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LAMINATED SHEET MATERIAL

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This invention relates to improved sheet materials and more particularly to coated and laminated sheet materials for packaging.

Many sheet materials have been developed for packaging which have a film of material either superficially adhered to the surface of a base sheet of paper, paper board, foil, regenerated cellulose, sheet metal, or the like, as a coating, or intercalated between two or more layers of any of such flexible base sheets as a laminant. The film has certain physical properties which alone or combined with properties of the base sheet provide a sheet material with certain functional characteristics. In packaging, for example, one of the most common films in use as a coating or a laminant are those comprised primarily of wax. The wax film provides a moisture and moisture vapor barrier, which makes the sheet material extremely useful in food packaging, and in other types of packaging where moisture is detrimental.

Wax coatings and laminants have comprised paraffin and microcrystalline waxes alone or in combination with wax compatible materials that modify the properties of the wax coating or add other functional properties to the sheet material. For example, paraffin wax coatings have been improved by the addition of rubber or polyisobutylene. Such coatings are heatsealing, flexible, stretchable, etc. Microcrystalline wax which has been used widely for laminating simply because of its adhesiveness, has been modified with ester gum, rosin esters, polyethylene, polyisobutylene, etc.

The art has continuously searched for modifiers or additives to improve the adhesive and flexing properties of wax films, particularly at low temperature. This latter requirement has become increasingly important with the growth of the frozen food industry. Paper and paper board laminated with microcrystalline wax will delaminate at temperatures of 10° F. to 50° F., depending on the wax used. Wax additives have been found which improve the adhesion to some degree, but these are usually high cost materials and require special blending. Flexibility has been obtained by adding plasticizers to wax, such as oil, but this has been at the sacrifice of seal strength. Though low temperature adhesion is particularly desirable in laminated sheets, it is also desirable in wax base coated sheets, particularly where the sheet is heatsealed. Frozen food carton overwraps are examples of sheets which must remain sealed at low temperature.

It is an object of this invention to provide a

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sheet material having a wax film, or wax-base film, either as a coating or as a laminant, which has improved adhesion to the sheet material, and still a further object is to provide a film of improved flexibility, film strength, and seal strength particularly at low temperatures. It is a further object of this invention to provide laminated sheet materials which will not delaminate at temperatures as low as 5° F. It is another object to provide heatsealable coated sheets having high seal strength at such temperatures. Other objects and advantages will be apparent from the following description of our invention.

Sheet materials of our invention have a film of a hydrocarbon wax which is substantially nonreactive with urea. The hydrocarbon wax is a novel wax of the type disclosed in a copending application of inventor, Rumberger Serial No. 110,892, filed August 17, 1949. Generally this wax is obtained by reacting a paraffin or microcrystalline petroleum wax with urea in the presence of a urea solvent to form a urea-wax complex with any of the reactive components of the starting wax. The urea-wax complex is separated from the nonreactive wax, as by filtration, thus a novel wax results which is substantially nonreactive with urea. This novel wax can be applied to sheet materials by conventional hot melt coating or waxing methods. These waxes are generally believed to comprise branched chain paraffins and cyclic compounds, and are substantially free from straight chain paraffins.

Laminated sheets of cellophane (regenerated cellulose) of our invention will not delaminate at temperatures as low as 5° F. or even below 0° F. in some cases. They are flexible at these temperatures hence do not crack. Cellophane laminated sheets using a wax or wax base laminant have never been available heretofore which would not delaminate and crack at such low temperatures. The poor adhesion of waxes to impervious sheets such as cellophane, foil, sheet metal and the like, has always presented a problem which is overcome by our sheet materials.

The wax films in our sheet materials provide as good a moisture and moisture-vapor barrier as previously known films, and further provide as good a barrier in a flexed sheet as in a flat sheet. With prior sheet materials, because of the brittleness of the wax film this was never the case, particularly at low temperatures. Since sheet materials of our invention find their greatest use as container walls, either in the form of sealed wrappers, bags, cartons, cans etc. where

the sheets are bent and formed, this improved property is very important.

The following specific examples will illustrate the superior properties of sheet materials of our invention.

EXAMPLE 1

Various microcrystalline waxes manufactured by the indicated companies were treated with urea and water. In each case the urea-wax ratio was about 3 parts urea to 1 part wax which was sufficient to remove all of the reaction wax. The amount of water used was about 2% based on the weight of the urea. The wax was first melted by heating to about 200° F. before the urea and water were added. The mixture was then stirred and held at about 170° F. to 190° F. until a white precipitate formed. This was the urea-reactive wax complex. The mixture was filtered, removing thereby the complex and any non-reacted urea. The nonreactive wax (N-wax) filtrate was heated to drive off any water and then was ready for coating.

Two sheets of moisture proof cellophane were laminated with about 15 lbs. per ream (24 x 36—500 sheets) of each type of N-wax by hot melt application, as well as each type of wax.

TABLE I

Flexibility and seal strength of wax laminated cellophane

Description of Laminant	Yield percent	M. P. °F.	Flexibility °F.	Seal Strength gms. per inch at—			
				95°F.	73°F.	45°F.	0°F.
Quaker State Micro:							
Regular		145	13	520	750	800	50
N-wax	70	130	−2	309	565	689	1,279
Bareco Oil Co.:							
170/75 Regular		171	75		10		
N-wax	60	142	−2	285	605	970	874
180/85 Regular		180	84		0		
N-wax	50	158	5		628	430	200
190/95 Regular		189	97		0		
N-wax	30	170	15		772	131	43
Socony-Vacuum Magnowax:							
Regular		160	29	440	759	865	150
N-wax	86	143	1	358	726	890	175

In the table the values for flexibility were obtained by flexing a wax strip 0.03" thick at decreasing temperatures and noting the temperature at which the strip cracked. Melting points were determined by A. S. T. M. method D87–42. Seal strength is the force in gms. required to separate a laminated sheet 1" wide at the temperature indicated.

From Table I it is readily apparent that in every case sheets made from N-wax are superior to those made from the corresponding commercial microcrystalline wax. It is further seen that only the sheets laminated with N-waxes have both low temperature flexibility and seal strength, and hence are superior to sheets made from the waxes having components reactive with urea. Even Magnowax which contains only about 14% of material which is reactive with urea showed a marked improvement in flexibility after removal of this material.

The N-waxes used in Example 1 were prepared by treating the original wax with an excess of urea. These N-waxes are therefore characterized by the fact that they are substantially free from normal paraffins naturally occurring in microcrystalline wax some of which would melt above 150° F. Since, however, removal of any

reactive material improves the original wax, there may be instances where only a partial removal of the higher melting paraffins with urea will produce an improved wax film as a coating or laminant.

In this regard we have found that sheet materials having wax films wherein N-wax is an additive have unique and unexpected properties. Many sheet materials are coated with paraffin wax having no components melting above 150° F., e. g., bread wrappers, and wax wrapping papers. We have found that a minor portion of N-wax added to the paraffin wax will not only improve such a sheet as to flexibility and heat-sealing strength, but will also increase the blocking temperature.

EXAMPLE 2

A 25# basis weight sulfite base sheet was coated with 4# per ream of paraffin wax modified with 10% of the N-wax from Bareco 170/175 used in Example 1 which was de-oiled which N-wax has a melting point of 155° F. De-oiling was carried out by crystallizing out and separating any wax from an ethylene dichloride solution, 1 part wax to 10 parts dichloride, at 0° F. The crystallization was repeated. The coated sheets were tested for blocking temperature and seal strength and the results compared to a straight paraffin coated sheet.

TABLE II

Blocking temperature and seal strength of wax coated sheets

Description of Coating	Blocking Temp. °F.	Seal Strength gms. per inch at 73°F.
Paraffin	90–95	80–100
Paraffin plus N-wax	110–115	170–200

Where special conditions demand properties not present in our sheet materials when using N-wax alone it can be modified with conventional wax modifiers. For example, the melting point of the laminant may be raised by adding high molecular weight polyisobutylene, rubber, polyethylene, butyl rubber, and the like. In order to take maximum advantage of the improved flexibility of our N-wax laminated sheet we prefer to add branched chain polyethylene or polyisobutylene. With these branched chain modifiers we can get flexibility in our sheet materials at temperatures below 5° F. and yet have a laminant that will not flow at temperatures as high as 150° F.

Particularly desirable applications for our sheet materials are wax coated cartons which are subject to refrigeration. Paper milk bottles for example are generally heavily coated with wax to prevent leakage. The heavy coating tends to break or flake off under refrigeration causing wax flakes to fall into the milk. Bottles made of our sheet material, that is sheets coated with N-wax, or even a paraffin wax modified with N-wax, would obviate this problem because of the improved cohesion and adhesion of the coating as evidenced by seal strength. Another use of N-wax or such modified paraffin wax is in making frozen food cartons. So-called "tin cans" are lined with wax for certain applications, e. g., beer cans. Here again the low temperature properties of our coatings are very desirable. The improved coated sheet of Example 2 is excellent as a bread wrapper because of the high blocking temperature together with improved seal strength.

Many other variations and modifications in our sheet material will be obvious to those skilled in the art and no limitations are intended by the above examples and illustrations except such as are contained in the following claims.

We claim:

1. A sheet material comprising a base sheet and a superficial film of wax on said base sheet which wax film is substantially nonreactive with urea.

2. A sheet material comprising a base sheet and a superficial film of a wax, said wax film consisting of a wax substantially free from normal paraffins.

3. A laminated sheet material comprising at least two base sheets and a film of wax intercalated therebetween which wax is substantially nonreactive with urea.

4. A container wall comprising at least two sheets of material adhered together by a film of wax intercalated therebetween, which wax is substantially free from normal paraffins.

5. An improved sheet material for milk bottles comprising a paperboard having a superficial film of wax thereon which wax is substantially nonreactive with urea.

6. A laminated sheet material comprising at least two sheets of regenerated cellulose adhered together by a film of wax substantially free from normal paraffins.

7. A coated sheet material comprising a base sheet and a superficial film of a wax comprising paraffin wax to which has been added a minor portion of a wax substantially free from normal paraffins.

8. A container wall comprising a base sheet having superficial wax film thereon, said wax film comprising a homogeneous wax which is substantially free from normal paraffin.

9. A sheet material comprising a base sheet having superficial wax film thereon, said wax film comprising a homogeneous wax which is substantially free from normal paraffin.

10. A sheet material comprising a base sheet and a superficial film of a wax, said wax film comprising a microcrystalline wax substantially free from normal paraffins.

11. A coated sheet material comprising a base sheet and a superficial film of a wax comprising paraffin wax having no components melting in excess of 150° F. to which has been added a minor portion of a de-oiled microcrystalline wax substantially free from normal paraffins.

12. A sheet material comprising a base sheet and a superficial film of wax, said wax film comprising a mixture of normal and iso-paraffinic wax components wherein the highest melting of said components is iso-paraffinic.

13. A coated sheet material comprising a base sheet and a superficial film of substantially oil-free paraffin wax having no components melting in excess of 150° F. to which has been added a minor portion of a microcrystalline wax substantially free from normal paraffins.

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