(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 777 934 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
17.09.2014 Bulletin 2014/38

(21) Application number: **12847115.8**

(22) Date of filing: **09.11.2012**

(51) Int Cl.:
B32B 29/00 *(2006.01)* ***B65D 65/40*** *(2006.01)*

(86) International application number:
PCT/JP2012/079176

(87) International publication number:
WO 2013/069788 (16.05.2013 Gazette 2013/20)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **10.11.2011 JP 2011246162**
11.01.2012 JP 2012002670
11.01.2012 JP 2012002671
23.01.2012 JP 2012011279
17.02.2012 JP 2012032254
28.05.2012 JP 2012120377

(71) Applicant: **Nippon Paper Industries Co., Ltd**
Kita-ku
Tokyo 114-0002 (JP)

(72) Inventors:
- **OKAMOTO Masashi**
Tokyo 114-0002 (JP)
- **NODA Takaharu**
Tokyo 114-0002 (JP)
- **NAKAYAMA Takeshi**
Tokyo 114-0002 (JP)
- **KATO Masatsugu**
Tokyo 114-0002 (JP)
- **CHATANI Akinobu**
Tokyo 114-0002 (JP)
- **FUKUNAGA Masaaki**
Tokyo 114-0002 (JP)
- **SATO Yukiko**
Tokyo 114-0002 (JP)
- **HAYAKAWA Junichi**
Tokyo 114-0002 (JP)

(74) Representative: **Grünecker, Kinkeldey,**
Stockmair & Schwanhäusser
Leopoldstrasse 4
80802 München (DE)

(54) BARRIER PAPER PACKAGING MATERIAL

(57) A paper based barrier packaging material simultaneously having both of an excellent gas barrier property and an excellent water vapor barrier property, the paper based barrier packaging material including a plurality of coating layers formed on a paper base material, wherein the coating layers include a water vapor barrier layer on the paper base material and a gas barrier layer formed on the water vapor barrier layer, and the coating layers are each formed by using as a binder resin a water soluble polymer or a water suspendable polymer.

EP 2 777 934 A1

Description

Technical Field

[0001] The present invention relates to a paper barrier material used for a food packaging material, a food container, a food cup or the like.

Background Art

[0002] It is important to impart a gas barrier property (in particular, an oxygen barrier property) to a paper packaging material for the purpose of protecting packaged various products from the degradation due to gas, such as oxidation due to oxygen.

[0003] Paper packaging materials have hitherto been provided to which a gas barrier property is imparted by laminating a metal foil or a film on a paper base material. Examples of the material forming the barrier layer include: a metal foil or a metal vapor deposited film made of a metal such as aluminum; a resin film made of polyvinyl alcohol, ethylene-vinyl alcohol copolymer, polyvinylidene chloride or polyacrylonitrile; a film coated with such a resin; and a ceramic vapor-deposited film which is further coated with a vapor-deposited inorganic oxide such as silicon oxide or aluminum oxide.

[0004] In addition to the foregoing, as paper packaging materials with a gas barrier property imparted thereto, paper gas barrier materials having a gas barrier layer made of a water soluble polymer and an inorganic layered compound have been disclosed in Patent Literature 1 and Patent Literature 2. A paper gas barrier material in which a barrier layer made of a specific vinyl alcohol-based polymer is provided on a coating layer is disclosed in Patent Literature 2.

[0005] It is also important to impart a waterproofness (in particular, a water vapor barrier property) to a paper packaging material for the purpose of protecting various products to be packaged from the degradation due to water vapor.

[0006] A paper packaging material has been proposed in which a water vapor barrier property is imparted by extrusion lamination of or pasting of a resin film excellent in water vapor barrier property onto a paper base material, or alternatively, by extrusion lamination of or pasting of, for example, a film coated with such a resin excellent in water vapor barrier property on a paper base material. A packaging paper having a moistureproof layer composed of a synthetic resin latex, a wax and inorganic fine particles is disclosed in Patent Literature 3.

[0007] Moreover, as a packaging material in which both of a gas barrier property and a water vapor barrier are imparted to a paper packaging material, a packaging material is known in which a resin having a gas barrier property and a resin having a water vapor barrier property are laminated on a paper base material.

Citation List

Patent Literature

[0008]

Patent Literature 1: Japanese Patent Laid-Open No. 2009-184138
Patent Literature 2: Japanese Patent Laid-Open No. 2003-094574
Patent Literature 3: Japanese Patent Laid-Open No. 2005-162213

Disclosure of the Invention

Technical Problem

[0009] A packaging material in which by extrusion lamination of a resin having a gas barrier property and a resin having a water vapor barrier property on a paper base material (base paper), both barrier layers are formed on the paper base material has a problem that the packaging material cannot cope with the required quality because the types and the like of the resins capable of being extrusion laminated are limited. A packaging material in which multilayers are laminated on a paper base material in order to establish the compatibility between the gas barrier property and the water vapor barrier property finds difficulty in recycling of the paper and the laminated layers. The multilayer laminated packaging material also offers a problem such that the carbon dioxide emission amount in the production thereof is large. Moreover, in the multilayer laminated packaging material, specific adhesive resins are sometimes required to be used between the respective laminated layers, to offer another problem that the production of the multilayer laminated packaging material is cumbersome.

[0010] On the other hand, in a packaging material in which a paper base material is coated with a resin having a gas barrier property and a resin having a water vapor barrier property, the types and the like of the usable resins are scarcely

limited, and various required qualities can be coped with. However, a packaging material to which both of the gas barrier property and the water vapor barrier property are imparted, for example, in the case where the moistureproof layer of Patent Literature 3 is disposed on the packaging material having a gas barrier property of Patent Literature 1 or Patent Literature 2, offers a problem that although a satisfactory water vapor barrier property is obtained, no gas barrier property is obtained. Additionally, in the case where the gas barrier layer of Patent Literature 1 or Patent Literature 2 is disposed on a moistureproof paper having the moistureproof layer of Patent Literature 3, the surface tension of the moistureproof layer, hence the gas barrier layer is not uniformly formed due to repellency, and hence no sufficient gas barrier property can be obtained.

[0011] Accordingly, the present invention takes as its object the provision of a paper based barrier packaging material simultaneously having both of an excellent gas barrier property and an excellent water vapor barrier property.

Solution to Problem

[0012] The main constitution of the present invention is as follows.

1. A paper based barrier packaging material including a plurality of coating layers disposed on a paper base material, wherein the plurality of coating layers includes a water vapor barrier layer on the paper base material and a gas barrier layer formed on the water vapor barrier layer; and in each of these coating layers, a water soluble polymer or a water suspendable polymer is used as a binder resin.
2. The paper based barrier packaging material according to 1., wherein the water vapor barrier layer and the gas barrier layer are different in coating material composition from each other.
3. The paper based barrier packaging material according to 2., wherein the binder resin of the water vapor barrier layer is a styrene-butadiene-based synthetic resin.
4. The paper based barrier packaging material according to 3., wherein the binder resin in the water vapor barrier layer includes kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more.
5. The paper based barrier packaging material according to 4., wherein the water vapor barrier layer includes a pigment having an average particle size of 5 μm or less.
6. The paper based barrier packaging material according to 4., wherein the coating material forming the water vapor barrier layer includes a cross-linking agent.
7. The paper based barrier packaging material according to any one of 1. to 6., wherein the binder resin of the gas barrier layer is a polyvinyl alcohol resin.
8. The paper based barrier packaging material according to 7., wherein the gas barrier layer includes kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more.
9. The paper based barrier packaging material according to 7., wherein the coating material forming the gas barrier layer includes a cross-linking agent.
10. The paper based barrier packaging material according to 1., wherein the coating amount of the water vapor barrier layer is 4 to 30 g/m^2 in terms of dry weight and the coating amount of the gas barrier layer is 0.2 to 10 g/m^2 in terms of dry weight.

Advantageous Effects of Invention

[0013]

(1) The present invention have succeeded in realizing both barrier properties, namely, a water vapor barrier and a gas barrier property, by sequentially forming by coating a water vapor barrier layer on a paper base material and further a gas barrier layer on the water vapor barrier layer. The present invention can provide a paper based barrier packaging material exhibiting an excellent gas barrier property and an excellent water vapor barrier property by forming a water vapor barrier layer and a gas barrier layer with coating layers of the coating materials using as binders polymers (aqueous coating materials) including water as dispersion media.
The coating materials forming the gas barrier layer and the water vapor barrier layer exhibit the functions to prevent the permeation of water vapor and the permeation of gas (oxygen), respectively, each in a form of a film formed by drying and solidifying. In the two types of the barrier layers, the coating layers made of the aqueous coating materials are satisfactory in the compatibility between the layers, and are strongly resistant to the interfacial separation due to the water vapor or the gas tending to permeate one of the layers from the other layer, so as to enable both functions to be satisfactorily maintained.
(2) By forming one or both of the water vapor barrier layer and the gas barrier layer by using a coating material to which, as a pigment having a large particle size, kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more was added, the barrier property against water vapor or gas is improved.

(3) The use of a coating material including a pigment as added thereto, having an average particle size of 5 μm or less improves the barrier property against water vapor or gas.
(4) As the polymer for the coating layer forming the water vapor barrier layer, a styrene-butadiene-based synthetic resin is suitable. As the polymer for the coating layer forming the gas barrier layer, a polyvinyl alcohol resin is suitable. As a paper based barrier packaging material, the combination of the resins is excellent in which the coating layer mainly composed of the polyvinyl alcohol resin is formed on the coating layer, formed on a paper base material, mainly composed of the styrene-butadiene-based synthetic resin.
(5) The styrene-butadiene synthetic resin or the polyvinyl alcohol resin including a cross-linking agent added thereto improves both barrier properties.

Description of Embodiments

[0014] The present invention is a paper based barrier packaging material (hereinafter, sometimes referred to as a "packaging material") including a water vapor barrier layer and a gas barrier layer disposed in this order on a paper base material (hereinafter, sometimes referred to as a "base paper"). The two types of the barrier layers are each formed by applying an aqueous coating material, and to the coating material, a polymer binder as a main additive, a pigment, a cross-linking agent and the like are added.

[0015] The water vapor barrier layer or the gas barrier layer is formed by coating with a coating material including a polymer as a binder resin and using water as a dispersion medium. To the coating layers forming the two types of the barrier layers, it is preferable to add kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more, a pigment having an average particle size of 5 μm or less, a cross-linking agent and the like.

[0016] The reasons for the fact that the paper based barrier packaging material of the present invention including the water vapor barrier layer formed on a paper base material and further the gas barrier layer on the water vapor barrier layer simultaneously has both of an excellent water vapor barrier property and an excellent gas barrier property are inferred as follows.

[0017] There are many instances where for the formation of the gas barrier layer, a water soluble polymer resin is used. In the case where the gas barrier layer and the water vapor barrier are disposed in this order on the paper base material, the moisture or the like in the air permeating through the paper base material operates to degrade the gas barrier layer including the water soluble polymer. On the other hand, in the case where a water vapor barrier layer including a resin satisfactory in waterproofness and a gas barrier layer are disposed in this order, the moisture passing through the paper base material is blocked by the water vapor barrier layer, and hence the moisture effect on (the degradation of) the gas barrier layer can be prevented. Accordingly, the paper based barrier packaging material of the present invention has a satisfactory water vapor barrier property and a satisfactory gas barrier property.

[0018] The paper based barrier packaging material of the present invention is usually used in such a way that the side of the gas barrier layer is the side of the content (article to be packaged) and the side of the paper layer is the atmospheric side (outer surface). The permeation of the atmospheric moisture into the interior can be prevented, and hence when the article to be packaged is a dry substance, the structure of the present invention is effective. When a wet article is packaged, further a resin extrusion laminated layer or a film laminate layer is additionally formed on the gas barrier layer to be the inner side.

<On the Paper Base Material>

[0019] In the present invention, the paper base material is a sheet includes pulp, a filler, and various additives. Examples of the pulp include: chemical pulps such as leaf bleached kraft pulp (LBKP), needle bleached kraft pulp (NBKP) and sulfite pulp; mechanical pulps such as stone-ground pulp and thermomechanical pulp; and non-wood fibers obtained from kenaf, bamboo, hemp and the like. These materials can be appropriately mixed to be used. Among these, the chemical pulps such as leaf bleached kraft pulp (LBKP) and needle bleached kraft pulp (NBKP) are preferable. The chemical pulps are suitable, for example, for the reasons that contamination of the base paper hardly occurs, temporal discoloration hardly occurs when used paper containers are collected as waste paper raw materials to be recycled, and chemical pulps have a high degree of whiteness to result in satisfactory surface touch at the time of printing so as to enhance the value in use as packaging materials.

[0020] Examples of the usable filler include heretofore known fillers such as white carbon, talc, kaolin, clay, heavy calcium carbonate, precipitated calcium carbonate, titanium oxide, zeolite and synthetic resin fillers. If necessary, the following papermaking internal aids can also be used: aluminum sulfate; various anionic, cationic, nonionic, or amphoteric yield improvers; a freeness improver, a paper-strengthening agent and an internal sizing agent. Moreover, if necessary, a dye, a fluorescent whitening agent, a pH adjuster, an antifoaming agent, a pitch control agent, a slime control agent and the like can also be added.

[0021] The method of the production (paper making) of the paper base material is not particularly limited; paper base

materials can be produced by using heretofore known fourdrinier former, on-top hybrid former and gap former machines, and by performing paper making with acidic paper making, neutral paper making, alkaline paper making methods. The paper base material is preferably a material generally used for coated papers, having a basis weight of about 25 to 400 g/m^2. Moreover, the surface of the paper base material can be treated with various chemicals. Examples of the chemicals to be used may include: oxidized starch, hydroxyethyl etherified starch, oxygen-modified starch, polyacrylamide, polyvinyl alcohol, a surface sizing agent, a waterproofing agent, a water retention agent, a thickener and a lubricant; these can be used each alone or in combinations of two or more thereof. The method of the surface treatment of the paper base material is not particularly limited; however, heretofore known coating apparatuses such as a rod metering size press, a pond type size press, a gate roll coater, a spray coater, a blade coater and a curtain coater can be used.

<On the Binder (Polymer)>

[0022] The polymer to be used as the main component of the coating layer forming the water vapor barrier layer or the gas barrier layer is suitably a resin for which water can be used as a dispersion medium. Examples of the dosage form include a polymer aqueous solution and a form of a polymer emulsion. The polymer corresponds to the binder of the coating material for forming a coating layer.

<On the Water Vapor Barrier Layer>

[0023] As the resins to be included in the water vapor barrier layer, the following resins can be used each alone or as mixtures of two or more thereof: copolymers such as styrene-butadiene-based, styrene-acrylic, ethylene-vinyl acetate-based, butadiene-methyl methacrylate-based, vinyl acetate-butyl acrylate-based copolymers; maleic anhydride copolymer; and acrylic acid-methyl methacrylate-based copolymer. Among these, styrene-butadiene-based resin is preferable from the viewpoint of the water vapor barrier property.

[0024] In the present invention, styrene-butadiene-based synthetic resin is a resin synthesized with emulsion polymerization by using styrene and butadiene as the main constituent monomers in combination with various comonomers aiming at modification. Examples of the comonomer include: methyl methacrylate, acrylonitrile, acrylamide and hydroxyethyl acrylate; and unsaturated carboxylic acids such as itaconic acid, maleic acid and acrylic acid.

[0025] The resins are used as emulsion-type coating materials prepared by emulsification with water as a dispersant. Examples of the emulsifier include anionic surfactants such as sodium oleate, rosin acid soap, sodium alkyl allyl sulfonate and sodium dialkyl sulfosuccinate. These can be used each alone or in combinations with nonionic surfactants. Moreover, if necessary, amphoteric or cationic surfactants may also be used.

[0026] In the present invention, the coating material to form the water vapor barrier layer preferably does not include water-repellent components such as a hydrocarbon, a silicone-based resin, a fluorine-based resin, a fatty acid and an ester between a fatty acid and an alcohol. It is to be noted that conventional packaging materials having a water vapor barrier property are generally provided with water-repellent component-containing resins. The water-repellent component degrades the affinity between the water vapor barrier layer and the gas barrier layer, and accordingly, the moisture or gas permeating from one of these layers unpreferably promotes interfacial peeling.

(On the Pigment for Addition to Water Vapor Barrier Layer)

[0027] In the present invention, the inclusion of a pigment in the water vapor barrier layer improves the water vapor barrier property, and also improves the adhesion between the water vapor barrier layer and the gas barrier layer.

[0028] Examples of the pigment include an inorganic pigment and an organic pigment. Examples of the inorganic pigment include: kaolin, clay, engineered kaolin, delaminated clay, heavy calcium carbonate, precipitated calcium carbonate, talc, titanium dioxide, barium sulfate, calcium sulfate, zinc oxide, silicic acid, silicates, colloidal silica and satin white. Examples of the organic pigment include a dense-type pigment, a hollow-type pigment, or a core-shell type pigment. These pigments can be used each alone or as mixtures of two or more thereof.

[0029] The pigments flat in shape and large in size are suitable. The water vapor barrier property is improved by using a pigment large in particle size and a pigment small in particle size in combination.

[0030] Among these pigments, inorganic pigments such as flat-shaped kaolin improve the water vapor barrier property. In particular, kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more is more preferable. A flat pigment is distributed parallel to the coating layer, the water vapor permeating into the water vapor barrier layer is blocked by the flat pigment with respect to the movement in the thickness direction and is made to move in a detour so as to elongate the path of the passage of the water vapor through the water vapor barrier layer, and hence the barrier property is improved. When the aspect ratio of the added pigment is small, the number of times of detour of the water vapor in the coating layer is decreased, accordingly the distance of the movement of the water vapor is reduced, and consequently the pigment small in aspect ratio is inferior to the flat pigment having a large particle size.

[0031] A flat pigment can be expected to have the same effect as described above on the gas barrier layer.

[0032] As a flat pigment, in addition to kaolin, mica and montmorillonite can also be used. However, the dispersion of mica or montmorillonite is lower in concentration than the dispersion of kaolin, accordingly the coating liquid for the water vapor barrier layer using mica or montmorillonite is low in concentration so as for the pigment to find difficulty in orientation in the formed water vapor barrier layer, and hence kaolin is more suitable than mica or montmorillonite.

[0033] By adding a pigment having an average particle size of 5 μm or less to the water vapor barrier layer, in addition to the above-described flat pigment, the water vapor barrier property can be further improved. The pigment having a small particle size is not required to be flat.

[0034] In the present invention, from the viewpoint of the improvement of the water vapor barrier property and the adhesiveness to the gas barrier layer, it is preferable to further include a pigment having an average particle size of 5 μm or less in the water vapor barrier layer including kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more. In this way, a structure is obtained in which a pigment having an average particle size of 5 μm or less is interposed between the kaolin particles present in a multilayered manner, having an average particle size of 5 μm or more and an aspect ratio of 10 or more, and consequently, the water vapor being forced to move along the flat plane of kaolin is blocked in its movement by the smaller pigment particles. Specifically, in the case where the pigments different in flatness and average particle size are included in the water vapor barrier layer, a state occurs in which in the water vapor barrier layer, the pigment of smaller particle size is filled in the voids formed between the adjacent flat pigment particles large in particle size, accordingly the water vapor passes all the way around the pigments, and hence the water vapor barrier layer including the pigments different in average particle size exhibits a higher water vapor barrier property as compared to the water vapor barrier layer including no pigment smaller in particle size.

[0035] In the present invention, the mixing ratio between kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more and the pigment having an average particle size of 5 μm or less is preferably 50/50 to 99/1 in terms of dry weight. When the ratio of kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more is smaller than the foregoing range, the detour distance of the water vapor in the coating layer is short, and hence no sufficient water vapor barrier property can be obtained. On the other hand, the ratio of kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more is larger than the foregoing range, the voids formed by the large particle size pigment in the coating layer cannot be sufficiently filled by the pigment having an average particle size of 5 μm or less, and hence no improvement of the water vapor barrier property is found.

[0036] In the present invention, as the pigment having an average particle size of 5 μm or less the following pigments can be used each alone or as mixtures of two or more thereof: inorganic pigments such as kaolin, clay, engineered kaolin, delaminated clay, heavy calcium carbonate, precipitated calcium carbonate, talc, titanium dioxide, barium sulfate, calcium sulfate, zinc oxide, silicic acid, silicates, colloidal silica and satin white; and organic pigments such as a dense-type pigment, a hollow-type pigment, or a core-shell type pigment. Among these pigments, heavy calcium carbonate is preferable.

[0037] When a pigment is included in the water vapor barrier layer, the mixing amounts of the resin and the pigment are such that a resin is used in an amount of preferably 5 to 200 parts by weight and more preferably 20 to 150 parts by weight (dry weight) in relation to 100 parts by weight (dry weight) of the pigment. In the water vapor barrier layer, it is possible to use, in addition to the resin and the pigment, various usually used aids such as a dispersant, a thickener, a water retention agent, an antifoaming agent, a waterproofing agent, a dye and a fluorescent dye.

(Cross-Linking Agent)

[0038] In the present invention, it is preferable to add a cross-linking agent typified by a multivalent metal salt to the water vapor barrier layer. The cross-linking agent causes a cross-linking reaction with the binder included in the water vapor barrier layer, and accordingly the number of the bonds (the number of the cross-linked points) in the water vapor barrier layer is increased. In other words, the water vapor barrier layer becomes dense in structure, and consequently exhibits a satisfactory water vapor barrier property.

[0039] In the present invention, the type of the cross-linking agent is not particularly limited; the cross-linking agent appropriately according to the type of the binder included in the water vapor barrier layer from the following can be used: multivalent metal salts (the compounds produced by bonding the multivalent metals such as copper, zinc, silver, iron, potassium, sodium, zirconium, aluminum, calcium, barium, magnesium and titanium with the ionic substances such as carbonate ion, sulfate ion, nitrate ion, phosphate ion, silicate ion, nitrogen oxide and boron oxide); and amine compounds, amide compounds, aldehyde compounds, and hydroxy acids. As long as the mixing amount of the cross-linking agent allows the concentration and the viscosity of the coating material to fall within ranges permitting coating operation, the cross-linking agent can be mixed without being particularly limited with respect to the mixing amount thereof. From the viewpoint of the development of the cross-linking effect, it is preferable to use a multivalent metal salt when a styrene-based water vapor barriering resin exhibiting excellent effects in the water vapor barrier property, such as a styrene-butadiene-based resin or a styrene-acrylic-based resin is used; in particular, potassium alum is more preferable.

[0040] The addition amount of the cross-linking agent is 1 to 10 parts by weight and more preferably 3 to 5 parts by weight in relation to 100 parts by weight of the binder resin used in the water vapor barrier layer. When the addition amount of the cross-linking agent is less than 1 part by weight, no sufficient effect is obtained, and when the addition amount of the cross-linking agent is larger than 10 parts by weight, the viscosity of the coating liquid is remarkably increased to make the coating operation difficult.

[0041] In the present invention, when a cross-linking agent is added to the coating liquid to form the water vapor barrier layer, it is preferable to add the cross-linking agent to the coating liquid after the cross-linking agent is dissolved in a polar solvent such as ammonium hydroxide solution. By dissolving the cross-linking agent in a polar solvent, bonding occurs between the cross-linking agent and the polar solvent, and hence even when the cross-linking agent is mixed in the coating liquid, the cross-linking reaction with the latex does not occur instantly, so as to allow the thickening of the coating material to be suppressed. In this case, it is inferred that by drying after the coating operation on paper, polar solvent component is evaporated, the cross-linking reaction with the binder occurs, and the dense water vapor barrier layer is formed.

(Contact Angle)

[0042] In the present invention, the contact angle with water of the surface of the water vapor barrier layer disposed on the paper base material is preferably less than 90°, more preferably less than 85° and furthermore preferably less than 80°. When the contact angle with water is 90° or more, it is difficult to dispose a uniform gas barrier layer on the water vapor barrier layer, and it is difficult to exhibit a high gas barrier property. When the contact angle with water is less than 90°, it is possible to suppress the repulsion between the water vapor barrier layer and the gas barrier layer so as to suppress the peeling between these two layers. The contact angle serves as a measure with which the affinity between the water vapor barrier layer and the gas barrier layer is inferred.

[0043] The method for regulating the contact angle with water of the surface of the water vapor barrier layer is not particularly limited; however, examples of such a method include a method using a resin having a low contact angle with water for the water vapor barrier layer, and a method in which a pigment or the like is added to the resin for the water vapor barrier layer.

<On the Gas Barrier Layer>

[0044] In the present invention, the water soluble polymer used as the binder resin of the coating material to form the gas barrier layer can be exemplified by completely saponified polyvinyl alcohol, partially saponified polyvinyl alcohol, ethylene copolymerized polyvinyl alcohol, polyvinylpyrrolidone, starch, methyl cellulose, carboxymethyl cellulose and sodium alginate. Among these, from the viewpoint of the gas barrier property, polyvinyl alcohol and carboxymethyl cellulose are preferable, and polyvinyl alcohol is furthermore preferable.

(On the Pigment)

[0045] In the present invention, examples of the pigments used in the gas barrier layer include: inorganic pigments such as kaolin, clay, engineered kaolin, delaminated clay, heavy calcium carbonate, precipitated calcium carbonate, talc, titanium dioxide, barium sulfate, calcium sulfate, zinc oxide, silicic acid, silicate, colloidal silica, satin white and mica; and organic pigments such as a dense-type pigment, a hollow-type pigment and a core-shell type pigment. These can be used each alone or as mixtures of two or more thereof. Among these, from the viewpoint of the gas barrier property, it is preferable to use an inorganic pigment.

[0046] It is more preferable to use an inorganic pigment (in particular, kaolin) having an average particle size of 3 μm or more and an aspect ratio of 10 or more, and it is particularly preferable to use an inorganic pigment (in particular, kaolin) having an average particle size of 5 μm or more and an aspect ratio of 50 or more. When a pigment is included in the gas barrier layer, a gas such as oxygen passes around the pigment. Consequently, as compared to the gas barrier layer formed of a water soluble polymer including no pigment, the gas barrier layer formed of a water soluble polymer including a pigment has a satisfactory water vapor barrier property and an excellent gas barrier property in a high-humidity atmosphere.

[0047] In the present invention, the mixing ratio (in terms of dry weights) between the pigment and the water soluble polymer included in the gas barrier layer is preferably such that the ratio pigment /water soluble polymer is 1/100 to 1000/100. When the proportion of the pigment falls outside the foregoing range, no sufficient gas barrier property is exhibited.

(On the Cross-Linking Agent)

[0048] In the present invention, it is preferable to add a cross-linking agent typified by a multivalent metal salt or the like to the gas barrier layer. The cross-linking agent bonds the hydroxyl groups in the water soluble polymer to each other through cross-linked structure, hence the amount of the hydroxyl groups having the loosened bonds (or broken bonds) when the humidity becomes high is decreased to improve the waterproofness of the whole layer, and thus the degradation of the oxygen barrier property under a high humidity can be suppressed.

[0049] In the present invention, the type of the cross-linking agent is not particularly limited; the cross-linking agent appropriately according to the type of the binder included in the water vapor barrier layer from the following can be used: multivalent metal salts (the compounds produced by bonding the multivalent metals such as copper, zinc, silver, iron, potassium, sodium, zirconium, aluminum, calcium, barium, magnesium and titanium with the ionic substances such as carbonate ion, sulfate ion, nitrate ion, phosphate ion, silicate ion, nitrogen oxide and boron oxide); and amine compounds, amide compounds, aldehyde compounds, and hydroxy acids. As long as the mixing amount of the cross-linking agent allows the concentration and the viscosity of the coating material to fall within ranges permitting coating operation, the cross-linking agent can be mixed without being particularly limited with respect to the mixing amount thereof. From the viewpoint of the development of the cross-linking effect, it is preferable to use a multivalent metal salt and it is more preferable to use potassium alum when a styrene-based water vapor barriering resin exhibiting excellent effects in the water vapor barrier property, such as a styrene-butadiene-based resin or a styrene-acrylic-based resin is used.

[0050] The addition amount of the cross-linking agent is 1 to 10 parts by weight and more preferably 3 to 5 parts by weight in relation to 100 parts by weight of the resin used in the gas barrier layer. When the addition amount of the cross-linking agent is less than 1 part by weight, no sufficient effect is obtained, and when the addition amount of the cross-linking agent is larger than 10 parts by weight, the viscosity of the coating liquid is remarkably increased to make the coating operation difficult.

(Additives)

[0051] In the present invention, when a pigment is mixed in a water soluble polymer, it is preferable to add and mix a pigment which is water-dispersed and slurried.

[0052] In the present invention, in the gas barrier layer, it is possible to use, in addition to the water soluble polymer and the pigment, various usually used aids such as a dispersant, a thickener, a water retention agent, an antifoaming agent, a waterproofing agent, a dye and a fluorescent dye.

<On the Coating Operation>

[0053] In the present invention, the coating methods of the water vapor barrier layer and the gas barrier layer are not particularly limited, and heretofore known coating apparatuses can be used. Examples of such a coating apparatus include: a blade coater, a bar coater, a roll coater, an airknife coater, a reverse roll coater, a curtain coater, a spray coater, a size press coater and a gate roll coater. As the method for drying the coating layer, usual methods using the following are used: a steam heating heater, a gas heater, an infrared heater, an electric heater, a hot air heating heater, a microwave, a cylinder dryer and the like.

[0054] In the present invention, the coating amount of the water vapor barrier layer is preferably set at 4 to 30 g/m^2, more preferably 6 to 25 g/m^2 and furthermore preferably 10 to 20 g/m^2 in terms of dry weight. When the coating amount is 3 g/m^2 or less, there occur a problem that it is difficult for the coating liquid to perfectly coat the base paper, and hence no sufficient water vapor barrier property is obtained, and a problem that the gas barrier layer penetrates into the paper base material, and hence a uniform gas barrier property is not obtained. On the other hand, when the coating amount is 30 g/m^2 or more, the drying load at the time of coating operation becomes large, unpreferably from the viewpoint of both of the operational aspect and the cost aspect.

[0055] In the present invention, the coating amount of the gas barrier layer is preferably set at 0.2 to 10 g/m^2 in terms of dry weight. When the coating amount is less than 0.2 $/m^2$, no uniform gas barrier layer can be formed, and hence there is problem that no sufficient gas barrier property is obtained. On the other hand, the coating amount is 10 g/m^2 or more, the drying load at the time of coating operation becomes large, unpreferably from the viewpoint of both of the operational aspect and the cost aspect.

[0056] In the present invention, it is possible to dispose a sealant layer made of a polymer such as polyethylene, polypropylene or polyvinyl acetate on the paper based barrier packaging material including a water vapor barrier layer and a gas barrier layer disposed on a paper base material. The method for laminating the sealant layer is not particularly limited; it is possible to use a conventional, heretofore known methods such as a melt-extrusion lamination method, a dry lamination method using a film and a direct melt coating method.

Examples

[0057] Hereinafter, the present invention is specifically described with reference to Examples, but of course, the present invention is not these Examples. It is to be noted that unless otherwise specified, parts and % in Examples represent parts by weight and % by weight, respectively. For the coating liquids obtained and the functional papers obtained, tests were performed on the basis of the following evaluation methods. The test results are shown in Table 1 and Table 2.

(Evaluation Methods)

[0058]

(1) Water vapor permeability: The water vapor permeability was measured under the conditions of a temperature of 40 ± 0.5°C and a relative humidity of 90 ± 2%, with a water vapor permeability tester (L80-4000, manufactured by Dr. Lyssy, Inc.).
(2) Oxygen permeability: The oxygen permeability was measured with the OX-TRAN2/21, manufactured by Mocon, Inc. under the conditions of 23°C and 0% RH and the conditions of 23°C and 85% RH.
(3) Contact angle: The surface contact angle after an elapsed time of 0.1 second from the dropping of a drop of water was measured in an atmosphere of 23°C and 50% RH, with a dynamic surface contact angle measurement apparatus (Dynamic Absorption and Contact Angle Tester DAT1100, manufactured by Fibro System AB).
(4) Average particle size: A sample slurry was dropwise mixed in a pure water including 0.2% by weight of sodium hexametaphosphate added as a dispersant to prepare a uniform dispersion, and the particle size of the sample was measured by using the resulting dispersion with a laser particle size analyzer (Mastersizer Type S, manufactured by Malvern Instruments Ltd.).
(5) Aspect ratio: The images of a pigment in the planar direction and the cross-sectional direction of the pigment were photographed with a SEM (scanning electron microscope), and the diameter and the length of the pigment orientation plane were measured and the aspect ratio was derived with the relation [aspect ratio = diameter/thickness of the pigment orientation plane].

[Example 1]

(Preparation of Paper Base Material)

[0059] A raw material pulp was prepared by mixing, with a weight ratio of 80/20, a leaf bleached kraft pulp (LBKP) having a Canadian standard freeness (CSF) of 500 ml and a needle bleached kraft pulp (NBKP) having a CSF of 530 ml. To a raw material pulp slurry, polyacrylamide (PAM) having a molecular weight of 2,500,000 as a dry paper-strengthening agent in an amount of 0.1% in relation to the bone-dry weight of the pulp, alkyl ketene dimer (AKD) as sizing agent in an amount of 0.35% in relation to the bone-dry weight of the pulp, a polyamide epichlorohydrin (PAEH)-based resin as a wet paper-strengthening agent in an amount of 0.15% in relation to the bone-dry weight of the pulp, and further polyacrylamide (PAM) having a molecular weight of 10,000,000 as a yield improver in an amount of 0.08% in relation to the bone-dry weight of the pulp were added; and then paper making was performed with a duo former FM-type paper making machine at a rate of 300 m/min to yield a paper having a basis weight of 59 g/m^2. Next, both faces of the obtained paper were coated with polyvinyl alcohol (PVA117, manufactured by Kuraray Co., Ltd.) regulated to a solid content concentration of 2% in an amount of 1.0 g/m^2 by using a rod metering size press, and dried to yield a base paper having a basis weight of 60 g/m^2. The base paper obtained was subjected to a smoothing treatment with a chilled calender at a rate of 300 min/m and at a linear load of 50 kgf/cm, in a single pass.

(Preparation of Coating Liquid for Water Vapor Barrier Layer)

[0060] To large particle size engineered kaolin (Barrisurf HX, particle size: 9.0 μm, aspect ratio: 80-100, manufactured by Imerys Minerals Ltd.), sodium polyacrylate was added as a dispersant (in an amount of 0.2 part in relation to inorganic pigment), and the resulting mixture was dispersed with a Serie mixer to prepare a large particle size kaolin slurry having a solid content concentration of 55%. In the kaolin slurry obtained, a styrene-butadiene-based latex (PNT7868, manufactured by Zeon Corp.) was mixed in an amount of 100 parts (solid content) in relation to the pigment to yield a coating liquid A having a solid content concentration of 50%.

(Preparation of Coating Liquid for Oxygen Barrier Layer)

[0061] Polyvinyl alcohol (PVA117, manufactured by Kuraray Co., Ltd.) was regulated so as to have a solid content

concentration of 10% to yield a coating liquid B.

(Preparation of Paper Based Barrier Packaging Material)

[0062] The base paper obtained was single-side coated with the coating liquid A so as to have a coating amount (dry amount) of 12 g/m^2 at a coating speed of 300 m/min with a blade coater and dried; subsequently, the coated side was single-side coated with the coating liquid B so as to have a coating amount (dry amount) of 2.0 g/m^2 at a coating speed of 300 m/min with a roll coater to yield a paper based barrier packaging material.

[Example 2]

[0063] In the coating liquid for the oxygen barrier layer, to the large particle size engineered kaolin (Barrisurf HX, manufactured by Imerys Minerals Ltd.), sodium polyacrylate was added as a dispersant (in an amount of 0.2 part in relation to the inorganic pigment), and the resulting mixture was dispersed with a Serie mixer to prepare a large particle size kaolin slurry having a solid content concentration of 55%. A paper based barrier packaging material was obtained in the same manner as in Example 1 except that a coating liquid was used which was prepared by mixing the obtained kaolin slurry and the coating liquid B in a ratio of pigment:coating liquid B = 100:100 in terms of the solid content so as for the solid content concentration to be 10%.

[Example 3]

[0064] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the oxygen barrier layer, potassium alum (aluminum potassium sulfate dodecahydrate, manufactured by Kanto Chemical Co., Inc.) was dissolved so as for the concentration to be 5%, the obtained potassium alum aqueous solution was mixed in an amount of 3 parts in terms of the solid content in relation to polyvinyl alcohol, to prepare a coating liquid having a solid content concentration of 10%, and the thus obtained coating liquid was used.

[Example 4]

[0065] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the oxygen barrier layer, the kaolin slurry prepared in Example 2 was mixed in the coating liquid B in a ratio of pigment:coating liquid B = 100:100 in terms of the solid content, and further the potassium alum aqueous solution dissolved in Example 3 was mixed in an amount of 3 parts in terms of the solid content in relation to polyvinyl alcohol, to prepare a coating liquid having a solid content concentration of 10%, and the thus obtained coating liquid was used.

[Example 5]

[0066] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, a coating liquid in which a heavy calcium carbonate slurry (FMT-75, average particle size: 1.6 μm, aspect ratio: 1, manufactured by Fimatec Ltd.) was mixed in and stirred with the pigment of the coating liquid A so as for the pigment mixing ratio to be 75:25 was used.

[Example 6]

[0067] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the potassium alum aqueous solution dissolved in Example 3 was mixed in an amount of 3 parts in relation to the pigment in the coating liquid obtained in Example 5 to prepare a coating liquid having a solid content concentration of 50%, and the thus obtained coating liquid was used.

[Example 7]

[0068] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the oxygen barrier layer, the coating liquid obtained in Example 4 was used, and in the coating liquid for the water vapor barrier layer, the coating liquid obtained in Example 5 was used.

[Example 8]

[0069] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the oxygen barrier layer, the coating liquid obtained in Example 4 was used, and in the coating liquid for the water vapor barrier layer, the coating liquid obtained in Example 6 was used.

[Example 9]

[0070] A paper based barrier packaging material was obtained in the same manner as in Example 2 except that in the coating liquid for the oxygen barrier layer, the large particle size engineered kaolin in the coating liquid obtained in Example 2 was altered to mica (B-82, particle size: 180 μm, manufactured by Matsuo Sangyo Co., Ltd.).

[Example 10]

[0071] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the oxygen barrier layer, the large particle size engineered kaolin in the coating liquid obtained in Example 1 was altered to montmorillonite (Nikka Knight A-36, particle size: 400 μm, manufactured by Toshin Chemicals Co., Ltd.).

[Example 11]

[0072] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the large particle size engineered kaolin in the coating liquid obtained in Example 1 was altered to mica (B-82, particle size: 180 μm, manufactured by Matsuo Sangyo Co., Ltd.), the pigment dispersion concentration was altered to 20%, and the coating liquid concentration was altered to 30.

[Example 12]

[0073] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the large particle size engineered kaolin in the coating liquid obtained in Example 1 was altered to montmorillonite (Nikka Knight A-36, particle size: 400 μm, manufactured by Toshin Chemicals Co., Ltd.), the pigment dispersion concentration was altered to 20%, the coating liquid concentration was altered to 30%, and the coating amount was altered to 9 g/m^2.

[Example 13]

[0074] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the styrene-butadiene-based latex in Example 1 was altered to an acrylic-styrene-based copolymer emulsion (Saivinol X-511-374E, manufactured by Saiden Chemical Industry Co., Ltd.).

[Example 14]

[0075] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the latex was altered to a styrene-butadiene-based latex (L7360, manufactured by Asahi Kasei Chemicals Corp.).

[Example 15]

[0076] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the pigment used in the coating liquid was altered from the large particle size engineered kaolin (Barrisurf HX, manufactured by Imerys Minerals Ltd.) to the large particle size engineered kaolin (Capim CC, particle size: 8.0 μm, aspect ratio: 10 to 15, manufactured by Imerys Minerals Ltd.).

[Example 16]

[0077] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the pigment used in the coating liquid was altered from the large particle size engineered kaolin (Barrisurf HX, manufactured by Imerys Minerals Ltd.) to a fine particle kaolin (Hydragloss,

average particle size: 0.3 μm, aspect ratio: 10 to 15, manufactured by KaMin LLC).

[Example 17]

[0078] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the pigment used in the coating liquid was altered from the large particle size engineered kaolin (Barrisurf HX, manufactured by Imerys Minerals Ltd.) to a second grade kaolin (KCS, average particle size: 3.6 μm, aspect ratio: 10 to 15, manufactured by Imerys Minerals Ltd.).

[Example 18]

[0079] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the latex used in the coating liquid was altered to a styrene-butadiene-based latex (PNT7889, manufactured by ZEON Corp.).

[Example 19]

[0080] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the latex used in the coating liquid was altered to a styrene-butadiene-based latex (L7360, Asahi Kasei Chemicals Corp.).

[Example 20]

[0081] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the latex used in the coating liquid was altered to an acrylic copolymer latex (E316, manufactured by Asahi Kasei Chemicals Corp.).

[Example 21]

[0082] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the coating liquid for the water vapor barrier layer, the latex used in the coating liquid was altered to an acrylic copolymer aqueous emulsion (EK-61, manufactured by Saiden Chemical Industry Co., Ltd.).

[Example 22]

[0083] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that the coating amount of the coating liquid A was altered from 12 g/m^2 to 6 g/m^2 in terms of dry weight.

[Example 23]

[0084] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that the coating amount of the coating liquid A was altered from 12 g/m^2 to 15 g/m^2 in terms of dry weight.

[Example 24]

[0085] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that the coating amount of the coating liquid B was altered from 2 g/m^2 to 1 g/m^2 in terms of dry weight.

[Example 25]

[0086] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that the coating amount of the coating liquid B was altered from 2 g/m^2 to 4 g/m^2 in terms of dry weight.

[Example 26]

[0087] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the preparation of the coating liquid for the water vapor barrier layer, the mixing amount of the styrene-butadiene-based latex (PNT7868, manufactured by ZEON Corp.) was altered from 100 parts to 50 parts (solid content) in relation to the

pigment.

[Example 27]

[0088] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that in the preparation of the coating liquid for the water vapor barrier layer, the mixing amount of the styrene-butadiene-based latex (PNT7868, manufactured by ZEON Corp.) was altered from 100 parts to 150 parts (solid content) in relation to the pigment.

[Example 28]

[0089] A paper based barrier packaging material was obtained in the same manner as in Example 2 except that in the preparation of the coating liquid for the oxygen barrier layer, the mixing amount of the kaolin slurry was altered in such a way that the ratio in terms of the solid content was altered from pigment:coating liquid B = 100:100 to 150:100.

[Example 29]

[0090] A paper based barrier packaging material was obtained in the same manner as in Example 2 except that in the preparation of the coating liquid for the oxygen barrier layer, the mixing amount of the kaolin slurry was altered in such a way that the ratio in terms of the solid content was altered from pigment:coating liquid B = 100:100 to 50:100.

[Comparative Example 1]

[0091] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that the gas barrier layer and the water vapor barrier layer were disposed in this order on the paper base material.

[Comparative Example 2]

[0092] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that no water vapor barrier layer was disposed.

[Comparative Example 3]

[0093] A paper based barrier packaging material was obtained in the same manner as in Example 1 except that no gas barrier layer was disposed.

[Table 1]

	Coating amount of water vapor barrier layer	Contact angle after coating of water vapor barrier layer	Water vapor permeability	Coating amount of oxygen barrier layer	Oxygen permeability (under dry condition)	Oxygen permeability (under high humidity)
	g/m^2	°	$g/m^2 \cdot day$	g/m^2	$g/m^2 \cdot day$	$g/m^2 \cdot day$
Example 1	12.0	75	250	2.0	1.0	200
Example 2	12.0	75	250	2.0	1.0	80
Example 3	12.0	75	250	2.0	1.0	150
Example 4	12.0	75	250	2.0	1.0	50
Example 5	12.0	75	200	2.0	1.0	200
Example 6	12.0	75	150	2.0	1.0	200

(continued)

	Coating amount of water vapor barrier layer	Contact angle after coating of water vapor barrier layer	Water vapor permeability	Coating amount of oxygen barrier layer	Oxygen permeability (under dry condition)	Oxygen permeability (under high humidity)
	g/m^2	°	$g/m^2 \cdot day$	g/m^2	$g/m^2 \cdot day$	$g/m^2 \cdot day$
Example 7	12.0	75	200	2.0	1.0	50
Example 8	12.0	75	150	2.0	1.0	50
Example 9	12.0	75	250	2.0	1.0	80
Example 10	12.0	75	250	2.0	1.0	80
Example 11	9.0	75	300	2.0	1.0	200
Example 12	9.0	75	300	2.0	1.0	200
Example 13	12.0	90	250	2.0	1.0	300
Example 14	12.0	80	250	2.0	1.0	250

[Table 2]

	Coating amount of water vapor barrier layer	Contact angle after coating of water vapor barrier layer	Water vapor permeability	Coating amount of oxygen barrier layer	Oxygen permeability (under dry condition)	Oxygen permeability (under high humidity)
	g/m^2	°	$g/m^2 \cdot day$	g/m^2	$g/m^2 \cdot day$	$g/m^2 \cdot day$
Example 15	12.0	75	280	2.0	1.0	220
Example 16	12.0	75	380	2.0	1.0	320
Example 17	12.0	75	330	2.0	1.0	280
Example 18	12.0	75	260	2.0	1.0	200
Example 19	12.0	75	250	2.0	1.0	200
Example 20	12.0	80	300	2.0	1.0	240
Example 21	12.0	80	300	2.0	1.0	240
Example 22	7.0	70	350	2.0	1.0	300
Example 23	15.0	75	200	2.0	1.0	150
Example 24	12.0	75	250	1.0	2.0	250
Example 25	12.0	75	250	3.0	0.5	150
Example 26	12.0	70	280	2.0	1.0	220
Example 27	12.0	80	220	2.0	1.0	180
Example 28	12.0	75	250	2.0	2.0	150

(continued)

	Coating amount of water vapor barrier layer	Contact angle after coating of water vapor barrier layer	Water vapor permeability	Coating amount of oxygen barrier layer	Oxygen permeability (under dry condition)	Oxygen permeability (under high humidity)
	g/m^2	∘	$g/m^2 \cdot day$	g/m^2	$g/m^2 \cdot day$	$g/m^2 \cdot day$
Example 29	12.0	75	250	2.0	0.5	230
Comparative Example 1	12.0	75	250	2.0	10000↑	10000↑
Comparative Example 2	-	-	10000↑	2.0	1.0	10000↑
Comparative Example 3	12.0	75	250	-	10000↑	10000↑

<Discussion of the Results>

[0094] From the test data of Examples and Comparative Examples, the following properties can be listed.

(1) From the data of Example 1 and Comparative Examples 1, 2 and 3, it can be seen that Example 1 in which a water vapor barrier layer was formed on a paper base material and further a gas barrier layer was formed on the water vapor barrier layer is low in water vapor permeability and oxygen permeability. In contrast, in Comparative Example 2 in which only the gas barrier layer is disposed, the oxygen permeability and the water vapor permeability are extremely large, and both of these barrier property functions are not exhibited; in Comparative Example 3 in which only the water vapor barrier layer is disposed and Comparative Example 1 in which the water vapor barrier layer is disposed on the gas barrier layer, the water vapor barrier property exhibits the same degree of function as in Example 1, but the gas barrier property is not observed at all. This shows the result that the moisture permeating the paper base material degraded the gas barrier layer. Accordingly, this shows the result clearly demonstrating the usefulness of the present invention in which the water vapor barrier layer is disposed on the paper base material, and further the gas barrier layer is disposed on the water vapor barrier layer.
(2) In Examples 6 and 8 in each of which potassium alum, a cross-linking agent, was added to the coating material for the water vapor barrier layer, the water vapor barrier property is more improved than Example 1.
(3) In Examples 5 and 7 in each of which large and small pigments, namely, large particle size kaolin having a large flatness and heavy calcium carbonate fine particles were used in combination in the coating material for the water vapor barrier layer, the water vapor barrier property is more improved than in Example 1.
(4) It has been able to be verified that kaolin, mica (Example 11) and montmorillonite (Example 12), which are large particle size pigments having an aspect ratio of 80 or more, are effective; in particular, kaolin having a large particle size and an aspect ratio of 80 or more exhibited a more excellent water vapor barrier property than other pigments.
(5) From the results of Examples 2, 3, 4, 7, 8, 9 and 10 in which large particle size kaolin, mica and montmorillonite (these are large particle size pigments) and calcium alum (cross-linking agent) were used each alone or in combination in the gas barrier layer, it is possible to suppress the degradation of the gas barrier property performance to a small extent in a high humidity environment.
(6) In the cases where the contact angle of a water drop on the water vapor barrier layer is 90 degrees (Example 13) or 80 degrees (Examples 14, 21 and 22), to be larger than the contact angles of a water drop of 75 degrees in Example 1 and the like, the degradation of the gas barrier property performance becomes somewhat larger in a high humidity environment, and accordingly the smaller the contact angle of a water drop, the more effectively the degradation of the gas barrier property performance due to the humidity change can be prevented.
(7) The results of Examples 1, 15, 16 and 17 reveals a tendency of the water vapor barrier performance to depend on the particles size of the pigment added to the water vapor barrier layer. The gas barrier performance in a high humidity environment also shows a similar dependence on the particle size.
(8) The results of Examples 1, 14, 18, 19, 20 and 21 has verified that as the binder resin used in the coating material to form the water vapor barrier layer, the styrene-butadiene-based copolymer and the acrylic copolymer are useful.
(9) It has been able to be verified that the coating amount (dry weight) of the water vapor barrier layer falling within a range from 6 to $15g/m^2$ and the coating amount (dry weight) of the gas barrier layer falling within a range from 1

to 4 g/m^2 allow a sufficient water vapor barrier property and a sufficient gas barrier property to be exhibited, respectively.

Claims

1. A paper based barrier packaging material comprising a plurality of coating layers disposed on a paper base material, wherein the plurality of coating layers includes a water vapor barrier layer on the paper base material and a gas barrier layer formed on the water vapor barrier layer; and in each of these coating layers, a water soluble polymer or a water suspendable polymer is used as a binder resin.

2. The paper based barrier packaging material according to claim 1, wherein the water vapor barrier layer and the gas barrier layer are different in coating material composition from each other.

3. The paper based barrier packaging material according to claim 2, wherein the binder resin of the water vapor barrier layer is a styrene-butadiene-based synthetic resin.

4. The paper based barrier packaging material according to claim 3, wherein the binder resin in the water vapor barrier layer includes kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more.

5. The paper based barrier packaging material according to claim 4, wherein the water vapor barrier layer includes a pigment having an average particle size of 5 μm or less.

6. The paper based barrier packaging material according to claim 4, wherein the coating material forming the water vapor barrier layer includes a cross-linking agent.

7. The paper based barrier packaging material according to any one of claims 1 to 6, wherein the binder resin of the gas barrier layer is a polyvinyl alcohol resin.

8. The paper based barrier packaging material according to claim 7, wherein the gas barrier layer includes kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more.

9. The paper based barrier packaging material according to claim 7, wherein the coating material forming the gas barrier layer includes a cross-linking agent.

10. The paper based barrier packaging material according to claim 1, wherein the coating amount of the water vapor barrier layer is 4 to 30 g/m^2 in terms of dry weight and the coating amount of the gas barrier layer is 0.2 to 10 g/m^2 in terms of dry weight.

Amended claims under Art. 19.1 PCT

1. (amended) A paper based barrier packaging material comprising a plurality of coating layers disposed on a paper base material, wherein the plurality of coating layers includes a water vapor barrier layer <u>formed</u> on the paper base material and a gas barrier layer formed on the water vapor barrier layer; and in each of these coating layers, a water soluble polymer or a water suspendable polymer is used as a binder resin.

2. (original) The paper based barrier packaging material according to claim 1, wherein the water vapor barrier layer and the gas barrier layer are different in coating material composition from each other.

3. (original) The paper based barrier packaging material according to claim 2, wherein the binder resin of the water vapor barrier layer is a styrene-butadiene-based synthetic resin.

4. (amended) The paper based barrier packaging material according to claim 3, wherein the water vapor barrier layer includes kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more.

5. (amended) The paper based barrier packaging material according to claim 4, wherein the water vapor barrier layer includes a pigment having an average particle size of 5 μm or less.

6. (original) The paper based barrier packaging material according to claim 4, wherein the coating material forming the water vapor barrier layer includes a cross-linking agent.

7. (original) The paper based barrier packaging material according to any one of claims 1 to 6, wherein the binder resin of the gas barrier layer is a polyvinyl alcohol resin.

8. (original) The paper based barrier packaging material according to claim 7, wherein the gas barrier layer includes kaolin having an average particle size of 5 μm or more and an aspect ratio of 10 or more.

9. (original) The paper based barrier packaging material according to claim 7, wherein the coating material forming the gas barrier layer includes a cross-linking agent.

10. (original) The paper based barrier packaging material according to claim 1, wherein the coating amount of the water vapor barrier layer is 4 to 30 g/m^2 in terms of dry weight and the coating amount of the gas barrier layer is 0.2 to 10 g/m^2 in terms of dry weight.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/079176

A. CLASSIFICATION OF SUBJECT MATTER
B32B29/00(2006.01)i, *B65D65/40*(2006.01)i

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)
B32B29/00, B65D65/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2012
Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2008-87784 A (Dainippon Printing Co., Ltd.), 17 April 2008 (17.04.2008), claims; paragraphs [0006], [0014], [0017] to [0028]; fig. 2 (Family: none)	1-3,10 4-6
Y	JP 2000-177244 A (Fuji Photo Film Co., Ltd.), 27 June 2000 (27.06.2000), claim 3; paragraphs [0007], [0017] (Family: none)	4-6
Y	JP 2005-162213 A (Daio Paper Corp.), 23 June 2005 (23.06.2005), claims; paragraphs [0034], [0035] (Family: none)	4-6

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* 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 application or patent 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
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 November, 2012 (27.11.12)	04 December, 2012 (04.12.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/079176

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2000-303386 A (Oji Paper Co., Ltd.), 31 October 2000 (31.10.2000), claims; paragraphs [0004], [0012], [0013], [0015] (Family: none)	6
A	JP 2004-17993 A (Dainippon Printing Co., Ltd.), 22 January 2004 (22.01.2004), entire text (Family: none)	1-10
A	JP 2002-326321 A (Toppan Printing Co., Ltd.), 12 November 2002 (12.11.2002), entire text (Family: none)	1-10

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2009184138 A **[0008]**
- JP 2003094574 A **[0008]**
- JP 2005162213 A **[0008]**