

TITLE OF THE INVENTION:

PACKAGING BAG ✓

BACKGROUND OF THE INVENTION:

The present invention relates to a packaging bag, and more particularly, to a packaging bag suitable as a food packaging bag for wrapping food such as ham and sausage upon the production thereof.

In general, ham and sausage have been produced by filling raw materials thereof in a bag composed of a shrinkable film and then heat-treating the raw materials in the bag in a retainer. Before these foods are marketed, a printed label is attached onto a surface of the bag filled with food. Since the adhesion strength of the printed label to the surface of the food-filled bag is adversely affected by water present on a label-adhesive surface of the surface of the food-filled bag, it is desirable that water can be readily removed from the surface of the food-filled bag taken out of the retainer to such an extent that it is unnecessary to dry the surface of the bag before the label is attached thereto. Also, packaging bags whose surfaces have a good water-releasing or removing property and are excellent in label adhesion strength even after washed with water, have been demanded for packaging not only food but also various other products. In addition, the packaging bags have been required to have an excellent pinhole resistance upon transportation thereof.

As a result of the present inventor's studies, it has been found that by laminating (A) as an outermost layer, a blend resin layer comprising a polyester resin containing a specific



amount of a polyethylene naphthalate-forming unit and a polyester resin containing a specific amount of a polyethylene terephthalate-forming unit, or a polyester resin layer containing a specific amount of a polybutylene terephthalate-forming unit, (B) a gas-barrier resin layer and (C) as an innermost layer, a heat-sealable resin layer in this order, and heat-sealing the obtained laminated film, the thus obtained packaging bag shows excellent label adhesion strength and pinhole resistance. On the basis of the above-mentioned finding, the present invention has been attained.

SUMMARY OF THE INVENTION:

It is an object of the present invention to provide a packaging bag capable of exhibiting excellent label adhesion strength and pinhole resistance.

To attain the aim, in a first aspect of the present invention, there is provided a packaging bag produced by heat-sealing an unstretched laminated film comprising at least (A) a blended resin layer comprising a polyester resin containing not less than 70 mol % of a polyethylene naphthalate-forming unit and a polyester resin containing not less than 70 mol % of a polyethylene terephthalate-forming unit, or a polyester resin layer containing not less than 70 mol % of a polybutylene terephthalate-forming unit; (B) a gas-barrier resin layer; and (C) a heat-sealable resin layer,

the resin layers (A), (B) and (C) being laminated in this order, such that the resin layer (A) is disposed as an outermost layer and the resin layer (C) is disposed as an innermost layer.



In a second aspect of the present invention, there is provided a packaging bag produced by heat-sealing an unstretched laminated film comprising (A) a blended resin layer comprising a polyester resin containing not less than 70 mol % of a polyethylene naphthalate-forming unit and a polyester resin containing not less than 70 mol % of a polyethylene terephthalate-forming unit, or a polyester resin layer containing not less than 70 mol % of a polybutylene terephthalate-forming unit; (D) an adhesive resin layer; (B) a gas-barrier resin layer; (D) an adhesive resin layer; and (C) a heat-sealable resin layer,

the resin layers (A), (D), (B), (D) and (C) being laminated in this order, such that the resin layer (A) is disposed as an outermost layer and the resin layer (C) is disposed as an innermost layer.

In a third aspect of the present invention, there is provided a food packaging bag comprising the packaging bag defined in the first or second aspect.

DETAILED DESCRIPTION OF THE INVENTION:

The present invention is described in detail below.

The packaging bag according to the present invention can be produced by heat-sealing an unstretched laminated film. The unstretched laminated film has a multi-layered structure comprising at least (A) a blended resin layer comprising a polyester resin containing not less than 70 mol % of polyethylene naphthalate-forming units and a polyester resin containing not less than 70 mol % of polyethylene terephthalate-



forming units, or a polyester resin layer containing not less than 70 mol % of polybutylene terephthalate-forming units; (B) a gas-barrier resin layer; and (C) a heat-sealable resin layer, wherein the resin layers (A), (B) and (C) are laminated in this order. Further, in the preferred embodiment of the present invention, adhesive resin layers may be interposed between the adjacent resin layers.

The respective polyester resins constituting the resin layer (A) may include not only homopolymers but also copolymers.

As the polyester resin composed of homopolymers, i.e., as polyethylene naphthalate (PEN) resins, polyethylene terephthalate (PET) resins or polybutylene terephthalate (PBT) resins, there may be exemplified any known resins which can be ordinarily used for the production of films.

As to the polyester resin composed of copolymers, the content of PEN-forming unit, PET-forming unit or PBT-forming unit in each polyester resin is preferably 85 to 99 mol %.

Components of the above-mentioned copolymers are as follows. That is, as dicarboxylic acid components of the copolymers, there may be exemplified isophthalic acid, phthalic acid, 2,6-naphthalene dicarboxylic acid, adipic acid, sebacic acid, oxycarboxylic acids (such as p-oxybenzoic acid), or the like. As glycol components of the copolymers, there may be exemplified ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, 1,4-cyclohexane dimethanol, neopentyl glycol, polyethylene oxide glycol, polypropylene oxide glycol, polytetramethylene oxide glycol or the like. Any two or more

kinds of these dicarboxylic acid components and glycol components may be used in combination.

In the case where the resin layer (A) comprises the blended resin, the weight ratio of PEN resin to PET resin may be usually selected from the range of 1:0.5 to 1:2.

As the polyester resins composed of copolymers, the polyester resins containing not less than 70 mol % of polybutylene terephthalate-forming units are preferred. In this case, as a copolymerizing component of the polyester resins, there may suitably be used polytetramethylene oxide glycol having a number-average molecular weight of preferably 300 to 6,000, more preferably 500 to 2,000. By using copolymerized PBT resins satisfying the above requirements, it is possible to produce films exhibiting not only a good flexibility without damage to heat resistance, but also a higher pinhole resistance than that of homopolymerized PBT resins because of an excellent low-temperature stretchability thereof. Such copolymerized PBT resins preferably have a melting point of 200 to 223°C, while the homopolymerized PBT resins have a melting point of 225°C.

The polyester resins constituting the resin layer (A) may further contain an anti-blocking agent composed of organic or inorganic particles in order to enhance an anti-blocking property of the resultant packaging bags when stored in stack.

As the anti-blocking agents composed of organic particles, there may be exemplified particles composed of homopolymers or copolymers of polystyrene, polyethylene, polyamides, polyesters, polyacrylic esters, polymethacrylic esters, epoxy resins, polyvinyl acetate, polyvinyl chloride or the like. The organic

particles may further contain a cross-linking agent. As the anti-blocking agents composed of inorganic particles, there may be exemplified talc, kaolin, silica, calcium carbonate, glass powder or the like.

The anti-blocking agents may have an average particle size of usually about 1 to about 10 μm . The amount of the anti-blocking agent used is usually 100 to 10,000 ppm, preferably 1,000 to 5,000 ppm based on the resin. In the present invention, the use of the anti-blocking agents composed of organic particles is preferred. Among them, the use of organic particles composed of polyacrylic esters or polymetacrylic esters is more preferred.

The gas-barrier resin layer (B) is composed of any resin selected from the group consisting of polyamides (PA), saponified products of ethylene-vinyl acetate copolymer (EVOH), polyethylene terephthalate (PET), polyethylene naphthalate (PEN) and polycarbonates (PC). Among these resins, polyamides (PA) or saponified products of ethylene-vinyl acetate copolymer (EVOH) are preferred, and polyamides (PA) are more preferred.

In the present invention, there may be used polyamides obtained by polycondensation between the respective raw materials, i.e., by polycondensation of (1) lactam having not less than 3-membered ring, (2) polymerizable ω -amino acid or (3) diamine, with dicarboxylic acid.

Specific examples of the lactams having not less than 3-membered ring may include ϵ -caprolactam, ϵ -anthocaprolactam, α -pyrrolidone, α -piperidone or the like. Specific examples of the polymerizable ω -amino acids may include 6-amino hexanoic acid,

7-amino heptanoic acid, 11-amino undecanoic acid, 9-amino nonanoic acid or the like.

Specific examples of the diamines may include hexamethylene diamine, nonamethylene diamine, undecamethylene diamine, dodecamethylene diamine, metaxylylene diamine or the like.

Specific examples of the dicarboxylic acids may include terephthalic acid, isophthalic acid, adipic acid, sebacic acid, dodecane dibasic acid, glutaric acid or the like.

Specific examples of the polyamides used in the present invention may include nylons 4, 6, 7, 8, 11, 12, 6·6, 6·10, 6·11, 6·12, 6T, 6/6·6, 6/12, 6/6T and 6I/6T, or the like.

As materials of the heat-sealable resin layer (C), there may be usually used high-density polyethylene (HDPE), medium-density polyethylene (MDPE), low-density polyethylene (LDPE), polypropylene (PP), ethylene-vinyl acetate copolymer (EVA), ethylene-methacrylic acid copolymer (EMA), ethylene-ethyl acrylate copolymer (EEA), ethylene-methyl methacrylate copolymer (EMMA), ethylene-acrylic acid copolymer (EAA), ethylene-ethyl methacrylate copolymer (EMAA), adhesive polyethylene, ionomer resins, saponified products of EVA, linear low-density polyethylene (L-LDPE) or copolymers thereof. Among these compounds, linear low-density polyethylene (L-LDPE) is preferably used.

The linear low-density polyethylene (L-LDPE) is a copolymer of ethylene with α -olefin having 3 to 13 carbon atoms and has an ethylene content of 86 to 99.5 mol %. The L-LDPE is a low medium-density polyethylene unlike conventional high-pressure processed LDPE. The high pressure-processed LDPE and the L-LDPE

are different from each other in that the high pressure-processed LDPE has a multi-branched molecular structure while the L-LDPE has a linear molecular structure. In the production of the L-LDPE, as the α -olefins to be copolymerized with ethylene, there may be used butene-1, pentene-1, hexene-1, octene-1, 4-methyl pentene-1 or the like. The copolymerization of ethylene with these α -olefins may be carried out by a low medium pressure process using a so-called Ziegler-Natta catalyst.

Specific examples of commercially available products of the above-mentioned linear low-density polyethylenes (L-LDPE) may include UNIPOL (Union Carbide Corp.), DOWLEX (Dow Chemical), SQULERE (du Pont, Canada), MARLEX (Philips Corp.), NEOZEX and ULTZEX (Mitsui Petrochemical Co., Ltd.), NISSEKI LINILEX (Nippon Petrochemical Co., Ltd.), STAMILEX (DSM) or the like.

The adhesive resin layer may be composed usually of modified polyolefin resins (APO). Such APOs can be produced by copolymerizing and/or graft-polymerizing a polyolefin resin composed mainly of an ethylene component and/or a propylene component with α -, β -unsaturated carboxylic acid or derivatives thereof.

As the polyolefin resins, there may be exemplified polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-butene-1 copolymer, ethylene-vinyl acetate copolymer, ethylene-acrylic acid copolymer, ethylene-ethyl acrylate copolymer, ethylene-sodium acrylate copolymer or the like.

As the α -, β -unsaturated carboxylic acid or derivatives thereof to be copolymerized with the polyolefin resin, there may be exemplified acrylic acid, methacrylic acid, methyl



methacrylate, sodium acrylate, zinc acrylate, vinyl acetate, glycidyl methacrylate or the like. These α -, β -unsaturated carboxylic acid or derivatives thereof may be present in the molecular chain of the polyolefin resins in an amount of not more than 40 mol %.

As the α -, β -unsaturated carboxylic acid or derivatives thereof to be grafted to the polyolefin resin, there may be exemplified acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, fumaric acid, anhydrides of these acids, esters of these acids or the like. Among these compounds used for modifying the polyolefin resins, maleic anhydride is especially preferred. The amount of these compounds grafted is 0.01 to 25 % by weight, preferably 0.05 to 1.5 % by weight based on the weight of the polyolefin resin.

The graft polymerization may be carried out by ordinary methods, i.e., by usually melt-mixing the polyolefin resin with the α -, β -unsaturated carboxylic acid or derivatives thereof at a resin temperature of 150 to 300°C. In the graft polymerization, in order to effectively carry out the reaction, it is preferred that organic peroxides such as α, α' -bis-*t*-butylperoxy-*p*-diisopropyl benzene be added to the reaction mixture in an amount of 0.001 to 0.05 % by weight based on the total weight of the polyolefin resin and the α -, β -unsaturated carboxylic acid or derivatives thereof.

In the unstretched laminated film, the resin layer (A) composed of a blend of polyethylene naphthalate resin and polyethylene terephthalate resin or composed of polybutylene terephthalate resin, is disposed so as to be an outermost layer

of the packaging bag, the resin layer (C) composed of heat-sealable resin is disposed so as to be an innermost layer of the packaging bag, and the resin layer (B) composed of gas-barrier resin is disposed so as to be an intermediate layer interposed between the resin layers (A) and (C). The thickness of the resin layer (A) is usually 5 to 100 μm , preferably 10 to 70 μm . The thickness of the resin layer (B) is usually 5 to 50 μm , preferably 10 to 30 μm . The thickness of the resin layer (C) is usually 20 to 100 μm , preferably 30 to 70 μm . The thickness of the adhesive layer which may be interposed between the adjacent resin layers in the preferred embodiment of the present invention, is usually 2 to 30 μm , preferably 5 to 15 μm .

The packaging bag according to the present invention may be produced, for example, by first forming into a tubular body of the laminated film by a down-flow water-cooling molding method using a co-extrusion cylindrical die and then heat-sealing an end portion of the tubular body. The laminated film may be produced by T-die method. The heat-sealing may be usually conducted by a gusseting process. The co-extrusion molding method and the gusseting process themselves are well known in the art, and suitable procedures thereof are briefly described below.

That is, in the co-extrusion molding method, a water vessel equipped with inner sizing rings is usually disposed beneath the cylindrical die. Further, a guide plate and a take-up roll are successively arranged underneath the water vessel. A plurality of raw resins are co-extruded through the cylindrical die while substantially preventing the resins from being stretched. After

the co-extruded resins are passed between the sizing rings for cooling, the resultant laminated film of a tubular shape is passed through the guide plate and fed to the take-up roll so as to fold and take up the film in the form of a double film. Accordingly, the obtained laminated film is substantially unstretched. Further, in the preferred embodiment, the laminated film exhibits a heat shrinkage percentage (JIS K 6734) of not more than 5 % in any of machine direction (MD) and transverse direction (TD).

The gusseting process is a process for folding and sealing an end portion of a tubular body of the film. In an ordinary gusseting process, the tubular film is formed into a rectangular shape at its open end, and a pair of opposed walls are folded inside from nearly a centerline of each wall. Another pair of walls are collapsed and overlapped over the folded opposed walls in an aligned manner to form gussets therebetween. The thus-obtained folded tubular film is heat-sealed along its gusseted end portion using a heat seal bar.

The packaging bag according to the present invention can be suitably applied to food packaging bags used, for example, for the production of ham and sausage, beverage packaging bags filled with natural water, etc., and the like. Especially, since the outermost layer of the packaging bag is composed of a specific polyester resin, the packaging bag can exhibit an excellent label adhesion strength even immediately after taken out of a retainer. Such a technical advantage of the packaging bag according to the present invention is considered to be imparted by the outermost layer which is composed of a resin

having an extremely high water-releasing or removing property. However, as described in Comparative Examples hereinafter, such a technical advantage of the packaging bag according to the present invention cannot be achieved, for example, by the use of PET resins or PEN resins similar to PBT resins. Accordingly, the effect of the present invention attained by the use of the specific blended resin or the PBT resin is an extremely unexpected result.

In particular, when the outermost layer of the packaging bag according to the present invention is composed of a polyester resin containing not less than 70 mol % of polybutylene terephthalate-forming units, the laminated film itself can exhibit an excellent anti-curl property. Specifically, a packaging bag whose outermost layer is composed of resins other than the above-specified polyester resin tends to cause curling at an open end thereof, thereby failing to be suitably filled with raw materials. Whereas, the packaging bag according to the present invention whose outermost layer is composed of the polyester resin containing not less than 70 mol % of polybutylene terephthalate units, is free from such disadvantages experienced in conventional packaging bags.

EXAMPLES:

The present invention will now be described in more detail with reference to the following examples, but the present invention is not restricted to those examples and various modifications are possible within the scope of the invention.

Example 1:

A laminated film having a multi-layered structure: PBT layer (8 μm)/an APO layer (6 μm)/an NY (nylon 6) layer (16 μm)/an APO layer (6 μm)/an L-LDPE layer (44 μm) was formed into a tubular shape by a down-flow water-cooling molding method using a five-layer co-extrusion cylindrical die. In the production of the laminated film, polymethyl methacrylate (PMMA) particles having an average particle size of 6 μm as an anti-blocking agent were added to the raw PBT resin in an amount of 2,000 ppm. The extrusion temperature was 240°C, the water-cooling temperature was 28°C and the take-up speed of film was 15 m/min. The thus-obtained tubular laminated film was cut into a predetermined length. The cut tubular film was subjected to gusseting process where it was heat-sealed linearly along one peripheral end thereof, thereby obtaining a gusseted bag having an outermost layer composed of PBT and an innermost layer composed of L-LDPE.

After previously cooked raw materials of ham were filled in the gusseted bag, the bag was placed in a retainer to heat-treat the raw materials, thereby obtaining ham of a rectangular shape having a square section of 8 cm x 8 cm at nearly a longitudinal center thereof and a whole length of 35 cm. The label adhesion strength, anti-blocking property, pinhole resistance and anti-curl property of the thus-obtained packaged ham product were evaluated by the following methods. The results are shown in Table 2.

(1) Label adhesion strength:

A label was attached onto a surface of the packaging bag of the ham product immediately after taken out of the retainer, and measured with respect to a peel strength (g/15 mm) thereof.

(2) Pinhole resistance:

Ten cases of the packaging bags (ten bags each case) were subjected to refrigerated transportation test at -20°C (by cruising over the whole Shikoku district). The pinhole resistance of the packaging bags was evaluated by determining the number of bags broken upon transportation.

(3) Anti-blocking property:

Two packaged ham products whose surfaces were dried were stacked one over another to measure a sliding property thereof. The measurement was conducted using a tension tester, and the sliding property measured was expressed by grams. The less the grams, the higher the sliding property and the more excellent the anti-blocking property.

(4) Anti-curl property:

Curling was visually observed at an open end of each gusseted bag.

Examples 2 and 3 and Comparative Examples 1 to 3:

The same procedure as defined in Example 1 was conducted except that kinds of resins used for the outermost layer were changed to those shown in Table 1, thereby obtaining gusseted bags and then packaged ham products. The copolymerized PBT resin used in Example 3 had a melting point of 222°C, and contained as a copolymerizing component, 2.5 mol % of

polytetramethylene-oxide glycol having a number-average molecular weight of 1,000. Incidentally, the raw material of the outermost layer were mixed with 2,000 ppm of PMMA particles having an average particle size of 6 μm in the same manner as in Example 1. The label adhesion strength, anti-blocking property and pinhole resistance of the thus-obtained packaged ham products were evaluated in the same manner as in Example 1. The results are shown in Table 2.

Table 1

Examples and Comparative Examples	Layer structure
Example 1	PBT/APO/NY/APO/L-LDPE
Example 2	PEN and PET blend (weight ratio of 1:1)/APO/NY/APO/L-LDPE
Example 3	Copolymerized PBT/APO/NY/APO/L-LDPE
Comparative Example 1	PET/APO/NY/APO/L-LDPE
Comparative Example 2	PEN/APO/NY/APO/L-LDPE
Comparative Example 3	NY/APO/NY/APO/L-LDPE

Table 2

Examples and Comparative Examples	Label adhesion strength (g/15 mm width)	Anti-blocking property (g)	Pinhole resistance (number)	Anti-curl property (direction)
Example 1	632	232	0	none
Example 2	571	251	0	curled (inwardly)
Example 3	632	235	0	none
Comparative Example 1	272	247	2	curled (inwardly)
Comparative Example 2	318	258	2	curled (inwardly)
Comparative Example 3	22	240	9	curled (inwardly)



THIS SHEET HAS BEEN
REPLACED

WHAT IS CLAIMED IS:

1. A packaging bag comprising a heat-sealed, unstretched laminated film comprising:

(A) as an outermost layer, a blended resin layer comprising a polyester resin containing not less than 70 mol % of polyethylene naphthalate-forming units and a polyester resin containing not less than 70 mol % of polyethylene terephthalate-forming units, or a polyester resin layer containing not less than 70 mol % of polybutylene terephthalate-forming units;

(B) a gas-barrier resin layer; and

(C) as an innermost layer, a heat-sealable resin layer, said resin layers (A) to (C) being disposed in this order.

2. A packaging bag according to claim 1, wherein said polyester resin of said resin layer (A) contains 70 to 99 mol % of polybutylene terephthalate-forming units.

3. A packaging bag according to claim 2, wherein a copolymer component unit of said resin layer (A) comprises polytetramethylene oxide glycol having a number-average molecular weight of 300 to 6,000.

4. A packaging bag according to claim 1, wherein said resin layer (A) contains an anti-blocking agent.

5. A packaging bag according to claim 1, which is used for food-packaging.

This Sheet Has Been Replaced

