Abstract: This invention provides the use of a water vapor barrier as coating for paper or cardboard as substrate for lowering the water vapor transmission rate (WVTR) of the substrate under tropical conditions, for example 37.8°C and 90% relative humidity, wherein the barrier improvement factor (BIF), which is the ratio of WVTR uncoated substrate/WVTR coated substrate, is at least 80.
Use of a high performance water vapor barrier coating for paper under tropical conditions

The present invention refers to the use of a water vapor barrier as coating for paper or paperboard as substrate for lowering the water vapor transmission rate (WVTR) of the substrate under tropical conditions, for example 37.8°C and 90% relative humidity, wherein the barrier improvement factor (BIF), which is the ratio of WVTR uncoated substrate/WVTR coated substrate, is at least 80.

The application of coatings to improve water vapor barrier characteristics of paper or paperboard is well known in the art. Such water-vapor barriers can be polymers or mixtures of polymers and other ingredients, for example copolymers based on styrene and acrylates in combination with waxes are known. The use of paper or paperboard coated with water vapor barriers, under tropical conditions is also known. Yet, there is still a need for improved performance with regard to water vapor transmission rates of coated paper or paperboard under tropical conditions.

Therefore, it is an object of the present invention to provide a very high barrier to water vapor on paper or paperboard as substrate, while the substrate still has acceptable blocking behaviour and still forms film easily, in a conventional paper coating operation.

This object is solved by the use of a water vapor barrier according to claim 1.

The use of the present invention of a water vapor barrier as coating for paper or paperboard as substrate for lowering the water vapor transmission rate (WVTR) of the substrate under tropical conditions, is characterized in that the barrier improvement factor (BIF), which is the ratio of WVTR uncoated substrate/WVTR coated substrate, is at least 80.

The water vapor barrier can be any water vapor barrier comprising at least one polymer and a wax.

Preferably, the polymer is an acrylic polymer. Acrylic polymers can be polymers formed from at least one acrylic monomer and optionally other ethylenically unsaturated monomers. The term acrylic polymer shall also encompass acrylic core shell polymers.
Examples of acrylic monomers are (meth)acrylic acid and alkali or ammonium salts thereof, (meth)acrylamide, (meth)acrylonitrile, alkyl (meth)acrylates such as ethyl (meth)acrylate, butyl (meth)acrylate, hexyl (meth)acrylate or 2-ethylhexyl (meth)acrylate, di(alkylamino)alkyl (meth)acrylates such as dimethylaminooethyl acrylate or diethylaminooethyl acrylate and amides formed from di(alkylamino) alkylamines and (meth)acrylic acid.

Examples of other ethenically unsaturated monomers are styrene monomers such as styrene, vinyl monomers such as vinyl alcohol, vinyl chloride or vinyl acetate, olefin monomers such as ethylene, propylene, butadiene or isoprene, and maleic monomers such as maleic acid, maleic anhydride or maleimide.

Preferred acrylic polymers are formed from at least one acrylic and one styrene monomer.

More preferably, the polymer is an acrylic core shell polymer. Acrylic core shell polymers comprise an acrylic polymer and a stabilizing polymer, wherein the acrylic polymer is formed in the presence of the stabilizing polymer.

The acrylic polymer of the core shell polymer can have a weight average molecular weight (Mw) of from 75'000 g/mol to 350'000 g/mol, preferably from 80'000 g/mol to 200'000 g/mol, more preferably from 90'000 g/mol to 150'000 g/mol, as determined by gel permeation chromatography, and a glass transition temperature (Tg) of below 50 °C, preferably of below 30 °C, more preferably of below 20 °C.

Preferably, the acrylic polymer of the core shell polymer is formed from at least one acrylic monomer and at least one styrene monomer. The weight ratio of styrene monomer/acrylic monomer of the acrylic polymer of the core shell polymer can be from 1/99 to 99/1, preferably from 20/80 to 80/20, more preferably from 50/50 to 60/40. Examples of acrylic polymers of the core shell type polymer are copolymers formed from 50/50 (w/w) styrene/butyl acrylate, from 55/45 (w/w) styrene/butylacrylate, from 60/40 (w/w) styrene/2-ethylhexyl acrylate, from 30/30/40 (w/w/w) styrene/methyl methacrylate/2-ethylhexyl acrylate and from 55/45 (w/w) styrene/2-ethylhexyl acrylate.

A preferred acrylic polymer of the core shell polymer is 55/45 (w/w) styrene/2-ethylhexyl acrylate having a weight average molecular weight (Mw) of around 100'000 g/mol, as
determined by gel permeation chromatography, and a glass transition temperature \( (T_g) \) of about 15\(^\circ\)C.

Any suitable stabilizing polymer can be used. Preferably, the stabilizing polymer has a weight average molecular weight \( (M_w) \) of from 2'000 g/mol to 50'000 g/mol, more preferably from 3'000 g/mol to 20'000 g/mol, most preferably from 6'000 g/mol to 10'000 g/mol, and a glass transition temperature \( (T_g) \) of from 75 to 150\(^\circ\)C, preferably of from 85 to 120\(^\circ\)C, more preferably of from 95 to 110\(^\circ\)C. Preferably, the stabilizing polymer is also an acrylic polymer.

Examples of stabilizing polymers are 65/35 (w/w) styrene/ acrylic acid, ammonium salt; 43/43/14 (w/w/w) isobutyl methacrylate/methyl methacrylate/acrylic acid, ammonium salt; 43/43/14 (w/w/w) butyl acrylate/methyl methacrylate/acrylic acid, ammonium salt; and 80/20 (w/w) ethylene/acrylic acid, ammonium salt.

An example of a stabilizing polymer is 65/35 (w/w) styrene acrylic acid, ammonium salt copolymer having a weight average molecular weight \( (M_w) \) of 8'000 g/mol, as determined by gel permeation chromatography, and a glass transition temperature \( (T_g) \) of about 105\(^\circ\)C.

The weight ratio of stabilizing polymer/acrylic polymer of the core shell polymer is 10/90 to 90/10. Preferably, it is 10/90 to 60/40. More preferably, it is 20/80 to 50/50. Most preferably, it is 25/75 to 40/60.

An example of an acrylic core shell polymer comprises 70 weight parts 55/45 (w/w) styrene/2-ethylhexyl acrylate copolymer having \( M_w \) of 100'000 g/mol and \( T_g \) of about 15\(^\circ\)C as acrylic polymer, and 30 weight parts 65/35 (w/w) styrene/acrylic acid, ammonium salt copolymer having \( M_w \) of 8'000 g/mol and \( T_g \) of about 105\(^\circ\)C as stabilizing polymer.

The acrylic core shell polymer can be prepared by polymerizing the monomers forming the acrylic polymer in the presence of the stabilizing polymer and a suitable initiator. Preferably, the stabilizing polymer and part of the initiator is charged to a vessel and the remaining initiator and the monomers are fed to the vessel. Usually, the polymerization is performed in water as solvent. The initiator can be any suitable initiator such as a peroxide, a persulfate, an azo compound, a redox couple or mixtures thereof. Preferably, the initiator is a persulfate, more preferably, it is ammonium persulfate. Preferably, the molar ratio of initiator or initiators/
monomer or monomers is between 0.0001 % and 1%.

The wax can be any kind of suitable wax or wax mixture. Examples of wax are natural wax, chemically modified wax and synthetic wax.

Examples of natural wax are vegetable wax such as carnauba wax or candilla wax, animal wax such as bee wax or wool wax, and mineral wax such as paraffin and ceresin.

An example of a chemically modified wax is hydrated jojoba wax. Examples of synthetic waxes are polyethylene wax and polyethyleneglycol wax.

Preferably, the wax is a natural wax, a synthetic wax or a mixture thereof. A preferred wax is a mixture of paraffin wax and carnauba wax. An aqueous emulsion thereof is commercially available as "Aquabead 525E" from Micropowders, Inc. (USA). Another preferred wax is a mixture of paraffin and polyethylene. An aqueous emulsion thereof is commercially available as "Michem 60233" from Michelman, Inc. (USA).

The weight ratio of the polymer and the wax can range from 1/99 to 99/1, preferably from 50/50 to 95/5, more preferably from 70/30 to 90/10, most preferably from 75/25 to 85/15.

The coating weight of the water vapor barrier can range from 0.1 to 20 g/m² on the paper or paperboard, preferably from 4 to 18 g/m², more preferably from 6 to 16 g/m², most preferably from 11 to 14 g/m². The values refer to the weight of the barriers after drying.

The total amount of the polymer and the wax in the water vapor barrier after drying (coating) ranges from 50 to 100% by weight based on the weight of the water vapor barrier after drying, preferably from 80 to 100%, more preferably from 90 to 100%, most preferably from 95 to 100%.

Almost any paper or paperboard can be used. Preferred paper substrates are Vegetable Parchment Paper or Candy Wrap Paper.
Vegetable Parchment Papers are made from a paper of pure cellulose, treated with sulfuric acid. The acid treatment swells the fibers and a homogenous film is formed. Typical basis weights of such papers range from 40-200 g/m$^2$.

Candy Wrap Paper can also be called twist paper and is typically made with kraft paper and range in basis weights from 30-40 g/m$^2$. Such papers are highly opaque due to presence of titanium dioxide pigment, either as a filler in the bulk of the paper, or on the surface.

Commercially available examples of vegetable parchment are Sulpack available from Ahlstrom Corporation of Helsinki, Finland, Pergamenata, sold by Fedrigoni Cartiere Spa of Verona, Italy, and Virtual, sold by CTI Paper of Sun Prairie, Wisconsin, USA.

Commercially available examples of Candy Wrap Paper are Ascoflex, available from Ahlstrom Corporation of Helsinki, Finland, and Twistlux from Cham-Tenero Paper Mills, Inc., of Cham, Switzerland.

Preferred papers are Sulpack (120 g/m$^2$) and Ascoflex (40 g/m$^2$), both available from Ahlstrom Corporation of Helsinki, Finland.

The paper or paperboard is coated with the water vapor barrier by methods known in the art. The water vapor barrier can be applied in form of a solution, emulsion or dispersion to one side of the paper or paperboard. Preferably, it is applied in form of an aqueous emulsion, more preferably, in form of an aqueous emulsion having a solid content in the range of from 1 to 60%, more preferably of from 30 to 55%. The water vapor barrier can be applied by coating applications known in the art such as a bar coater application, rotation application, spray application, curtain application, dip application, air application, knife application, blade application, roll application or film press. Bar coater or film press are preferred. After application of the water vapour barrier, usually in form of an aqueous emulsion, the barrier is dried. Drying can be accomplished by either contact or contact-less drying or through a combination of several methods. Examples of contact-less drying are forced hot air drier or Infra-Red drier, whereas examples of contact drying are drum drier. The water vapor barrier can be applied to both sides of the paper. However, preferably, it is only applied to one side of the paper.
Preferably, the water vapor barrier is applied in the form of an aqueous emulsion having a solid content in the range of 5 to 80% by weight based on the weight of the emulsion, more preferably in the range of from 20 to 60%, most preferably in the range of from 30 to 50%.

Tropical conditions refer to temperatures well above 30°C and a high relative humidity. High relative humidity can be 60 to 99% relative humidity, preferably 70 to 95% relative humidity, more preferably 75 to 90% relative humidity. The temperature can be in the range of from 30 to 60°C, preferably, from 30 to 45°C, more preferably, from 35 to 45°C.

The water vapor transmission rate (WVTR) of paper is the mass of water vapor transmitted per unit time per unit area from one face of the paper to the other. The barrier improvement factor (BIF) is the ratio of WVTR uncoated substrate/WVTR coated substrate. The higher the barrier improvement factor (BIF) the more efficient is the barrier against transmission of water vapor.

The water-vapor transmission rates (WVTR) used to determine the barrier improvement factor (BIF) are measured using TAPPI method T 464 om-95, which is a method for the gravimetric determination of the water vapor transmission rate (WVTR) of a paper at 37.8°C with an atmosphere of 90% relative humidity on one side and a desiccant (approaching 100% relative humidity) on the other. The coated papers are conditioned for 24 hours.

The barrier improvement factor (BIF) is at least 80, preferably, it is at least 90, more preferably, it is at least 100, most preferably, it is at least 125. There is no particular restriction to the upper limit, but barrier improvement factors (BIF) of less than 250, preferably less than 200, are preferred.

The use of a water vapor barrier as coating for paper or paperboard as substrate for lowering the water vapor transmission rate (WVTR) of the substrate under tropical conditions, wherein the barrier improvement factor (BIF), which is the ratio of WVTR uncoated substrate/WVTR coated substrate, is at least 80, has the advantage that a very efficient water vapor barrier is provided for this specific conditions. This particular good performance of the barrier is achieved at very low coat weights, for example at coat weights of 11 g/m². Further, paper sheets coated with the water vapor barrier do not block and form films easily.
Examples

Example 1:

Example 1: Preparation of an aqueous emulsion of a core shell polymer

Butyl acetate (250 g) is charged to a reactor and heated to reflux (125°C). tert-Butyl perbenzoate (7.8 g) is added to the reactor. A monomer feed consisting of styrene (162.5 g) and glacial acrylic acid (87.5 g) is prepared. An initiator feed consisting of tert-butyl-perbenzoate (23.4 g) is prepared. The monomer feed is added to the reactor within 5 hours and the initiator feed is added to the reactor within 5.5 hours. Once the feeds are completed, the reaction mixture is held for a further 1 hour at 125°C. A mixture of 20% by weight aqueous ammonia (100 g) and water (700 g) is added to the reactor whilst distilling off butyl acetate. The distillate is split and the water returned to the reactor and the butyl acetate to the receiver. The temperature of the reaction mixture falls to 93°C during distillation and rises to 100°C when all the butyl acetate has been removed. When distillation is complete, the reaction mixture is cooled to below 40°C, the obtained solution of 65/35 (w/w) styrene/acrylic acid, ammonium salt is adjusted to 25% by weight solid content and pH 9.0.

The 25% by weight aqueous solution of styrene/acrylic acid, ammonium salt copolymer (576 g) and water (71 g) is charged to a reactor, heated to 85°C and degassed with nitrogen for 30 minutes. Ammonium persulfate (0.5 g) is added. A monomer feed consisting of styrene (184.8 g) and 2-ethylhexyl acrylate (151.2 g) is prepared. An initiator feed consisting of ammonium persulfate (1.5 g) and water (15.0 g) is prepared. The monomer feed is added to the reactor within 3 hours and the initiator feed is added to the reactor within 4 hours. The temperature of the reaction mixture is kept at 85°C during polymerisation. Once the feeds are completed, the contents is held for a further 1 hour at 85°C before being cooled to below 40°C and Acidid 4DLG, a biocide containing chlorinated and non-chlorinated methyl isothiazolones, (0.9 g) is added.

The obtained core shell polymer consists of 70 weight parts 55/45 (w/w) styrene/2-ethylhexyl acrylate copolymer having $M_w$ of 100'000 g/mol and $T_g$ of about 15°C and of 30 weight parts 65/35 (w/w) styrene/acrylic acid, ammonium salt copolymer having $M_w$ of 8'000 g/mol and $T_g$ of about 105°C. The aqueous emulsion of the core shell polymer has a solid content of about 46% (w/w), a pH of 8.5 and a viscosity at 25°C (Brookfield 20 rpm) of 700 mPa x s.
Example 2: Preparation of a water-vapor barrier coating composition
The aqueous emulsion of the core shell polymer of example 1 and "Aquabead 525E", which is commercially available by Micro Powders Inc (USA) and which is an aqueous emulsion of a mixture of refined paraffin wax (CAS No. 63231-60-7) and Carnauba wax (CAS No. 8015-86-9), are mixed under light agitation to obtain a water-vapor barrier coating composition, which is an aqueous emulsion of a 80/20 (w/w) mixture of the core shell polymer of example 1 and the wax mixture of "Aquabead 525E". The obtained water-vapor barrier coating composition has a solids content of approximately 40% (w/w), a pH of 8.5 to 9.5 and a viscosity at 25°C (Brookfield 20 rpm) of 50 to 300 mPa s.

Example 3: Coating of paper with the water-vapor barrier coating composition of example 2
Sulpack (basis weight 120 g/m²), a Vegetable Parchment Paper commercially available from Ahlstrom Corporation, Helsinki, Finland, is coated with the water-vapor barrier coating composition of example 2 on the back side of the basestock using a hand drawdown coater with Meyer rods, and dried using a contact-less laboratory dryer (infrared and hot air at 130°C) to yield coatings having a dry coat weight of 5, 8, 11 and 14 g/m², respectively.

Example 4: Coating of paper with the water-vapor barrier coating composition of example 2
Example 3 is repeated except that Ascoflex (basis weight 40 g/m²), a Candy Wrap Paper commercially available from Ahlstrom Corporation, Helsinki, Finland, is used instead of Sulpack.

Example 5: Measurement of water-vapor transmission rate (WVTR)
The water-vapor transmission rate (WVTR) is measured using TAPPI method T 464 om-95. In the following, the test is briefly described: The coated paper sheets of examples 3 and 4 are placed on a test dish having a desiccant placed in the base with the uncoated side of the paper sheets facing the desiccant. The space between the edges of the paper and the test dish is sealed with wax. The test dish is placed in a testing room maintained at 37.8°C and 90% relative humidity with air continuously circulating over the exposed coated side of the paper sheets for 24 hours. The weight of the assembly is measured before and after conditioning. The results for the WVTR values are the average of three measurements. The barrier improvement factor (BIF) is defined as WVTR uncoated paper/WVTR coated paper.
<table>
<thead>
<tr>
<th>Coat weight [g/m²]</th>
<th>Vegetable Parchment Paper</th>
<th>Candy Wrap Paper</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>WVTR [g/(m² x day)]</td>
<td>BIF</td>
</tr>
<tr>
<td>0</td>
<td>2324</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>94</td>
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<td>72.6</td>
</tr>
<tr>
<td>11</td>
<td>18</td>
<td>129.1</td>
</tr>
<tr>
<td>14</td>
<td>18</td>
<td>129.1</td>
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</table>

Table 1: Water vapor transmission rates (WVTR) for Vegetable Parchment Paper and Candy Wrap Paper coated with the water vapor barrier coating composition of example 2.

It can be seen that a barrier improvement factor (BIF) of at least 80 is reached with 11 g/m² coat weight when using Vegetable Parchment Paper and Candy Wrap Paper as base paper. A barrier improvement factor (BIF) of at least 100 is reached with 11 g/m² coat weight when using Vegetable Parchment Paper and with 14 g/m² coat weight, when using Candy Wrap Paper. Thus, very high barrier improvement factors (BIF) can be obtained at very low coat weights.

Example 6: Measurement of Cobb (900 seconds) values
The Cobb value (900 seconds) is measured using TAPPI Test Method T441 om-98. The Cobb (900 seconds) value refers the mass of water adsorbed per unit area of paper after 900 seconds.

<table>
<thead>
<tr>
<th>Coat weight [g/m²]</th>
<th>Vegetable Parchment Paper</th>
<th>Candy Wrap Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cobb Value (900 seconds) [g/m²]</td>
<td>Cobb Value (900 seconds) [g/m²]</td>
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<tr>
<td>0</td>
<td>81</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>16</td>
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<tr>
<td>8</td>
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<tr>
<td>11</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>14</td>
<td>0.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Table 2: Cobb Values for Vegetable Parchment Paper and Candy Wrap Paper coated with the water vapor barrier coating composition of example 2.

The Cobb (900 seconds) Values are extremely good. Cobb (900 seconds) Values of below 1 g/m² at a coat weight of 8 g/m² or higher can be obtained.

**Example 7: Blocking test**

A blocking test is performed in analogy to ASTM D918-99. In the following the test is briefly described: Eight samples (30 x 40 mm) are cut from the coated paper sheets of examples 3 and 4. The samples are stacked in the following order: face to face, face to back, back to back, interleaving material, face to face, face to back, back to back, and conditioned at 60°C, 50% relative humidity and 3.4 kPa for 21 hours.

After conditioning, the paper sheets are examined by slipping or peeling the sheets apart and rated for blocking resistance as follows: no blocking, slight blocking and considerable blocking.

"No blocking" means that there is no adhesion or coadhesion between contiguous surfaces and the surfaces slide freely upon one another. The surfaces of the papers are also not marred when sheets are separated.

"Slight blocking" means that there is a slight adhesion. Adjacent surfaces do not slide freely, and upon separation of the sheets the surfaces show an occasional evidence of slight marring. "Slight blocking" is classified as a "pass" by the ASTM D918-99 method.

"Considerable blocking" means that there is adhesion or coadhesion of contiguous surfaces. The layers may be separated with difficulty and surfaces will be definitely marred or partially destroyed upon separation.
Table 3: Blocking behaviour of Vegetable Parchment Paper and Candy Wrap Paper coated with the water vapor barrier coating composition of example 2.

All coated papers passed the ASTM Blocking test. Only the sheets having a coat weight of 11 g/m² or higher for Vegetable Parchment Paper, respectively, of 8 g/m² or higher for Candy Wrap Paper show a slight blocking tendency.
Claims

1. Use of a water vapor barrier as coating for paper or paperboard as substrate for lowering the water vapor transmission rate (WVTR) of the substrate under tropical conditions, wherein the barrier improvement factor (BIF), which is the ratio of WVTR uncoated substrate/WVTR coated substrate, is at least 80.

2. The use of claim 1 wherein the water vapor barrier comprises at least one polymer and a wax.

3. The use of claim 1 or 2 wherein the polymer is an acrylic polymer.

4. The use of any of claims 1 to 3 wherein the coating weight of the water vapor barrier ranges from 0.1 to 20 g/m².

5. The use of any of claims 1 to 4 wherein the substrate is a Candy Wrap Paper or a Vegetable Parchment Paper.

6. The use of any of claims 1 to 5, wherein the barrier improvement factor (BIF) is at least 90.

7. The use of claim 6, wherein the barrier improvement factor (BIF) is at least 100.
# INTERNATIONAL SEARCH REPORT

## A. CLASSIFICATION OF SUBJECT MATTER

**INV. D21H21/14 D21H19/72**

According to International Patent Classification (IPC) or to both national classification and IPC:

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched:

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Relevant to claim No.</th>
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* Special categories of cited documents:
  - **A** document defining the general state of the art which is not considered to be of particular relevance
  - **E** earlier document but published on or after the international filing date
  - **L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - **O** document referring to an oral disclosure, use, exhibition or other means
  - **P** document published prior to the international filing date but later than the priority date claimed
  - **T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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  - **&** document member of the same patent family

Date of the actual completion of the international search: 22 October 2007

Date of mailing of the international search report: 30/10/2007

Name and mailing address of the ISA/

Authorized officer:

Naes und, Per

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