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HEAT-SEALABLE WAXED PACKAGING MATERIAL AND PROCESS OF MAKING THE SAME

Herbert P. Cantelow, Oakland, Calif., assignor to Crown Zellerbach Corporation, San Francisco, Calif., a corporation of Nevada

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This invention relates to packaging material especially adapted for the packaging industry, and particularly flexible wrapper sheets.

More specifically, this invention relates to the production of a heat-sealable waxed packaging sheet which is substantially moisture-proof and which, when heat-sealed, will produce an exceptionally strong bond resistant to delamination. The invention relates also to a novel wax composition containing a relatively small proportion of partly oxidized polyethylene, which composition is employed for coating a base sheet to produce the packaging sheet in accordance with the present invention.

While various types of waxed wrappers have long been employed in packaging of foodstuffs and other products, such wrappers have proved not entirely satisfactory in providing a protective and moistureproof covering after being heat-sealed, due to the fact that the wax seal often fails or delaminates during the handling, shipping, or prolonged storage of the packaged goods.

Recent developments include wax compositions modified by the incorporation of small amounts of polyethylene. Thus, in the Hyde U.S. Patent No. 2,582,037, a paraffin-microcrystalline wax-polyethylene blend is employed as a coating for paper. The waxed surface of the paper has an improved gloss, flexibility and sealing qualities compared to a paper coated with paraffin wax alone. Although the above mentioned wax-polyethylene composition improves many properties of the sheets coated therewith, the coated products are still not all to be desired in giving a strong bond upon heat-sealing.

In order to improve the sealing strength to a certain degree, Thwaites et al. describe in their U.S. Patent No. 2,698,309 a paper coating composition comprising a mixture of refined paraffin wax, polyethylene, and a low-molecular weight polyethylene having a terminal hydroxyl group. The latter material may be prepared according to the Erchak U.S. Patent No. 2,504,400 wherein the hydroxyl group is caused to enter the polymer chain during polymerization of ethylene in the presence of isopropanol and hydrogen peroxide.

An object of this invention is to provide an improved packaging sheet, particularly a wrapper which will be capable of being heat-sealed to produce an exceptionally strong bond.

Another object of the invention is to provide an improved heat-sealable waxed wrapper, particularly adaptable for packaging foodstuffs and the like, which wrapper will be substantially moistureproof and thus, when sealed, will enable the food incased therein to maintain its original moisture content while being protected from outside moisture, vapor or dust as long as the bond obtained through heat-sealing remains unruptured.

An additional object of the invention is to provide methods of making heat-sealable waxed packaging sheets, which methods are simple, economical, and requiring only conventional equipment employed in the manufacture of waxed papers and the like.

A further object of the invention is to provide a novel wax coating composition which, when applied as a coating film on a base sheet, will produce a non-blocking film of

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wax capable of producing an exceptionally strong heat-sealing bond.

Briefly, we attain these objects and other advantages by coating at least one face of a base sheet of suitable weight for use as a packaging sheet, such as a wrapper, with a wax composition containing a small portion of partly oxidized polyethylene. The resultant waxed sheet presents a finished, glossy, non-blocking surface which is heat-sealable, and when heat-sealed will maintain its seal over a long period of time during handling, shipping or storage of the goods packaged therein. The important and novel feature of this invention is the fact that, due to some interaction between the two essential constituents of the coating composition, i.e. the wax and the partly oxidized polyethylene, which occurs under the heat-sealing temperature, a tenacious bond is set-up between the heat-sealed surfaces, this bond being resistant to delamination and being breakable only by rupturing the base sheet. Such interaction resulting in enhanced sealing is particularly effective with microcrystalline wax containing coating compositions, and especially with microcrystalline paraffin wax compositions.

In the carrying out of the invention, the base sheet is made preferably of fibrous cellulosic pulp, although regenerated cellulose, cellophane, glassine and the like may be also employed as base sheets. The basis weight of the sheet for the wrapper may vary from about 15 pounds to about 150 pounds per ream of 3000 square feet, or even higher as in the case of the paperboard to be employed as cartons for the packaging of various food products. However, a basis weight of from about 20 to 35 pounds per ream is considered most satisfactory for customary waxed paper wrappers. Any of the conventional "beater additives," such as sizing agents, wet strength resins, fillers, opacifying pigments, etc., may be incorporated in the pulp furnish from which the base sheet is made. A pulp furnish containing about 80% bleached softwood kraft or sulfite pulp and about 20% hardwood soda or kraft pulp has been found very suitable for the manufacture of the base sheet to be employed in the carrying out of this invention. The base sheet may be calendered, if desired, to impart thereto a smooth surface desirable for coating or printing.

After the base sheet is made, it is coated with the composition of this invention by any of the conventional procedures of making papers waxed on either one side or both sides thereof. If the composition is applied to one side only of the sheet, this may be accomplished by depositing a film of wax from aqueous emulsion, solvent solution, or from molten bath. Preferably, however, the sheet is passed through a bath of molten wax composition, then between a pair of squeeze rolls to remove the excess of wax, and finally through a chilling bath. As a result of this procedure, both sides of the sheet will be coated with a thin film of the wax composition.

The amount of wax-based coating necessary to obtain a film of adequate thickness for a satisfactory heat-sealable wrapper may vary from about 8 pounds to 25 pounds per ream (3000 square feet), such weight including the total amount on both sides of the base sheet, depending on the type of sheet used and its basis weight. For the usual flexible paper sheet employed for wrappers and having a basis weight of 20 to 35 pounds per ream, the amount of dry wax coating ranging from 10 to 18 pounds per ream for both sides of the sheet is generally sufficient.

The term "wax," as used herein, includes such waxes or wax-like materials which are capable of giving a flexible, non-blocking film characterized by a good moisture-vapor transmission resistance, and which are capable of

producing, in conjunction with the hereinbelow described partly oxidized polyethylene, a very strong heat-seal bond at a heat-sealing temperature of the mixture, resistant to delamination. The desirable waxes in the carrying out of this invention are microcrystalline wax containing compositions, and especially any of the well known microcrystalline-paraffin wax blends with or without minor amounts of the usual additives.

The term "partly oxidized polyethylene," as used herein, defines a polyethylene having in its carbon-to-carbon chain a certain number of oxygen-containing groups, mainly carbonyl groups, such as ketonic, aldehydic, or carboxylic groups. The partly oxydized polyethylene may be obtained by heating polyethylene while simultaneously working for agitating the same in the presence of an oxidizing medium, to uniformly expose the entire mass to such medium. This is preferably accomplished by hot-milling polyethylene in the presence of oxygen or other suitable oxidizing agent. During the treatment, certain changes in physical and chemical properties of polyethylene occur. Under mild conditions the white color of polyethylene changes to off-white. With longer reaction time and higher temperatures, the color changes further to yellow, brown, and even black, together with the development of a rancid odor. For instance, heating polyethylene in the presence of air at 160° C. for several hours first brings about lowering of its molecular weight because of chain breaking and then rapid increase of the molecular weight, viscosity and softening point because of cross-linking by oxygen. Continued oxidation, especially at higher temperatures, leads to degradation of the chains, liberation of volatile compounds such as carbon dioxide, water, and fatty acids, and the formation of a brittle, wax-like product. If desired, antioxidants may be employed during the thermal treatment in order to prevent oxidative degradation. The oxidation of polyethylene follows, in general, the pattern set by lower homologs, such as paraffinic waxes and oils. It is autocatalytic in nature, the rate of oxidation increasing as the amount of oxygen absorbed by the polyethylene increases.

Thus by controlling the reaction conditions of oxidation of polyethylene, it is possible to obtain a variety of products of a carbonyl oxygen concentration which as such carbonyl oxygen concentration increases results in gradually increase in acid number which may be up to 25, or even higher. The partly oxidized polyethylene must be compatible with most waxes to produce uniform blends therewith.

Particularly suitable for blending with wax in accordance with the present invention are emulsifiable, non-toxic solid polyethylenes, which have been only partly oxidized and having an average molecular weight from 500 to 30,000, preferably from 1000 to 5000, a carbonyl oxygen content determinable by acid number of up to 25, preferably from 10 to 20, a melting point in the range of about 190° F. to 220° F., Saybolt viscosity from 30 to 120 seconds at 140° C., color ranging from a translucent white to a slight green, and being substantially odorless or having merely a slight odor.

The two types of waxes which are customarily used in the manufacture of waxed papers or other flexible packaging sheets, and for laminating flexible sheets, and are particularly suitable for blending with polyethylene are the paraffin wax having a melting point in the broad range of about 120° F. to 200° F., and the preferred range of 130° F. to 160° F., and the microcrystalline wax having a broad melting point range of about 120 F. to 170° F and preferred range of 140° F. to 160° F. The combinations thereof in various proportions are also widely employed and are suitable in preparing the coating compositions of this invention, as is well known in the art.

The following Table I shows the most satisfactory wax coating compositions and proportions of their constituents expressed in percentages by weight.

Table I

	Broad Range	Preferred Range
5 Paraffin Wax.....	5-95	55-85.
Microcrystalline Wax.....	5-95	15-45.
Partly Oxidized Polyethylene.....	0.01-20	¹ 0.1-1.0. ² 0.1-5.0.

¹ (For food wrappers.)

10 ² (For coatings on other types of packaging sheets, the maximum being determined in accordance with weight of sheet.)

We have found that, for the same level of heat-seal strength, smaller amounts of polyethylene oxidized to a higher degree need to be admixed with the wax, and vice versa. We have also found that when a partially oxidized polyethylene having a slight rancid odor is employed for blending with wax, and the final coating film is to be entirely free of odor as may be required for wrapping food products, amounts up to about 0.7% by weight of partly oxidized polyethylene may be used to advantage without imparting any undesirable odor to the coated wrapper.

25 If desired, the above compositions may be further admixed with small amounts of unoxidized polyethylene, butyl rubbers, etc.

In preparing the wax coating compositions containing partly oxidized polyethylene, this is done in the usual manner of blending polyethylene with waxes; namely, the wax is usually melted and the predetermined quantity of polyethylene, preferably in finally divided form is added thereto and stirred until dissolved. The resulting uniform coating composition is then ready for use in the usual waxing operation. The waxed sheet may be wound in roll form for ease in handling, shipping and packaging.

When an article is to be wrapped and sealed, the waxed wrapper of adequate size for the package is used and placed so that the waxed side of the wrapper (if one side only of the wrapper is waxed) will form the outside of the package. The overlapping marginal portions of the wrapper and the closing folds in the same are so arranged that the wax film will be intermediate between the surfaces of the wrapper to be sealed. The sealing is then effected by the application of light pressure and heat for a short period of time sufficient to produce a strong bond. Although what actually transpires to produce the resulting exceptionally strong bond through heat-sealing is not clearly understood, it is evident that a physical or chemical interaction between the wax and the partly oxidized polyethylene and with the opposed surfaces of the base sheet takes place under the influence of the sealing heat and pressure. As it will be shown hereafter, the seal strength of the present composition is markedly greater than that produced by a wax composition containing the same amount of unmodified polyethylene in lieu of the partly oxidized material.

The heat-sealing operation should be carried out at a temperature above the cloud point (ASTM designation D97-47) of the wax composition, preferably at least 10° F. above such cloud point of the wax composition. Under such conditions, the partly oxidized polyethylene will be substantially dissolved in the wax.

Extensive tests have demonstrated that the strength of the bond produced by heat-sealing is such that it is impossible to pull the bonded areas apart except by rupturing the base sheet. In other words, no delamination occurs, after heat-sealing of the wrapper, for prolonged periods of time during handling or shipping of the packaged goods.

The following Table II shows some specific examples of the carrying out of the invention. In these examples the proportions are given as percentages by weight. It is to be understood, of course, that the invention is not limited entirely to these specific examples.

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Table II

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Paraffin wax.....		59.95	71.0	60.0	57.5
Microcrystalline wax.....	95.0	40.00	24.0	20.0	37.0
Partly oxidized polyethylene.....	5.0	0.05	5.0	20.0	0.5
Polyethylene.....					5.0
Sealing Strength, gms./in.....	33	150	¹ above 170	¹ above 170	¹ above 170

¹ (With these compositions, the sealing strength was so great that the paper to which the compositions were applied tore at the sealing strengths indicated, thus establishing that the sealing strengths of the compositions were above the readings obtained.)

In the above examples, the sealing strength was determined by the Standard Tappi method 642 S.M. 54, as measured in grams per inch, and the sealing strength readings were the average of three determinations. The paraffin wax had a melting point of 143° to 150° F., the microcrystalline wax had a melting point of 150° to 155° F., the partly oxidized polyethylene was AC-629 supplied by Semet Solvay Division of Allied Chemical & Dye Corp., New York city, having the following properties: average molecular weight about 2000; melting point 205-208° F.; viscosity (Saybolt furol seconds at 140° C., 30 cc. efflux) 40-50; color off-white; specific gravity 0.93; acid number 14-17; and saponification value 14-17; the polyethylene was DYNH, supplied by Bakelite Corporation and having a molecular weight of about 21,000.

Each of the wax coating compositions of the above examples was applied on both sides of the base sheets of paper of 30 lbs. per ream basis weight by conventional wax coating equipment in amount sufficient to give 15 lbs. of the total (both sides) dry wax film per ream of base sheet.

Each finished wrapper was employed for packaging a carton containing powdered milk, the marginal portions and the end-folds of the wrapper being heat-sealed using a conventional sealer, the platens of which were heated to 225° F. Slight pressure was applied between the hot platens for about 2 seconds, which was sufficient to produce a strong bond between the heat-sealed areas of the wrapper. The heat-sealed packages were stored at room temperature for a period of six months. At the end of this period, the bond was still very strong, and no delamination of the heat-sealed areas occurred.

For purposes of comparison, the procedures employed in the foregoing examples were repeated with the coating compositions containing unoxidized polyethylene DYNH, described above, as a substitute for and in the same amounts as the partly oxidized polyethylene.

The following Table III presents the results obtained from these tests.

Table III

	Ex. 1A	Ex. 2A	Ex. 3A	Ex. 4A	Ex. 5A
Paraffin wax.....		59.95	71.0	60.0	57.5
Microcrystalline wax.....	95.0	40.00	24.0	20.0	37.0
Polyethylene DYNH.....	5.0	0.05	5.0	20.0	5.5
Sealing Strength, gms./in.....	6.5	25.0	15.0	22.0	17.0

The compositions in the examples of Table III corresponding to the compositions of Table II have the same ordinal numbers, respectively, but are distinguished by the letter "A." The above results indicate that considerable improvements in sealing strengths were obtained when partly oxidized polyethylene was present in the coating composition, compared to those obtained in wax-polyethylene blends devoid of partly oxidized polyethylene.

A laminated sheet suitable as a composite wrapper, in which a superior heat-seal bond is provided between the adhesively secured sheets, can be made with the composition of this invention. For example, any suitable flexible sheet of paper can be strongly adhesively united to any other suitable flexible sheet, such as a sheet of metal foil, by coating the paper sheet on both sides with such com-

position, and then heat sealing the foil to such coated sheet in the manner described above. The composition on the coated side of the paper sheet which is not secured to the foil, enables heat-sealing of the composite wrapper about the goods. The composition of Example 3 is preferred for making such composite wrapper, and aluminum foil having a thickness of 0.0035 is preferred.

Although the heat-sealing of the sheets of the above examples was effected at 225° F. and the time during which the sheet was in contact with the heated platens was about 2 seconds, the platens could be heated to higher temperatures and the contact time correspondingly reduced. Thus, in commercial packaging operations it has been found to be practical to have the temperature of the platens as high as 360° to 440° F., but the contact time is then restricted to about one-half of a second.

The glossy, heat-sealable wax coating composition applied to at least one surface of the packaging sheet of this invention provides a coating film which is non-cohesive, non-tacky, and non-blocking at normal room temperature so that the sheet may be handled or shipped in roll form without any special precautions. The superior heat-sealing characteristics imparted by the blend of the wax and the partly oxidized polyethylene give as a result a highly satisfactory sheet possessing the desired feature of being capable of producing a bond at the heat-sealed areas of such exceptional strength that it will not break or delaminate during handling, shipping or storage of the packaged goods for a prolonged period of time. Furthermore, the sheet is flexible, has a very low moisture-vapor transmission rate, and good physical strength properties.

I claim:

1. A cellulosic packaging sheet having a coating composition on at least one surface thereof comprising as essential constituents (1) a wax, and (2) a minor proportion, based on the weight of wax, of partly oxidized polyethylene imparting enhanced sealing strength to such coating, said partly oxidized polyethylene resulting from the oxidation of polyethylene alone.

2. A waxed wrapper comprising a cellulosic base sheet having at least one entire surface thereof coated with a dry, flexible, non-blocking, heat-sealable film of a wax composition containing from 0.01 to 20% by weight based on said composition of a partly oxidized polyethylene, said film being capable of producing a strong bond at a heat-sealing temperature of said film, and said partly oxidized polyethylene resulting from the oxidation of polyethylene alone.

3. The wrapper of claim 2 wherein the wax composition comprises microcrystalline wax.

4. The wrapper of claim 2 wherein the wax composition comprises microcrystalline and paraffin waxes.

5. The wrapper as described in claim 2 wherein the amount of partly oxidized polyethylene is from 0.1 to 1% by weight of the composition.

6. The wrapper as described in claim 2 wherein the base sheet is a sheet of paper.

7. A composite packaging sheet comprising a sheet of paper, an aluminum foil, and an intermediate heat-sealed film adhesively uniting said paper sheet and foil, said film comprising essentially a wax composition containing from 0.01 to 20% by weight based on said composition of a partly oxidized polyethylene, said film being present in an amount sufficient to produce a strong bond resistant to delamination between said paper sheet and said foil at a heat-sealing temperature of said film, said partly oxidized polyethylene resulting from the oxidation of polyethylene alone.

8. In the process of making a heat-sealable waxed wrapper, the step which comprises coating at least one entire surface of a cellulosic base sheet with a flexible, non-blocking film of a wax composition containing from 0.01 to 20% by weight based on said composition of a partly oxidized polyethylene, the amount of applied wax composition being sufficient to produce a strong bond

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when the wrapper is heat-sealed, and said partly oxidized polyethylene resulting from the oxidation of polyethylene alone.

9. The process of claim 8 wherein the wax composition contains from 0.1 to 1% by weight of partly oxidized polyethylene.

10. A waxed wrapper comprising a paper sheet having at least one entire surface thereof coated with a dry, flexible non-blocking, heat sealable film of a wax composition including microcrystalline and paraffin waxes, and 0.1 to 1.0 percent by weight of a partly oxidized polyethylene, said partly oxidized polyethylene resulting from the oxidation of polyethylene alone and having an average molecular weight of about 500 to 30,000 with a measurable acid number of up to 25, and said film being capable of producing a strong heat sealed bond at a heat sealing temperature of said film.

11. The waxed wrapper of claim 10 in which the partly oxidized polyethylene has an average molecular weight of about 1000 to 5000 and an acid number of about 10 to 20.

12. The method of imparting enhanced sealing strength to a wax composition for coating a cellulosic packaging sheet which method comprises melting a wax, adding thereto a minor proportion, based on the weight of said wax, of partly oxidized polyethylene resulting from the oxidation of polyethylene alone, and stirring to dissolve said partly oxidized polyethylene in the wax.

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13. A paper packaging sheet having at least one surface thereof coated with a dry, flexible non-blocking coating of a wax composition containing 0.01 to 20 percent, based on the weight of the wax, of a partly oxidized polyethylene, said partly oxidized polyethylene resulting from the oxidation of polyethylene alone and having an average molecular weight of about 500 to 30,000 with a measurable acid number of up to 25.

14. A wrapping sheet material consisting of a cellulosic base sheet coated with a composition consisting essentially of a major proportion of a petroleum wax and a minor proportion of an oxidized polyethylene having an acid number of about 10 to 25.

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