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(12) (19) (CA) **Demande-Application**

(21) (A1) **2,231,627**
(22) 1998/03/10
(43) 1998/11/21

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(51) Int.Cl.[6] A22C 13/00, B65D 65/46
(30) 1997/05/21 (197 21 142.9) DE

(54) **BOYAU MULTICOUCHE A ORIENTATION BIAXIALE POUR ALIMENTS, RENFERMANT DEUX COUCHES BARRIERES POUR L'OXYGENE**

(54) **MULTILAYERED, BIAXIALLY ORIENTED FOOD CASING COMPRISING TWO OXYGEN-BARRIER LAYERS**

(57) L'invention porte sur au moins quatre boyaux alimentaires à quatre couches et orientation tubulaire biaxiale; la couche externe est essentiellement constituée dans chaque cas, d'au moins un (co)polyamide aliphatique et d'au moins un (co)polyamide partiellement aromatique, avec ou sans pigments, et d'une couche interne constituée essentiellement d'un (co)polyamide aliphatique; entre ces couches il y a une couche d'un copolymère d'éthylène/alcool vinylique ou d'un mélange du copolymère d'éthylène/alcool vinylique avec un (co)polyamide aliphatique ou partiellement aromatique et (ou) d'un (co)polymère oléfinique et (ou) d'une résine d'ionomère, et une couche constituée essentiellement d'un (co)polymère oléfinique avec ou sans agents de couplage, pigments et (ou) agents absorbants. Le boyau est une barrière efficace pour la vapeur d'eau et l'oxygène. Il convient particulièrement bien comme boyau synthétique pour les saucisses, mais peut également servir à envelopper des fromages ou de la nourriture pour animaux.

(57) The invention relates to an at least four-layer tubular biaxially oriented food casing having an outer layer which essentially consists of a mixture of in each case at least one aliphatic and one partly aromatic (co)polyamide with or without pigments, and an inner layer which essentially consists of aliphatic (co)polyamide, wherein, between these layers, a layer of an ethylene/vinyl alcohol copolymer or a blend of the ethylene/vinyl alcohol copolymer with an aliphatic or partly aromatic (co)polyamide and/or with an olefinic (co)polymer and/or an ionomer resin and a layer which essentially consists of an olefinic (co)polymer with or without coupling agents, pigments and/or UV absorbers are arranged. The casing has a high water-vapor and oxygen barrier. It is particularly suitable as synthetic sausage casing, but can also be used for packaging cheese or animal feed.

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97/K304 May 21, 1997

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Abstract:

Multilayer, biaxially oriented food casing having two oxygen-barrier layers

The invention relates to an at least four-layer tubular biaxially oriented food casing having an outer layer which essentially consists of a mixture of in each case at least one aliphatic and one partly aromatic (co)polyamide with or without pigments, and an inner layer which essentially consists of aliphatic (co)polyamide, wherein, between these layers, a layer of an ethylene/vinyl alcohol copolymer or a blend of the ethylene/vinyl alcohol copolymer with an aliphatic or partly aromatic (co)polyamide and/or with an olefinic (co)polymer and/or an ionomer resin and a layer which essentially consists of an olefinic (co-)polymer with or without coupling agents, pigments and/or UV absorbers are arranged. The casing has a high water-vapor and oxygen barrier. It is particularly suitable as synthetic sausage casing, but can also be used for packaging cheese or animal feed.

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Multilayered, biaxially oriented food casing comprising two oxygen-barrier layers

The invention relates to a multilayered, biaxially oriented food casing made of thermoplastics, and to a process for its production.

Food casings of the type mentioned at the outset are used in particular for producing cooked-meat sausage and scalded-emulsion sausage. In general, the longest possible storage life of the sausage is sought after. Casings have been developed for this which have a decreased permeability to water vapor and/or oxygen. The water vapor barrier prevents drying out during storage and the oxygen barrier prevents oxidation of the sausage emulsion. An increasing gray coloration of the emulsion surface indicates oxidation which causes the gradual spoilage of the sausage.

Sausages which are to be stored for longer than three months must be sterilized after stuffing. This sterilization is customarily carried out in a steam autoclave at a temperature of about 115 to 130°C. Even with sausage casings having an increased oxygen barrier, a sterilization is required, since in addition to aerobes, anaerobic microorganisms can also lead to spoilage. An ingress of atmospheric oxygen can obviously not be decreased by the sterilization.

A single-layer casing having a good water vapor and oxygen barrier may be produced from vinylidene chloride copolymers. However, these special VDC copolymers are expensive and poorly environmentally compatible on account of their chlorine content. Therefore, chlorine-free multilayer food casings have been developed in which in each case at least one polymer layer assures the water vapor barrier or oxygen barrier. These casings are generally produced by coextrusion. Thus, EP-A 0 467 039 discloses a tubular casing which consists of an outer layer of aliphatic polyamide, a central layer of polyolefin and a coupling component and an inner layer of aliphatic and/or partly aromatic (co)polyamides. For sausage goods which are to be stored for a relatively long period, however, the oxygen barrier itself of this casing is not sufficient.

Biaxially oriented tubular films having an outer layer of aliphatic polyamide, a central oxygen barrier layer of an ethylene/vinyl alcohol copolymer (EVOH) or of (partly) aromatic copolyamide and an inner layer of olefinic (co)polymers are described in EP-A 0 530 539. However, the polyolefin inner layer leads to an unsatisfactory adhesion of the casing to the sausage emulsion. In order to improve this adhesion, for the inner layer, use can be made of polyolefins which are modified with polar groups. It is also possible to blend the polyolefins with polar (co)polymers. However, all these measures have the disadvantage that they decrease the water-vapor barrier of the inner layer. A corona treatment of the olefinic inner layer likewise leads to an improved emulsion adhesion, it is at all events technically very complex. A further disadvantage of the tubular films as described in EP-A 0 530 539 is that the outer polyamide layer is water-vapor permeable, so that the central EVOH layer can absorb moisture. It is generally known that the oxygen permeation of the EVOH layer increases five hundred to one thousand times if the relative humidity increases from 0 to 100% (see J. Rellmann, H. Schenck in: Kunststoffe 82 [1992] 731). In the case of relatively long storage, in particular in a moist environment, the oxygen barrier of this casing is therefore scarcely greater than that of a single-layer polyamide casing. If the central layer consists of the (partly) aromatic copolyamide (e.g. poly[meta-xylylene adipamide] = nylon MXD6), although its oxygen barrier action is retained if the relative humidity is increased from 0 to 100%, the barrier action is too small in any case. A layer of nylon MXD6 still allows the passage of a tenth of the oxygen volume that penetrates a corresponding layer of nylon 6. In order to prevent oxidation during storage for several months, the oxygen barrier is not sufficient.

EP-A 0 530 549 likewise discloses a three-layer casing having a central EVOH layer. The outer layer here consists of olefinic (co)polymers, while the inner layer is formed of aliphatic polyamide. This casing also does not have a long-lasting oxygen barrier when it is filled with emulsion. The moisture present in abundance in the emulsion slowly migrates through the inner polyamide layer into the central EVOH layer and greatly reduces its oxygen barrier action.

In order to rectify these defects, casings having still more layers have been developed. Thus EP-A 0 603 676 describes a biaxially oriented five-layer tubular film. The layer sequence in this casing is symmetrical. Adjacent to each side of the central EVOH layer are layers of polyolefin, which are each in turn followed by one layer of aliphatic polyamide. The polyolefinic interlayers substantially protect the central layer from moisture. However, the protective action of the interlayers is not sufficient against the superheated steam used during the sterilization (see B.C. Tsai and J.A. Wachtel in ASC Symp. Ser. 423 [1990] 198). Although, after the sterilization, the moisture slowly diffuses again out of the casing, a residual moisture remains in the central layer, which greatly reduces the oxygen barrier.

To date, there is no chlorine-free polymer-based tubular food casing which has a high oxygen barrier which remains under all conditions of practice.

The object was therefore to provide a food casing having a high water-vapor and oxygen barrier which may be sterilized using superheated steam, without this substantially increasing the oxygen permeability.

The object is achieved by an at least four-layer tubular biaxially oriented food casing having

a) an outer layer which essentially consists of a mixture of in each case at least one aliphatic and one partly aromatic (co)polyamide with or without pigments, and
d) an inner layer which essentially consists of aliphatic (co)polyamide,

wherein, between these layers,

b) a layer of an ethylene/vinyl alcohol copolymer or a blend of the ethylene/vinyl alcohol copolymer with an aliphatic or partly aromatic (co)polyamide and/or with an olefinic (co)polymer and/or an ionomer resin and
c) a layer which essentially consists of an olefinic (co)polymer with or without coupling agents, pigments and/or UV absorbers

are arranged. The layer c) can also be present multiply, in particular twice, in the casing.

The content of aliphatic (co)polyamide in the outer layer is preferably 40 to 95% by weight, particularly preferably 60 to 90% by weight, in each case based on the total weight of the layer. Preferred aliphatic (co)polyamides are nylon 6 and nylon 6/66. Preferred partly aromatic (co)polyamides are poly(meta-xylylene adipamide) and nylon 6I/6T. Particularly preferably, the outer layer consists of a blend of 60 to 90% by weight of nylon 6 and/or nylon 6/66 and 40 to 10% by weight of nylon-MXD6. The content of partly aromatic (co)polyamide markedly decreases the oxygen permeability of the outer layer. The oxygen permeability decreases still further even here if the casing is exposed to moisture or is sterilized with superheated steam.

The layer can, in addition, further comprise generally conventional additives, in particular pigments. The layer may be colored by the pigments. Pigments can also decrease the tendency to blocking. The thickness of the outer layer is generally 12 to 30 μm, preferably 15 to 25 μm.

The ethylene/vinyl alcohol copolymer (EVOH) of the central layer b) preferably consists of 29 to 47 mol% ethylene units and 71 to 53 mol% vinyl alcohol units. In addition to 30 to 90% by weight of EVOH, the layer preferably comprises 70 to 10% by weight of at least one aliphatic and/or one partly aromatic (co)polyamide. Suitable co-polyamides are, for example, nylon 6/69, nylon 6/12 and nylon 6I/6T. Suitable olefinic copolymers are, for example, ethylene/acrylic acid or ethylene/methacrylic acid copolymers. If the hydrogen atoms in a greater or lesser proportion of the carboxyl groups of these copolymers are replaced by metal cations (for example Na^+ or 1/2 Zn^{2+}), suitable ionomer resins are attained. The EVOH gives the layer b) a high oxygen-barrier action. Said (co)polyamides and/or olefinic (co)polymers do not decrease the oxygen barrier, or only insignificantly, but in addition cause an improved suppleness of the layer. A layer of pure EVOH, in contrast, is relatively stiff, still stiffer than that of the layers a), c) and d). Thus an EVOH having a content of 32 mol% of ethylene units has a tensile modulus of elasticity of about 3800 N/mm^2, while moist nylon 6 has a tensile modulus of elasticity of about 700, that is gives much less resistance to mechanical extension. Improved suppleness of the layer b) leads to the casing being extensible and thus being able to be stuffed more readily. At the same time, it ensures that during stuffing or scalding of the emulsion no cracks form in the layer. Such cracks would greatly impair the barrier action. The layer b) generally has a thickness of 3 to 15 μm, preferably 6 to 12 μm.

The polyolefinic layer c) preferably consists of polyethylene, ethylene-α-olefin copolymers, polypropylene and/or ethylene/propylene copolymers. The polyolefins can be modified by functional groups. They then have a coupling effect between EVOH and polyamide. The same result is achieved if a coupling agent is mixed with the polyolefins. The coupling agents are generally organic polymers. They can therefore also form a separate layer on one or both sides of the polyolefinic layer c). The layer c) can, in addition, further contain color pigments and/or organic or inorganic UV absorbers. If only one layer c) is present, it is generally arranged between the layers b) and d). If two layers c) are present, one is present between the layer b) and the outer layer a), and between the layer b) and the inner layer d), respectively. In the case of a five-layer casing, the sequence of the individual layers is preferably a) - c) - b) - c) - d). The thickness of the (respective) olefinic layer(s) is 5 to 20 μm, preferably 8 to 12 μm.

Suitable aliphatic polyamides for the inner layer d) are, for example, nylon 6/69. The thickness of the layer d) is generally 4 to 15 μm, preferably 5 to 10 μm.

The food casings according to the invention can be produced by known processes. A particularly suitable process comprises the steps of

- extruding the individual layers through an annular coextrusion die to form a multilayer primary tube,
- cooling and solidifying the primary tube,

- heating the primary tube to a temperature required for orientation,
- orienting the primary tube in the longitudinal and transverse direction at this temperature and, if appropriate,
- heat-setting the oriented tube.

In this process, the starting materials for the individual layers are firstly melted and plastified in different extruders. The individual polymer melts are then fed to an annular coextrusion die. The so-called primary tube resulting in the extrusion is then solidified under intensive cooling. It is then reheated to a temperature required for orientation. The orientation itself is generally performed by the action of a pressurized gas (e.g. air) in the interior of the tube. In the machine direction (= longitudinal direction), the extension can be reinforced by suitably set roll pairs. The oriented tube is then customarily further heat-set. The heatsetting improves the dimensional stability of the tube.

The food casing according to the invention is used in particular as synthetic sausage casing, especially for cooked-meat sausages and scalded-emulsion sausages which are required to keep over long storage times, and in addition, for example, for packaging cheese or animal feed.

The examples below illustrate the invention. Data on the composition of the individual layers in percent are by weight.

The water vapor permeability was determined as specified in DIN 53122 by gravimetry at an H_2O partial pressure difference of 85% to 0% and a temperature of 23°C.

The oxygen permeability was determined as specified in DIN 53380 using an Oxtran® 10 instrument from Mocon at 53% relative humidity and 23°C.

The sausage casings were also tested under conditions of practice. For this purpose, the casings were soaked in water in sections for 30 minutes and then stuffed with fine-grained calf liver sausage emulsion. The sausages were then scalded and sterilized in a counterpressure steam autoclave for 60 minutes at a temperature of 115°C. After cooling, they were stored in a cold room at 6°C for a time period specified in the table below. At the end of the storage time, the sausages were sliced. A part of the casing was carefully taken off and the color of the emulsion surface was evaluated in comparison with a freshly stuffed sausage.

<u>Example 1</u>:
A four-layer primary tube was produced by coextrusion, having

a) an outer layer of 70% nylon 6/66 (Ultramid® C4, BASF AG), blended with 30% of nylon MXD6 (nylon MX 6007 of Mitsubishi Gas Chem.)
b) a central layer of 80% of an ethylene/vinyl alcohol copolymer containing 32 mol% ethylene units and 68 mol% vinyl alcohol units (Soarnol® DC of Nippon Gohsei), blended with 20% polyamide 6/69 (Grilon® CF62BS, Ems-Chemie),
c) a central layer of maleic-anhydride-grafted low density linear polyethylene (grafted LLDPE = Escor® CTR 2000 from Exxon Ltd.) and
d) an inner layer of nylon 6/66 (Ultramid® C4 of BASF AG).

The primary tube was rapidly cooled to about 15°C, then heated to about 90°C and biaxially oriented at this temperature. The area drawing ratio was 9.1 : 1. Heatsetting followed, in which the tube was initially squeezed flat air-tightly by a roller pair, then reinflated, passed through a heating chamber and finally squeezed flat again. The diameter of the heat-set tube was 45 mm, with a wall thickness of 45 µm. The layer a) made up 25 µm thereof, the layer b) 7 µm, the layer c) 8 µm and the layer d) 5 µm. The properties of the tube are summarized in the table.

Example 2:
As described in Example 1, a biaxially oriented heat-set four-layer tube having a diameter of 45 mm and a wall thickness of 50 µm was produced.

The outer layer a) consisted of 60% nylon 6/66, 30% nylon MXD6 and 10% nylon 6I/6T (Selar® PA 3426 from DuPont) and had a thickness of 25 µm. The central layer b) consisted of 50% of the ethylene/vinyl alcohol copolymer mentioned in Example 1, blended with 50% of the nylon 6/69 likewise mentioned in Example 1, and had a thickness of 12 µm. The olefinic layer c), and also the inner polyamide layer d) had the same thickness and consisted of the same material as the layers c) and d) in Example 1.

Example 3:
In a similar manner to Example 1, a biaxially oriented, heat-set, five-layer tube having a diameter of 45 mm and a wall thickness of 50 µm was produced. The outer layer a), the olefinic layer c) and also the inner polyamide layer d) had in this case the same composition and thickness as the layers a), c) and d) in Example 2. The layer b) in turn, had the same composition and thickness as the layer b) in Example 1.

Between the outer polyamide layer a) and the central layer b), however, lay, in addition, a further olefinic layer c) of the same composition as the first layer c), but this had a thickness of only 5 μm.

Comparison Example V1:

As described in Example 1, a biaxially oriented heat-set four-layer tubular casing having a diameter of 45 mm and a wall thickness of 45 μm was produced. The polyolefinic layer c) and the inner polyamide layer d) had the same composition and thickness as the layer c) and d) in Example 1. The outer polyamide layer a), however, consisted solely of nylon 6/66 (Ultramid® C4 from BASF AG); its thickness was 25 μm. The layer b) arranged between the layers a) and c) consisted of the ethylene/vinyl alcohol copolymer as described in Example 1 and had a thickness of 7 μm.

Comparison Example V2:

In similar manner to Example 1, a biaxially oriented heat-set three-layer tubular casing having a diameter of 45 mm and a wall thickness of 45 μm was produced. The outer and inner layers each consisted of nylon 6/66 and had a thickness of 30 μm and 5 μm, respectively. The central layer consisted of the grafted polyethylene mentioned in Example 1 and had a thickness of 10 μm.

Table

Example	Water-vapor permeability [g/m^2 day]	Oxygen permeability [cm^3/m^2 day bar]	Visual rating of the color of the emulsion surface after	
			4 weeks	12 weeks
1	4.7	5.3	0	0
2	4.6	5.1	0	0
3	3.2	3.2	0	0
V1	4.8	0.9	1	1
V2	3.8	15.3	1	2

In the rating of the color of the emulsion surface after the respective storage times, the values denote the following:

0 = No observable gray discoloration
1 = Slight gray discoloration
2 = Severe gray discoloration

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Patent claims

1. An at least four-layer tubular biaxially oriented food casing having

   a) an outer layer which essentially consists of a mixture of in each case at least one aliphatic and one partly aromatic (co)polyamide with or without pigments, and
   d) an inner layer which essentially consists of aliphatic (co)polyamide,

   wherein, between these layers,

   b) a layer of an ethylene/vinyl alcohol copolymer or a blend of the ethylene/vinyl alcohol copolymer with an aliphatic or partly aromatic (co)polyamide and/or with an olefinic (co)polymer and/or an ionomer resin and
   c) a layer which essentially consists of an olefinic (co)polymer with or without coupling agents, pigments and/or UV absorbers

   are arranged.

2. The food casing as claimed in claim 1, wherein the content of aliphatic (co)polyamide in the outer layer a) is 40 to 95% by weight, preferably 60 to 90% by weight, in each case based on the total weight of the layer.
3. The food casing as claimed in claim 1 or 2, wherein the thickness of the outer layer a) is 12 to 30 μm, preferably 15 to 25 μm.

4. The food casing as claimed in one or more of claims 1 to 3, wherein the ethylene/vinyl alcohol copolymer of layer b) consists of 29 to 47 mol% of ethylene units and 71 to 53 mol% of vinyl alcohol units.

5. The food casing as claimed in one or more of claims 1 to 4, wherein the layer b) consists of 30 to 90% by weight of at least one ethylene/vinyl alcohol copolymer and 70 to 10% by weight of at least one aliphatic and/or one partly aromatic (co)polyamide.

6. The food casing as claimed in one or more of claims 1 to 5, wherein the thickness of the layer b) is 3 to 15 μm, preferably 6 to 12 μm.

7. The food casing as claimed in one or more of claims 1 to 6, wherein the polyolefinic layer c) consists of polyethylene, polypropylene and/or ethylene/propylene copolymers.

8. The food casing as claimed in one or more of claims 1 to 7, wherein the thickness of the olefinic layer(s) c) is (in each case) 5 to 20 μm, preferably 8 to 12 μm.

9. The food casing as claimed in one or more of claims 1 to 8, wherein the thickness of the inner layer d) is 4 to 15 μm, preferably 5 to 10 μm.

10. The food casing as claimed in one or more of claims 1 to 9, wherein it is five-layered and has one olefinic layer c) in each case between the layer b) and the outer layer a) and between the layer b) and the inner layer d).

11. The food casing as claimed in one or more of claims 1 to 10, wherein it is heat-set.

12. A process for producing the food casing as claimed in one or more of claims 1 to 11, comprising the steps of

- extruding the individual layers through an annular coextrusion die to form a multilayer primary tube,
- cooling and solidifying the primary tube,
- heating the primary tube to a temperature required for orientation,
- orienting the primary tube in the longitudinal and transverse direction at this temperature and, if appropriate,
- heat-setting the oriented tube.

13. The use of the food casing as claimed in one or more of claims 1 to 11 as synthetic sausage casing or for packaging cheese and animal feed.

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