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(54) Title: COATED SUBSTRATE, MORE IN PARTICULAR COATED PAPER MATERIAL

(57) Abstract

The invention relates to a coated substrate having reduced oxygen and vapour permeability, said coated substrate comprising at least one layer of substrate and at least one layer of a blend of a) at least one film forming polymer, or a blend of such film forming polymer and at least one other polymer, and b) at least one reaction product of at least one EPDM rubber, at least one ethylene-vinyl acetate copolymer and at least one ethylene copolymer having short chain branching, applied to at least one surface of the substrate, to a process for preparing such a paper and to the use thereof as packaging material.

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Title: Coated substrate, more in particular coated paper material.

The present invention relates to a coated substrate, more in particular a coated paper material having reduced oxygen and vapour permeability and to a process for preparing such a coated substrate.

It is known in the art to coat packaging materials, such as paper, with a film-forming polymer, for example polyethylene, polypropylene, polyamide and other film-forming polymers or blends thereof or blends of these substances and one or more other polymers. The aim of coating papers with such polymers is to improve the resistance of the paper to liquid and to improve the oxygen and vapour permeability properties of the paper, i.e. to decrease the amount of oxygen that permeates the paper.

It is known that certain materials are susceptive to oxygen and tend to deteriorate when oxygen comes into contact with them. Examples of such materials are fat containing materials, like butter and margarine, other dairy products and bakery products, like biscuits and other food products like chips, sweets and confectionery. When exposed to oxygen for some time, the products become rancid due to oxidation, particularly of the triglycerides therein, and/or stale.

In order to prevent those problems, the products are usually packed in such way that no oxygen can enter the package. Suitable packaging materials for this purpose are PVC and laminated papers, provided that at least one of the layers is an aluminum layer.

The environmental disadvantages of using PVC are well known, whereas complicated laminates containing aluminum are relatively expensive to produce, resulting in increased costs of the packaging material. Other possibilities for packaging susceptible materials lie in the use of laminates containing

barrier materials, such as Saran™. The use of those materials is rather complicated, as it requires multilayer systems. Also these materials are rather expensive

One object of the present invention is to provide a material that is simple and easy to produce and has excellent barrier properties, i.e. a strongly reduced oxygen permeability and can thus be used extremely well as packaging material for products that are susceptible to oxygen.

The invention provides a coated substrate having reduced oxygen and vapour permeability, said coated substrate comprising at least one layer of substrate and at least one layer of a blend of

a. at least one film forming polymer, or a blend of such film forming polymer and at least one other polymer, and
b. at least one reaction product of at least one EPDM rubber, at least one ethylene-vinyl acetate copolymer and at least one ethylene copolymer having short chain branching,

applied to at least one surface of the substrate.

The substrates that can be used in the invention are the various sheet-like packaging materials used in the art, like paper and cardboard, but also other materials like plastics that do not possess sufficient barrier properties for oxygen and vapour.

Surprisingly, it has been found that excellent barrier properties for oxygen and vapour, i.e. a strongly reduced permeability of oxygen and vapour through the material, can be obtained. Even if the barrier properties of the separate materials, i.e. the substrate and the layer of film forming polymer, are low the combination of the layers has a good barrier value.

According to a preferred embodiment the said substrate has on its surface one or more functional groups. It has been found that said functional groups may interact or react with components of the blend, resulting in a superior barrier material.

Said functional groups may comprise hydroxy, carboxy, silane, amino, carboxylic acid and other comparable groups.

The functional groups may be present on the surface in the form of a coating of the surface of the substrate. It is also possible that the material of the substrate surface has already sufficient functional groups. Generally it is however preferred to have the functional groups present in a coating applied over the surface of the substrate.

The principle behind the improvement of the barrier properties is not entirely clear. It is assumed that the reaction product present in the blend reacts with the functional groups on the surface of the substrate, resulting in the improvement of the barrier properties.

Suitable components containing functional groups are for example paper size, a reactive polymer, like acrylate or methacrylate polymer, a silane and the like.

The substrate can suitably be paper, cardboard or another sheet-like cellulose based material suitable for packaging food or food ingredients. It may also be a film of polymer having functional surface groups. Suitably those functional surface groups may have been obtained by applying a material containing functional groups to the said surface of the substrate. However it is also possible to give the surface a specific treatment resulting in the presence of the said functional groups.

According to the invention, it is preferred to combine one layer of substrate with one layer of the said blend, as this provides already sufficient barrier properties. However, it is possible to combine more layers of substrate and/or of the blend in one structure. It is also possible to include other layers, for example to protect the other surface of the substrate against water.

According to a preferred embodiment of the present invention, the said blend of at least one film forming polymer and at least one reaction product of at least one EPDM rubber, at least one ethylene-vinylacetate copolymer and at least one

ethylene copolymer having short chain branching, is melt-extruded onto the surface of the paper. In the most preferred embodiment of the invention, the surface of the paper to which the blend is applied is sized, preferably with a modified starch and/or polymeric sizing agent.

In the present invention, the paper is preferably a conventional paper having a paper weight between 30 and 250 g/m^2. This paper is preferably sized with a sizing agent, such as a modified potato starch comprising a hydroxy-propyl modified starch ether, carboxymethyl cellulose and/or a polymeric sizing agent such as those based upon epichlorohydrin modified polyamide. Surprisingly, it has been found that sized paper gives excellent barrier properties. Paper having a layer of a waxy material already gave a strong decrease in oxygen and vapour permeability, but especially so-called grease proof paper, i.e. sized with hydroxy-propyl modified starch ether in combination with epichlorohydrin modified polyamide has an excellent performance.

The above-mentioned reaction product is for example described in European patent applications Nos. 287,140 and 316,037, the contents of which is incorporated herein by reference. The said reaction product is based upon at least three materials, namely an EPDM rubber, an ethylene-vinyl acetate copolymer and an ethylene copolymer having short chain branching. The last material may be an LLDPE, that is an ethylene/1-(C_4-C_8) alkylene copolymer, or another ethylene copolymer, wherein at least one comonomer is present with 4 or more atoms in a carbon chain. The ethylene/1-(C_4-C_8)alkylene copolymer may be any suitable copolymer, although the use of 1-hexene and 1-octene copolymers are preferred.

The term 'short chain branching' is used to exclude the materials having long chain branching, that is materials based on LDPE. The length of the side chains of the ethylene copolymer preferably varies between 2 and 10, preferably between 2 and 6 carbon and/or oxygen atoms.

Most preferred is the reaction product of the European patent application No. 316,037, which reaction product is defined as based upon 1-10 wt.% of EPDM rubber, 35-65 wt.% of ethylene-vinyl acetate copolymer and 30-60 wt.% ethylene/1-(C_4-C_8)alkylene copolymer.

However, it is also possible to use the material defined in European patent application No. 287,140, namely the reaction product of 30-70 wt.% of EPDM rubber, 30-70 wt.% of ethylene-vinyl acetate copolymer and 1-25 wt.% ethylene/1-(C_4-C_8) alkylene copolymer. Finally, it is also possible to use a combination of both reaction products.

The said reaction product can be prepared in the manner disclosed in the two cited European patent applications. More in particular this can be done by melt-mixing the components in the required ratio in a suitable extruder, providing sufficient shear and heat to obtain the reaction. The required melt temperature for the reaction is usually at least 150°C, more in particular between 175 and 275°C.

Said at least one film forming polymer can be any film-forming polymer that adheres to paper. The polymer or polymer blend is preferably chosen from the group of alkylene polymers, alkylene copolymers, polyamides, blends thereof, and blends of said polymers and other polymers or copolymers.

The film forming polymer is preferably a low density polyethylene, such as a high pressure polyethylene or an ethylene-1-alkylene copolymer, i.e. a copolymer of ethylene and at least one of the group of butylene, hexene and octene. Said film forming polymer may contain at least one other polymer, such as polypropylene or a copolymer of propylene. Preferred is the use of a blend of low density polyethylene and polypropylene. According to another preferred embodiment, a blend of polyamide, usually nylon 6, and polypropylene is used.

The amounts of the various components in the said polymer blend depend on the use. The amount of the reaction product mainly determines the barrier properties. Without being bound

to this, the inventors have the impression that the said reaction product reacts with the paper or the sizing thereof, which results in the surprising barrier properties. Suitable amounts for these reaction products are between 1 and 20 wt.%, preferably between 2.5 and 10 wt.% based upon the weight of the film forming polymer blend.

In case a combination of two or more film forming polymers is used, the ratio of these polymers will be determined by the required properties of the end product. According to the preferred embodiment, the low density polyethylene and the polypropylene are present in a ratio of 10/90 to 90/10, preferably 85/15 to 50/50.

The oxygen and vapour permeability of the coated paper depends to a degree on the thickness of the materials used and more in particular the thickness of the film forming polymer blend. Appropriately, the thickness of said film ranges between 10 and 75 μm. The thickness of the paper depends mainly on the application and the paper strength required for that use.

The components of the paper coating can be melt blended prior to the application thereof to the paper. This can be done in a conventional extruder suitable for this purpose.

The coated paper can be used as packaging material in various applications. Particularly important applications are those where presently aluminum containing paper laminates, or PVC are being used. Examples thereof are the packaging of fat-containing products, like dairy products and bakery products.

The invention is now elucidated in and by the following examples, without being limited thereto.

EXAMPLE

A blend of 7.5 wt.% of the reaction product described in Example 1 of European patent application No 316,037, 25 wt.% of propylene homopolymer and 50 wt.% of linear low density polyethylene (ethylene/1-octene copolymer) was prepared by

melt-blending the components. The blend was extruded onto the surface of three different types of 50 g/m^2 paper to form a 50µm layer.

Using unsized paper the oxygen permeability, determined at 23°C, 0% RH, was 570 cm^3/m^2/24h. With paper sized with a waxy material the oxygen permeability was 15.6 cm^3/m^2/24h and the paper sized with hydroxy-propyl modified starch ether in combination with epichlorohydrin modified polyamide gave a permeability of 6.6 cm^3/m^2/24h.

CLAIMS

1. Coated substrate having reduced oxygen and vapour permeability, said coated substrate comprising at least one layer of substrate and at least one layer of a blend of

a. at least one film forming polymer, or a blend of such film forming polymer and at least one other polymer, and

b. at least one reaction product of at least one EPDM rubber, at least one ethylene-vinyl acetate copolymer and at least one ethylene copolymer having short chain branching,

applied to at least one surface of the substrate.

2. Coated substrate according to claim 1, wherein the said ethylene copolymer having short chain branching is an ethylene/1-(C_4-C_8)alkylene copolymer.

3. Coated substrate according to claim 1 or 2, wherein said blend is melt-extruded onto the surface of the substrate.

4. Coated substrate according to claim 1-3, wherein said at least one surface of the substrate contains functional groups.

5. Coated substrate according to claim 4, wherein said functional groups have been chosen from the groups consisting of hydroxy, carboxy, silane, amino, carboxylic acid and other comparable groups.

6. Coated substrate according to claims 1-5, wherein said at least one film forming polymer is chosen from the group of alkylene polymers, alkylene copolymers, polyamides, blends thereof, and blends of said polymers and other polymers or copolymers.

7. Coated substrate according to claim 6, wherein the said at least one film forming polymer is low density polyethylene or a blend of low density polyethylene and at least one other polymer or copolymer.

8. Coated substrate according to claim 7, wherein a blend of a low density polyethylene and polypropylene or a copolymer of propylene is used.

9. Coated substrate according to claim 7 or 8, wherein the low density polyethylene is a high pressure polyethylene or a copolymer of ethylene and at least one of the group of butylene, hexene and octene.

10. Coated substrate according to claims 1-9, wherein the oxygen permeability as defined herein is not more than 20 $cm^3/m^2/24h$.

11. Coated substrate according to claim 1-10, wherein the said substrate has been selected from the group of paper, cardboard, and other materials like plastics that do not possess sufficient barrier properties for oxygen and vapour.

12. Substrate coated with a blend of low density polyethylene and polypropylene, having an oxygen and vapour permeability of not more than 20 $cm^3/m^2/24h$.

13. Process for the production of a coated substrate according to claim 1-12, said process comprising providing a layer of a blend of at least one film forming polymer and at least one reaction product of at least one EPDM rubber, at least one ethylene-vinyl acetate copolymer and at least one ethylene copolymer having short chain branching, on at least one surface of a substrate.

14. Process according to claim 13, wherein said blend is melt-extruded onto the surface of the substrate.

15. Process according to claim 13 or 14, wherein said at least one film forming polymer is chosen from the group of alkylene polymers, alkylene copolymers, polyamides, blends thereof, and blends of ssaid polymers and other polymers or copolymers.

16. Process according to claim 15, wherein the said at least one film forming polymer is low density polyethylene or a blend thereof with at least one other polymer or copolymer.

17. Process according to claim 16, wherein a blend of a low density polyethylene and polypropylene or a copolymer of propylene is used.

18. Process according to claim 16 or 17, wherein the low density polyethylene is a high pressure polyethylene or a copolymer of ethylene and at least one of the group of butylene, hexene and octene.

19. Coated substrate obtainable by the process of any one of the claims 13-18.

20. Packaging prepared in whole or in part from coated substrate according to claims 1-12.

21. Use of the coated substrate according to claims 1-12, as packaging material.

INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 93/00013

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 D21H27/10; D21H19/22; B65D65/38

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	D21H

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY. vol. 49, no. 10, April 1979, APPLETON US page 929 LAIHO ET AL. 'Possible resins and material combinations in co-extrusion coating.' see abstract & TAPPI SEMINAR NOTES INTERN. COEXTRUSION TRAINING SEMINAR (AMSTERDAM) JUNE 1978 Pages 37-46 ; LAIHO ET AL. * pages 37-38, 42 ; fig. 11 * ---	1-9,11, 13-21
Y	EP,A,0 287 140 (VAN DER GROEP) 19 October 1988 cited in the application see examples 54-55 ---	1-9,11, 13-21
A	DD,A,120 214 (BOHLMANN ET AL.) 5 June 1976 ---	
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° Special categories of cited documents :[10]

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
26 APRIL 1993	04. 06. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	SONGY Odile

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 316 037 (VAN DER GROEP) 17 May 1989 cited in the application	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

NL 9300013
SA 69693

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 26/04/93
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		NL-A- 8701208	16-12-88
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		JP-B- 4003785	24-01-92
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