates the properties of the wax compositions in which the polyethylenes are incorporated. Polypropylenes may be utilized for their greater increase in isotactic nature, and therefore, preferably belong in the relatively high density polyalkylenes although certain polypropylenes may have densities low enough to be in the relatively low class of polyalkylenes utilized in the compositions of the invention. The use of relatively low density polyalkenes results in an improvement in shock resistance. The use of low density polyethylene to incorporate and amplify the desirable properties contributed by isoparaflinic-naphthenic wax allows the use of harder, higher melting components than otherwise possible for the same quality, thus higher block of blend. Moreover, as the data contained in the working examples given hereinafter show, the combination of the two types of polyethylene also result in a substantial reduction in consumption without loss in coverage of the wax composition when it is utilized as a coating material on carton stock.

TABLE II
High Density Polyethylenes

Sample	Density	Cloud Point, ° F. ^a	Avg. Molecular Weight
F-----	0.917	>200	21,000
G-----	0.920	183	2,000
H-----	0.920	181	5,000
I-----	0.920	182	1,500
J-----	0.920	171	2,000
K-----	0.927	176	2,000
L-----	0.935	185	2,000
M-----	0.925	176	1,500

^a 1% polymer in wax.

The invention applies broadly to the modification of any petroleum wax with the high and low density polyalkenes. However, it is particularly useful with respect

to dairy food carton compositions which meet a stringent and interlocking series of requirements relative to their physical properties. Ordinary paraffin waxes have been found to be entirely too brittle when utilized alone at dairy storage temperatures. Their use, in unmodified form, as coating compositions is entirely unsatisfactory due to their brittle nature at low temperatures, which results in very excessive flaking and disintegration of the coating. One of the earlier modifications of such compositions was to combine a substantial amount of microcrystalline wax with paraffin wax. Microcrystalline waxes are obtained from residual lubricating oil fractions and comprise only minor amounts of normal paraffin waxes but over about 80% of highly branched and naphthenic waxes of relatively high molecular weight. These are characterized by their malcrystalline or microcrystalline structure as contrasted with the highly crystalline character of ordinary distillate normal paraffin waxes. The resulting blend, while an improvement over distillate paraffin waxes for use as carton coatings, still lacks many of the properties suitable for use as dairy carton coating compositions such as excessive absorption. Also, the melt viscosity was relatively high if more than a modest amount of microcrystalline wax was present. Also, low temperature flexibility of the composition was not improved to the most desirable extent. Still further improvements were, therefore, made by the combination of soft wax fractions obtained during the deoiling of crystalline waxes. The soft waxes so obtained comprise a mixture of isoparaflin and naphthenic waxes of relatively low molecular weight which are normally contaminated by the presence of substantial amounts of oil. Consequently, the soft waxes obtained in the deoiling of distillate paraffin waxes must be deoiled for use in the present invention. They provide wax compositions with greatly increased flexibility at low temperatures and reduce the viscosity in the melted state, thus facilitating their use in the standard carton-making machinery.

Still further improvements in the combined properties of carton wax compositions was provided by the further addition of heavy distillate waxes. These form a special variety in themselves since they not only have relatively high melting points but also comprise a minor amount of normal paraffin waxes while at the same being of essentially a crystalline paraffin wax structure. Thus, they provide the compositions with increased blocking point, improved cold flow properties and increased fracture resistance upon shock chilling. It is to this particular combination of waxes that the addition of both high and low density polyalkenes finds particular and special application.

The distillate paraffin waxes which form a major component in the present compositions preferably have melting points between about 122 and 142° F., preferably between 130 and 140° F. They are obtained normally by the well known operation of dewaxing the waxy distillate lubricating oil fractions obtained in petroleum refining. They comprise major amounts of normal paraffin waxes with minor amounts of non-normal paraffins, principally isoparaflins and naphthenes. The heavy distillate waxes are obtained from the highest boiling lubricating oil distillate fraction and normally have melting points between about 145 and 175° F. Residual microcrystalline waxes have only very minor amounts of normal paraffins present therein and largely predominate in highly branched and naphthenic waxes and have melting points in the order of 130-160° F., usually between about 140 and 150° F. The plastic waxes referred to hereinbefore are obtained as briefly described above, namely, by the deoiling and crude distillate waxes to obtain a so-called "soft wax" which contains up to about 30% by weight of oil. This oil is removed by ordinary deoiling operation at a reasonably low temperature so that the resulting wax obtained is highly isoparaflinic and naphthenic in nature and has a melting point in the order of 102-115° F. Consequently, the waxes which in total constitute greater than about

90% by weight of the present wax-polyalkene compositions, have the following preferred compositions:

	Percent by weight
Paraffin wax, 122–142° F., melting point.....	40–60
Heavy distillate wax, 142–175° F.....	5–20
Microcrystalline wax.....	10–20
Plastic wax.....	25–40

The wax-polyalkene compositions are so compatible as to entail little if any problems in their assembly. The waxes (assuming that more than one type of petroleum wax is utilized) are combined simply by melting the two waxes and stirring. The polyalkenes are preferably incorporated by suspending them in a basket or other perforated piece of apparatus and circulating the wax melt therethrough until the polyalkene is thoroughly dispersed throughout the wax. This is preferably done at a temperature between about 135 and 250° F. There does not appear to be any noticeable advantage to dispersing either the low or the high density polyethylene in wax prior to incorporation of the second polyalkene.

In view of some of the statements in the prior art, it was necessary to determine if the beneficial effects relative to shock resistance, blocking point and wax consumption were due to a combination of differing molecular weight polyalkenes or whether in fact the combination of high and low density polyalkenes was indeed responsible. In order to investigate this aspect, wax compositions were modified with a combination of high and low density polyethylenes having substantially the same average molecular weight namely, about 4,000. The wax composition utilized for this purpose was as follows:

	Percent
Distillate paraffin wax, 138–140° F. melting point....	45
Heavy distillate wax, 158–160° F. melting point.....	10
Isoparaflinic-naphthenic plastic distillate wax, 110° F. melting point.....	30
Residual microcrystalline wax, 145° F. melting point....	15

This composition was modified by the high and low density polyethylenes of the same average molecular weights and by a combination of these two polyethylenes, all as shown in Table III which follows:

TABLE III

Sample	Low Density Polyethylene	High Density Polyethylene	Impact Strength (inches of cracks at 45° F.)	Wax Absorption Into Board *	Cloud Point, ° F.
1.....	none	none	>30	0.129	-----
2.....	1.0	-----	4.5	0.132	160
3.....	1.20	-----	4.5	0.128	-----
4.....	-----	a 0.25	12.3	0.114	169
5.....	1.0	a 0.25	4.7	0.108	169
6.....	-----	b 0.25	>30	0.092	-----
7.....	1.0	b 0.25	6.5	0.092	-----

* 0.920 density, 5,000 mol wt.

b 0.927 density, 2,000 mol wt.

c g./sq. in.

According to the data given in the above table, it will be seen that the use of relatively low density polyethylene resulted in a wax composition having good impact strength but relatively high wax absorption of wax composition by a standard dairy carton board. When the relatively high density polyethylene was utilized (Sample 4) impact strength was sharply reduced while wax absorption was improved. However, when the two polyethylenes were combined in a single wax composition (Sample 5) it was found that impact strength was excellent and that wax absorption continued on a reduced basis.

The density of the low density polyethylene employed above was 0.880, while the density of the high density polyethylene was 0.920 or 0.927 at 20° C., as indicated.

Having found that the beneficial effects upon impact strength, wax consumption and wax adsorption were independent of molecular weight of the polyethylenes, fur-

ther tests were made upon combinations of polyethylenes having differing molecular weights, the same degree of improvement in both impact strength and wax consumption were obtained as long as both high and low density polyethylenes were present in the wax composition.

In another comparative test, cartons were waxed in a commercial machine, utilizing the same blend of waxes as above, in one case employing 1.2% of a low density polyethylene (Sample 3 in Table III). This required 56.0 lb. of wax for good coverage of 1,000 cartons. However, when 0.2% of the polyethylene content was replaced with an equal amount of high density (0.927), polyethylene, the resulting blend provided good coverage with only 50.9 lb. of the composition.

Half-gallon cartons were prepared utilizing the following: the same mixture of waxes employed in the tests described in Table III, modified with 1% low density polyethylene and 0.25% high density polyethylene (Sample 7, Table III). The wax composition including the polyethylenes had a melting point in the order of 138° F. and a blocking temperature of 106° F. Table IV which follows lists a number of important properties of this composition as applied to a standard milk carton board containing about 5% moisture when formed into half-gallon cartons.

TABLE IV

Performance on Half-Gallon Cartons (on Milk Carton Board, 5% Moisture)

Consumption, lbs. per 1,000 cartons.....	50.
Serpentine rating.....	Excellent.
Machine cracks.....	None.
Bottom fillet cracks.....	Do.
Firmness, initial.....	Firm.
Firmness, after 5 days.....	Do.
Bulge, inches.....	7/32.
Scuff resistance at 77° F.....	Excellent.
Filled carton dropped 6 times from 7 inches at 45° F.:	
Loose strings.....	None.
Loose flakes.....	1 small.
Total inches of cracks on bottom.....	2.

According to the above table it will be seen that the cartons formed from a composition of this invention exhibit excellent properties such as those widely demanded by dairy carton manufacturers and consumers. The most significant data insofar as this invention is concerned are the remarks relative to "loose strings," "loose flakes" and wax consumption, the other properties such as amount of cracking, serpentine rating, etc. being highly desirable but not necessarily essential.

I claim as my invention:

1. A composition of matter comprising at least 90% by weight of petroleum wax having a melting point between 125 and 145° F., 0.25–5% by weight of a lower density polyalkene having a density between about 0.870 and about 0.910 at 20° C. and 0.05–0.75% by weight of a higher density polyalkene having a density between about 0.915 and about 0.960, at 20° C., the monomeric alkenes from which the polyalkenes are prepared having 2–3 carbon atoms per molecule, each of the polyalkenes having average molecular weights between about 1,000 and about 12,000.

2. A composition of matter comprising at least 90% by weight of a petroleum wax having a melting point between about 125 and 145° F., said wax being a mixture of 40–60% by weight of a distillate paraffin wax having a melting point of 130–140° F., 5–20% by weight of heavy distillate wax having a melting point of 145–175° F., 10–20% by weight of a residual microcrystalline wax having a melting point of 140–150° F., and 25–40% by weight of an isoparaflinic naphthenic plastic distillate wax having a melting point of 102–115° F., 0.35–1.5% by weight of a lower density polyethylene having a density between about 0.870 and about 0.900 at 20° C. and 0.05–

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0.75% by weight of a higher density polyethylene having a density between about 0.915 and about 0.960, the average molecular weights of each of the polyethylenes being between about 1,000 and about 12,000.

3. A composition of matter comprising 40-60% by weight of a distillate paraffin wax having a melting point between about 122 and about 142° F., 5-20% by weight of a heavy distillate paraffin wax having a melting point between about 142 and about 175° F., 10-20% by weight of a residual microcrystalline wax, 25-40% by weight of an isoparaffinic-naphthenic plastic distillate wax having a melting point between about 102° F. and about 115° F., 0.35-1.5% by weight of a lower density polyethylene having a density between about 0.870 and about 0.900 at 20° C. and 0.05-0.75% by weight of a higher density polyethylene having a density between about 0.915 and about 0.960, the average molecular weights of each of the polyethylenes being between about 1,000 and about 12,000.

4. A wax composition comprising greater than 97% by weight of a mixture of waxes, said mixture including about 45% by weight based on the mixture of a distillate

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paraffin wax having a melting point of 138-140° F., about 10% by weight of the mixture of heavy distillate paraffin wax having a melting point of 158-160° F., about 30% by weight of the mixture of isoparaffinic-naphthenic distillate wax having a melting point of 102-115° F., about 15% by weight of the mixture of microcrystalline wax having a melting point of about 140-150° F., said mixture being modified with 0.35-1.5% by weight based on the mixture of a lower density polyethylene having a density between about 0.870 and about 0.9000 at 20° C. and 0.05-0.75% by weight based on the mixture of a higher density polyethylene having a density between about 0.915 and about 0.960, the average molecular weights of each of the polyethylenes being between about 1,000 and about 12,000.

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