3,042,640
POLYPROPYLENE AND WAX COATING FORMULATION

John J. Gersic, Elmhurst, and Lawrence B. Nelson, Garden City, N.Y., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

No Drawing. Filed Jan. 20, 1960, Ser. No. 3,478
8 Claims. (Cl. 260—28.5)

This invention is directed to a wax formulation for coating paper, cardboard, cartons and the like and is particularly concerned with a coating composition containing a substantial proportion of petroleum wax.

Many items have been packaged in paper and cartons in recent years which were formerly transported in bottles and boxes. In order to provide a leakproof container, the package is coated with a layer of paraffin wax. While substantial volumes of paraffin wax have been used for this purpose, certain defects in the wax coated container have annoyed the manufacturer and user of these packages. Continuous effort has been made through the years to improve the wax formulation by refinery treatment or additions to the wax or both and considerable improvement in the coating wax has been made. And yet in spite of this progress further improvement is desired and will have to be made to prevent competing types of packaging formulations from being developed and used as a replacement for the wax coating.

For bread wraps and paper sealed food containers, the wax formulation must be transparent to show printed matter, capable of being used as a heat seal and must not flow even when packaged hot. The wax formulation must show considerable ductility even at low temperature and high tensile strength. For coating milk containers the wax formulation must provide low temperature ductility and yet provide a hard surface even at elevated temperatures. The composition must not flake in the milk container and must not scuff on shelves or tables when rubbed across such surfaces.

Wax processing techniques have been developed to provide the correct amount of non-normals in the paraffin wax, thereby providing improved ductility. Oil has been added to the wax in some instances to improve ductility and removed from the wax in other instances to improve hardness and scuff resistance. Microcrystalline wax has been added to the paraffin to improve ductility and raise the tensile strength as well as the melting point. Microcrystalline wax has been divided into a plastic wax component and a hard ceresin wax component. The plastic wax has been added to provide better sealing in bread wrap formulations. The ceresin wax has been added to reduce scuffing and provide frictional feel in dairy wax formulations. Polyethylene has been added in varying molecular weights and amounts to provide various improvements.

For instance, U.S. Patent No. 2,031,036 discloses a paraffin wax mixed with 20% microcrystalline wax and a suspended colloid of natural and artificial resins, modified phenol-formaldehyde resins and other condensation and polymerization products on the market. This composition is shown to be useful for coating paper, cardboard or other material. The U.S. Patent No. 2,298,846 discloses the addition of plastic materials to wax to provide improved coating compositions for paper and sheet materials used to protect food stuffs. The plastics are polyalkylenes such as polyethylene, polybutylene, etc. The suggested waxes are crystalline paraffin, amorphous or microcrystalline, petrolatum, and high melting point waxes like carnauba wax.

Also, U.S. Patent No. 2,638,459 states that the tensile strength of paraffin wax used for coating paper bottles is important because of the strain to which the bottle is subjected in handling. Blocking should be avoided as wall as mottling, and a tendency toward scuffing, found particularly in paraffin wax, should be avoided. The patentees point out that the use of polyethylene has not been practical because the high molecular weight solid ethylene polymers dissolve with difficulty in molten paraffin wax even at the 150–160° F. normally used for waxing machine operations. The patentees state further that while solid ethylene polymers in melted condition are miscible with paraffins in all proportions, they tend to crystallize from solution at temperatures below about 230° F. The patent teaches that very small amounts of ethylene polymers having a molecular weight of 5,000–25,000 can be added to paraffin or microcrystalline wax and are effective in improving the wax.

And further, U.S. Patent No. 2,728,735 discloses a coating wax formed by mixing paraffin wax, ceresin or high-melting type paraffin wax obtained from petrolatum stock, and a polymerized olefin having a molecular weight greater than about 1,000 such as polyethylene of 1,000–100,000 molecular weight.

As indicated in the prior art discussion presented above, paraffin waxes and wax formulations are widely used as coating for paper and other materials. They form hard, glossy coatings that are good barriers to moisture vapor and to aqueous liquids. The largest single use is in the coating of dairy and juice containers. Other uses include frozen and dried food packaging. As indicated, however, the paraffin wax coatings are brittle and have an annoying tendency to crack and flake off under impact or other stress. While the ductility of paraffin waxes may be increased by additions of waxy isoparaffins, microcrystalline waxes, and lubricating oils, this improvement is obtained only at the sacrifice of other essential properties. The coatings are too soft or they rub off on clothing. They may feel "greasy" instead of being hard, glossy and plastic-like. This makes the container difficult to grasp. It is customary, therefore, to add only a limited amount of additive material for ductility improvement in order not to excessively debase other required properties.

We have discovered coating wax formulations possessing excellent ductility without debasement of other properties. These formulations comprise a major amount of a paraffin wax, a minor amount of microcrystalline or ceresin wax, and a critical amount of polymers of propylene alone or in combination with mineral oil.

The object of this invention is to provide an improved coating wax for application to paper and paperboard.

A further object of this invention is to provide an improved dairy coating wax formulation for application to milk cartons of paperboard.

A further object of this invention is to provide an improved coating wax for dip coating milk cartons which provides resistance to flaking and resistance to rub-off, has a non-greasy feel, provides improved handling and has exceptional ductility.

These and other objects of the invention will be more fully disclosed in the following detailed description of the invention.

Waxed dairy cartons are coated by a dipping procedure in which the preformed carton is immersed in a bath of molten wax and then allowed to drain to remove the excess wax. The resultant wax coating, when solidified, froms a glossy, liquid-resistant film on the paper carton which may be used to store milk, orange juice and other liquids. These containers are either coated at a central location and shipped to individual dairies for filling or are formed, dipped and filled at the dairy. The formed carton is dipped into the wax bath at a temperature between 150–180° F. The proper selection of dipping temperature is important and is made with consideration of the melt characteristics of the wax. When the carton is withdrawn from the wax bath, it is allowed to drain to remove excess wax. The draining period is critical in that if it is too short, an excessive amount of wax will be used, and if it is too long, too much wax will drain from the container walls and leave dry areas which are not protected with wax. Since the dipping and draining cycles are usually fixed, the temperature of the wax bath is regulated so that the wax has the proper viscosity and will deposit a coating of the proper thickness. One of the problems encountered in the past in choosing additives and components to add to the base dairy wax has been the viscosity of the resultant blend. If the resultant viscosity of the blend is too high, a suitable coating cannot be applied by a dipping procedure. Although present dairy wax formulations are applied between 150–180° F., it is possible for the wax baths of the dipping machines to be operated as high as 210° F. or more. However, at about 200–205° F., excessive amounts of the residual moisture from the paperboard are expelled, causing pinholes and bubbles to form in the coating. These bubbles result in a lack of protection in that particular area and the coating is unsuitable. Also, at these excessive temperatures, enough moisture is expelled from the paper during the dipping operation to cause it to become brittle. Thus, any blend prepared for dip coating dairy cartons must have a viscosity below a predetermined maximum level.

Most paraffin waxes used for coating purposes have a ductilities of 0.01 to 0.02 inch. Ductility is measured on an inclined plane as is disclosed in Modern Packaging, February 1953, in an article entitled "Tensile Strength for Waxes," by Roy T. Edwards. The addition of certain selected waxes or oils can increase this to 0.015 to 0.025 inch without making the wax unusually soft. However, we have found that ductilities greater than 0.025 inch, and preferably over 0.030 inch, are needed to reduce flaking in dairy cartons to a low level. The relationship of flaking to ductility is amply illustrated in the following table:

TABLE I

	Ductility (Elongation in Inches)	Grams Wax Flaked off Per 1,000 Cartons
WAX A	0.017	42.2
WAX B	0.025	6.1
WAX C	0.027	2.3

We have found that wax compositions suitable for coating purposes can be obtained by the following combinations:

(1) Paraffin wax, with or without microcrystalline wax or ceresin wax and a small amount of a liquid propylene polymer of low molecular weight.

(2) Paraffin wax, microcrystalline or ceresin wax or their combination, and a mixture of a liquid propylene polymer of low molecular weight with a higher molecular weight resinous or solid propylene polymer. The resinous polypropylene may be either isotactic, made by the polymerization of propylene with a stereo-specific catalyst; or it may be atactic, made by a random polymerization process.

(3) Same as (2) above, except that an atactic propylene resin is used which is produced during the polymerization of isotactic polypropylene and separated therefrom by solvent extraction and precipitation.

(4) Paraffin wax, microcrystalline wax or ceresin wax, and a mixture of atactic propylene resin and a mineral oil. We have found that only the atactic propylene resin will cooperate with a mineral oil to yield wax compositions of high ductility.

The paraffin waxes used in this invention are the normally available grades of coating wax having melting points of about 120–150° F. The oil content of these waxes may vary between about 0–3% although we prefer waxes with oil contents below 1% by weight.

Conventional microcrystalline wax is obtained from heavy distillate oils or residual lubricating oils by well known solvent precipitation procedures. The wax is obtained from the solvent solution by cooling the liquid to a temperature range of about 40–60° F., producing a wax which melts at about 150–170° F. The conventional microcrystalline wax may be considered to be made up of two components, a ceresin wax component melting at high temperature and a plastic wax component melting at an intermediate temperature. The ceresin wax component is composed predominantly of normal and slightly branched paraffins. The lower melting plastic wax component is composed of highly branched and cyclic hydrocarbons. Microcrystalline waxes have melting points in the range of 150–185° F. whereas the ceresin waxes usually melt at about 185–200° F. We prefer to add ceresin wax to microcrystalline wax in our formulations or use ceresin wax in place of microcrystalline wax. The ceresin wax imparts better appearance to the wax formulation and improved the feel or handleability of the coating.

The liquid propylene polymer oil can be obtained by polymerizing propylene in chloroform solution with a suspended aluminum halide catalyst. The molecular weight of the oil may vary from about 400–1500. The liquid polymer may be used as prepared or may be hydrogenated. In both instances the results were equally satisfactory.

The propylene polymer oil is prepared by polymerizing propylene in either hexane or chloroform using about 3% of suspended anhydrous aluminum chloride as a catalyst. Propylene at 12 p.s.i.g. is introduced into the stirred mixture which is kept at 110–120° F. until the reaction is complete, as indicated by the failure of the system to absorb more propylene. After the reaction mixture is allowed to settle and the aluminum chloride sludge drawn off, the liquid polymer is washed with water (5 gal./100 lbs.) and then with an equal amount of 5% sodium carbonate. This mixture is then stripped of solvent at atmospheric pressure and 300° F., followed by a vacuum stripping at 26 inches of Hg vacuum, and finally a filtration with Hyflo (trade name) filter aid.

Typical properties of the product oil prepared by the procedure described hereinabove are:

Color	Yellow to straw.
Molecular weight	670 to 850.
Viscosity—	
Cs. @ 100° F.	584 to 2200.
Cs. @ 210° F.	23.5 to 57.

The product oil contained about 0.80 to 0.95 double bonds per molecule.

Isotactic propylene resin, made with stereospecific catalyst is now commercially available. For example, the isotactic propylene resin manufactured and sold by the Hercules Powder Company under the trade name Pro-Fax may be used. Alternatively, the propylene resin manufactured and sold by Montecatini Soc., Gen., Milan, Italy, under the trade name Moplen may also be used. The molecular weight of this material may vary from about 100,000–500,000.

Atactic polypropylene is of random structure and not specifically oriented. This resin may have a molecular weight of about 5,000–100,000. A variety of nonspecific catalysts are available for preparation of atactic propylene resin and are well known to workers in this field. The atactic resin can also be obtained as a byproduct of the manufacture of isotactic polypropylene.

The mineral oil used in certain formulations with the atactic propylene resin is a 100–200 second (viscosity at 100° F. S.U.S.) commercially available U.S.P. grade oil. U.S.P. grade oils are not essential unless the coating is likely to come in contact with edible materials.

Example I

A 125/127 AMP commercial paraffin wax was subjected to the inclined plane ductility test and provided a ductility (elongation: inches) of 0.018.

Example II

A 133/135 AMP commercial paraffin wax was subjected to the ductility test and provided a ductility of 0.013 inch.

Example III

A ceresin wax having a melting point of 185° F. (ASTM designation: D127–49) was subjected to the ductility test and yielded a ductility of 0.013 inch.

Example IV

A blend of 80% 125/127 AMP paraffin wax and 20% ceresin wax of melting point 185° F. was subjected to the ductility test and showed a ductility of 0.022 inch.

Example V

A blend of 85% 125/127 AMP paraffin wax and 15% microcrystalline wax of melting point 160° F. was subjected to the ductility test and yielded a ductility of 0.020 inch.

Example VI

A blend of 80% 133/135 AMP paraffin wax and 20% ceresin wax of melting point 185° F. was subjected to the ductility test and yielded a ductility of 0.010 inch.

Example VII

A blend of 85% 133/135 AMP paraffin wax and 15% microcrystalline wax of melting point 160° F. was subjected to the ductility test and showed a ductility of 0.020 inch.

Example VIII

A blend of 77% 125/127 AMP paraffin wax, 20% ceresin wax of melting point 185° F., and 3% liquid propylene polymer of molecular weight 1140 (Staudinger method) was subjected to the ductility test and was found to have a ductility of 0.033 inch.

Example IX

A blend of 77% 125/127 AMP paraffin wax, 20% ceresin wax of 185° F. melting point, and 3% of a 1 to 1 mixture of liquid propylene polymer of molecular weight 680 (Staudinger method) and solid atactic propylene polymer of 5800 molecular weight (Staudinger method) was subjected to the ductility test and found to have a ductility of 0.043 inch.

Example X

A blend of 78% 125/127 AMP paraffin wax, 20% ceresin wax (M.P. 185° F.) and 2% of a 7 to 1 mixture of liquid propylene polymer of molecular weight 740 and solid atactic propylene polymer of 6500 molecular weight was subjected to the ductility test and yielded a ductility of 0.034 inch.

Example XI

A blend of 77% 133/135 AMP paraffin wax, 20% ceresin wax of a melting point 185° F. and 3% of a 7 to 1 mixture of liquid propylene polymer of molecular weight 740 and solid atactic propylene polymer of 300,000 molecular weight was subjected to the ductility test and yielded a ductility of 0.044 inch.

Example XII

A blend of 70% 125/127 AMP paraffin wax, 20% ceresin wax of a melting point of 185° F., and 10% of a 1 to 1 mixture of liquid propylene polymer of molecular weight 680 and solid atactic propylene polymer of 5800 molecular weight was subjected to the ductility test and yielded a ductility of 0.060 inch.

Example XIII

A blend of 75% 125/127 AMP paraffin wax, 20% ceresin wax of a melting point of 185° F., and 5% of a 1 to 1 mixture of liquid propylene polymer of molecular weight 680 and solid atactic propylene polymer of 5800 molecular weight was subjected to the ductility test and yielded a ductility of 0.060 inch.

Example XIV

A blend of 77% 133/135 AMP paraffin wax, 20% of microcrystalline wax of melting point 160° F., and 3% of a 7 to 1 mixture of 31° A.P.I. gravity mineral oil of viscosity at 100° F. of 142 S.U.S. and at 210° F. of 42.2 S.U.S. and a solid atactic propylene polymer of 305,000 molecular weight was subjected to the ductility test and showed a ductility of 0.039 inch.

Example XV

A blend of 77% 125/127 AMP paraffin wax, 20% microcrystalline wax of melting point 160° F., and 3% of a 7 to 1 mixture of 31° A.P.I. gravity mineral oil of viscosity at 100° F. of 142 S.U.S. and at 210° F. of 42.2 S.U.S. and a solid atactic propylene polymer of 300,000 molecular weight was subjected to the ductility test and was found to have a ductility of 0.052 inch.

Example XVI

A blend of 73% 133/135 AMP paraffin wax, 20% ceresin wax of melting point 185° F., and 7% of a 1 to 1 mixture of 31° A.P.I. gravity mineral oil of viscosity at 100° F. of 142 S.U.S. and at 210° F. of 42.2 S.U.S. and a solid atactic propylene polymer of 290,000 molecular weight was subjected to the ductility test and was found to have a ductility of 0.050 inch.

Example XVII

A blend of 79% 125/127 AMP paraffin wax, 20% ceresin wax of melting point 185° F., and 1% of a 1 to 3 mixture of isotactic propylene polymer (molecular weight about 200,000–450,000) and liquid propylene polymer (molecular weight 475) was subjected to the ductility test and was found to have a ductility of 0.036 inch.

Example XVIII

A blend of 64% 125/127 AMP paraffin wax, 20% ceresin wax of melting point 185° F., 15% microcrystalline wax of melting point 160° F. and 1% of a 1 to 1 mixture of isotactic propylene polymer (molecular weight about 200,000–450,000) and liquid propylene polymer (molecular weight 475) was subjected to the ductility test and was found to have a ductility of 0.034 inch.

Example XIX

A blend of 64% 125/127 AMP paraffin wax, 20% ceresin wax of melting point 185° F., 15% microcrystalline wax of melting point 160° F. and 1% of a 1 to 3 mixture of isotactic propylene polymer (molecular weight about 200,000–450,000) and liquid propylene polymer (molecular weight 475) was subjected to the ductility test and was found to have a ductility of 0.050 inch.

Example XX

A blend of 64% 125/127 AMP paraffin wax, 20% ceresin wax of melting point 185° F., 15% microcrystalline wax of melting point 160° F. and 1% of a 1 to 7 mixture of isotactic propylene polymer (molecular weight about 200,000–450,000) and liquid propylene polymer (molecular weight 475) was subjected to the ductility test and was found to have a ductility of 0.033 inch.

Example XXI

A blend of 64% 125/127 AMP paraffin wax, 20% ceresin wax of melting point 185° F., and 15% microcrystalline wax of melting point 160° F. was subjected to the ductility test and was found to have a ductility of 0.024 inch.

We have found that a wax blend suitable for dipping milk cartons on conventional dipping machines can be prepared by blending liquid polypropylene with parffin wax and either microcrystalline wax or ceresin wax. An improved formulation is obtained by using a mixture of liquid propylene polymer and solid propylene polymer. Using atactic polypropylene we have found that ordinary mineral oil can be substituted for the liquid polypropylene with satisfactory results. This was a completely unexpected discovery. The concentration of components must be within about the following ranges:

	Broad Operating Limits	Preferred Operating Limits
Microcrystalline or ceresin wax, percent	5–35	15–25
Paraffin Wax, percent	94–55	84–70
Liquid propylene polymer, percent	1–10	1–5

When liquid propylene resin or alternatively mineral oil is blended with solid propylene polymer the limits are as follows:

	Broad Operating Limits	Preferred Operating Limits
Microcrystalline or ceresin wax, percent	5–35	15–25
Paraffin Wax, percent	94–50	84–70
Liquid polypropylene or mineral oil and solid propylene polymer, percent (ratio varying from 1:1 to 1:7 solid to liquid)	1–15	1–10

When isotactic solid propylene polymer is used the liquid propylene polymer must be used and the limits are as follows:

	Broad Operating Limits	Preferred Operating Limits
Microcrystalline or ceresin wax, percent	5–35	15–25
Paraffin wax, percent	94–55	84–70
Liquid propylene polymer and solid propylene polymer, percent (ratio varying from 1:1 to 1:7 solid to liquid)	1–10	1–5

The concentration limits are defined in part by the performance requirements of the wax and the coating machines. The upper limits of microcrystalline wax and liquid polypropylene or mineral oil are dictated by the viscosity requirements that the blend must not exceed 50 Saybolt Universal seconds at 210° F. in order to permit coating operations at a temperature below 200° F. The upper limit of the liquid polypropylene is governed by the amount that the wax will hold as well as the degree of rub-off resistance desired. The larger the amount of liquid propylene polymer, the lower the rub-off resistance. The lower limits are determined in all cases by that concentration at which an improvement is noticeable or a desirable property obtained.

In practice it is generally not necessary or desirable to prepare a polymer which is entirely (100%) isotactic, i.e. stereospecifically oriented, nor is it necessary or desirable to prepare a polymer which is entirely randomly oriented or atactic. Within the same molecule there occur areas (a number of monomer units) which are atactic and others which are isotactic. The polymerization conditions determine the relative amounts of the two types. Using newly developed stereospecific catalysts, it is possible to control the reaction so that there is a predominance of the isotactic structure within most of the molecules. A small fraction of the molecules will, however, contain a predominance of atactic areas. The relative amounts of the atactic and isotactic areas determine the overall properties of the molecule. Therefore, when propylene polymer

is described as atactic or isotactic, it is intended and understood to cover situations in which the atactic or isotactic areas of the molecules predominate and not necessarily a molecule which is either fully randomly oriented or fully specifically oriented.

Commercial isotactic propylene polymers are prepared by a solution polymerization process using a stereospecific catalyst. At the end of the polymerization reaction the isotactic polymer is removed from the reactor as a solid which is not soluble in the polymerizing solution. For instance the polymerizing solution may be an aviation alkylate in which the propylene concentration may be about 15% by weight. The catalyst for the reaction may be titanium trichloride, aluminum triethyl or aluminum monoethyl dichloro or a combination of these or similar materials. Hydrogen at a concentration of about 15 p.p.m. can be used as a chain stopper. The reaction may be batch or continuous at normal or advanced pressure for a period of about 8–10 hours at a temperature of 150–200° F., the mixture being vigorously agitated during reaction. The reaction product is transferred to a solvent bath such as methyl alcohol from which the isotactic propylene polymer precipitates and is filtered therefrom. This product, when dried, is the isotactic propylene polymer. The polymer remaining in the solvent is separated by evaporation of the solvent or otherwise. This product, when dried, is the atactic propylene polymer. Further details of the manufacture of propylene polymer, the catalyst used or the separation of isotactic and atactic polymer is found in U.S. Patent No. 2,874,153 which issued February 17, 1959, as well as in the September 1957 issue of Scientific American which is devoted to the subject of "Giant Molecules."

It is understood that minor ingredients may be added to the wax blend in amounts sufficient to perform a particular function without impairing the effectiveness of the blend. For instance, well known oxidation-retarding materials, such as butylated hydroxy toluene, may be added in fractional amounts such as 0.0005%. Since the wax is maintained at elevated temperature for long periods of time, oxidation of various wax components may occur, and hence this may be resisted by adding an oxidation-retarding agent such as butylated hydroxy toluene to the blend.

The illustrations of the invention given hereinabove are merely for the purpose of demonstrating the invention. The only limitations intended are found in the attached claims.

We claim:

1. A wax composition for coating milk containers and similar articles consisting essentially of: about 94–55% by weight of paraffin wax having a melting point about 120–150° F., about 5–25% by weight of microcrystalline wax having a melting point about 150°–200° F., and about 1–10% by weight of a mixture of liquid propylene polymer and solid propylene polymer in which the solid to liquid ratio is between about 1 to 1 and about 1 to 7.

2. A wax composition for coating milk containers and similar articles consisting essentially of: about 84–70% by weight of paraffin wax having a melting point of about 120–150° C., about 5–35% by weight of microcrystalline wax having a melting point of about 150–200° F., and about 1–5% by weight of a mixture of liquid propylene polymer and solid propylene polymer in which the solid to liquid ratio is between about 1 to 1 and about 1 to 7.

3. Claim 1 in which the solid propylene polymer is an isotactic polymer.

4. Claim 1 in which the solid propylene polymer is an atactic polymer.

5. Claim 2 in which the solid propylene polymer is an isotactic polymer.

6. Claim 2 in which the solid propylene polymer is an atactic polymer.

7. A wax composition for coating milk containers and similar articles consisting essentially of: about 94–50%

by weight of paraffin wax having a melting point of about 120–150° F., about 5–35% by weight of microcrystalline wax having a melting point of about 150–200° F., and about 1–15% by weight of a mixture of liquid propylene polymer and solid atactic propylene polymer in which the solid to liquid ratio is between about 1 to 1 and about 1 to 7.

8. A wax composition for coating milk containers and similar articles consisting essentially of: about 84–70% by weight of paraffin wax having a melting point of about 120–150° F., about 15–25% by weight of microcrystalline wax having a melting point of about 150–200° F., and about 1–10% by weight of a mixture of liquid propylene polymer and solid atactic propylene polymer in which the solid to liquid ratio is between about 1 to 1 and about 1 to 7.

References Cited in the file of this patent

UNITED STATES PATENTS

2,808,382	Jakaitis	Oct. 1, 1957
2,835,659	Guillet	May 20, 1958
2,882,246	Leatherman et al.	Apr. 14, 1959

OTHER REFERENCES

Warth: The Chemistry and Technology of Waxes, 2nd edition, pages 502, 503, and 800, Reinhold Publishing Corporation (1956).